Inorganica Chimica Acta, 115 (1986) L35–L37

Axially Dissymmetric 2,2′-Diisocyano-1,1′-binaphthyl and its Platinum Complexes

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(Received November 28, 1985)

Molecules containing an axially dissymmetric 1,1-binaphthyl moiety have been proved to have high ability of chiral recognition [1]. There have been reported some chiral biphosphine ligands which contain the atropisomer 1,1′-binaphthyl structure as ligands in the transition-metal catalyzed asymmetric reactions [2]. Here we report the syntheses of axially dissymmetric 2,2′-diisocyano-1,1′-binaphthyl (DIBN) [**1**(*R*) and **1**(*S*)] and their platinum(II) complexes.

It is known that 2,2′-diamino-1,1′-binaphthyl (DABN) can be easily resolved into its antipodes [3]. (*R*) and (*S*)-2,2′-diisocyano-1,1′-binaphthyl (**1**) are prepared by a carbylamine synthesis utilizing phase transfer catalysis [4] *.

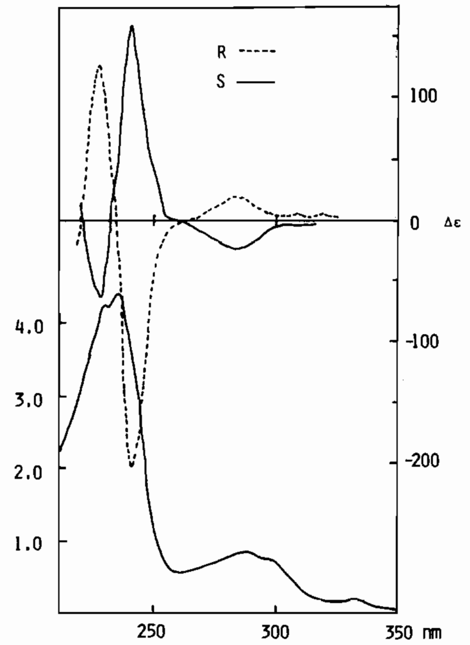

Fig. 1. Electronic and CD spectra of 2,2′-diisocyano-1,1′-binaphthyl (DIBN) in CH_2Cl_2.

TABLE I. Positional and Thermal Parameters for 2,2′-Diisocyano-1,1′-binaphthyl[a]

Atom	*x*	*y*	*z*	B_{eq}
N11	1974(3)	−1518(7)	5909(6)	5.9(0.1)
C10	2526(5)	−2567(10)	5461(10)	9.1(0.3)
C11	1352(4)	−187(7)	6472(6)	5.0(0.2)
C12	251(4)	−416(8)	6498(7)	5.4(0.2)
C13	−352(4)	883(9)	7021(6)	5.5(0.2)
C14	99(4)	2397(8)	7538(6)	4.9(0.2)
C15	−519(4)	3747(8)	8089(7)	5.8(0.2)
C16	−66(4)	5195(9)	8575(7)	6.5(0.2)
C17	1049(4)	5377(8)	8571(7)	6.4(0.2)
C18	1674(4)	4133(8)	8047(7)	5.7(0.2)
C19	1233(4)	2595(7)	7517(6)	4.5(0.1)
C120	1860(4)	1249(7)	6951(6)	4.4(0.1)
N21	2879(3)	2430(7)	4129(5)	5.5(0.1)
C20	2362(5)	2910(10)	3011(8)	7.4(0.2)
C21	3526(4)	1849(7)	5481(6)	4.7(0.1)
C22	4640(4)	1810(7)	5266(7)	5.1(0.2)
C23	5265(4)	1229(8)	6571(7)	5.4(0.2)
C24	4832(4)	720(7)	8070(6)	4.7(0.1)
C25	5482(4)	194(8)	9456(7)	5.9(0.2)
C26	5061(4)	−220(9)	10941(7)	6.3(0.2)
C27	3956(4)	−195(8)	11074(7)	6.1(0.2)
C28	3297(4)	301(8)	9782(6)	5.4(0.2)
C29	3714(4)	778(7)	8245(6)	4.6(0.2)
C210	3048(4)	1354(7)	6872(6)	4.4(0.1)

Atom	*x*	*y*	*z*	*B*
H12	−10(4)	−155(8)	622(6)	9.8(1.7)
H13	−107(3)	70(6)	713(5)	6.0(1.2)
H15	−138(4)	365(7)	797(6)	8.1(1.5)
H16	−58(4)	617(8)	894(6)	9.8(1.7)
H17	138(4)	655(9)	889(7)	10.7(1.8)
H18	252(3)	430(6)	795(5)	5.9(1.2)
H22	498(4)	228(7)	417(5)	7.2(1.4)
H23	612(3)	118(7)	639(6)	7.2(1.4)
H25	624(3)	9(6)	926(5)	4.4(1.0)
H26	564(4)	−64(8)	1175(7)	10.6(1.9)
H27	361(4)	−46(7)	1224(6)	7.7(1.5)
H28	250(3)	35(6)	993(5)	5.3(1.1)

[a] Positional parameters of nonhydrogen atoms are multiplied by 10^4 and hydrogen atoms by 10^3

Their electronic and CD spectra are shown in Fig. 1. Positional and thermal parameters are shown in Table I. The electronic spectrum showed absorption maxima at 285 and *ca.* 230 nm and the CD curve showed signed reflections of these spectral characteristics. A positive 285 nm Cotton effect corresponds to the (*R*)-configuration, and a nega-

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*The new complexes (1–4) were characterized by elemental analysis and IR spectroscopy. Specific rotation of 1 was measured in benzene: [1(*R*)], $[\alpha]_D^{23}$ −65°; and [1(*S*)], $[\alpha]_D^{23}$ +69°.

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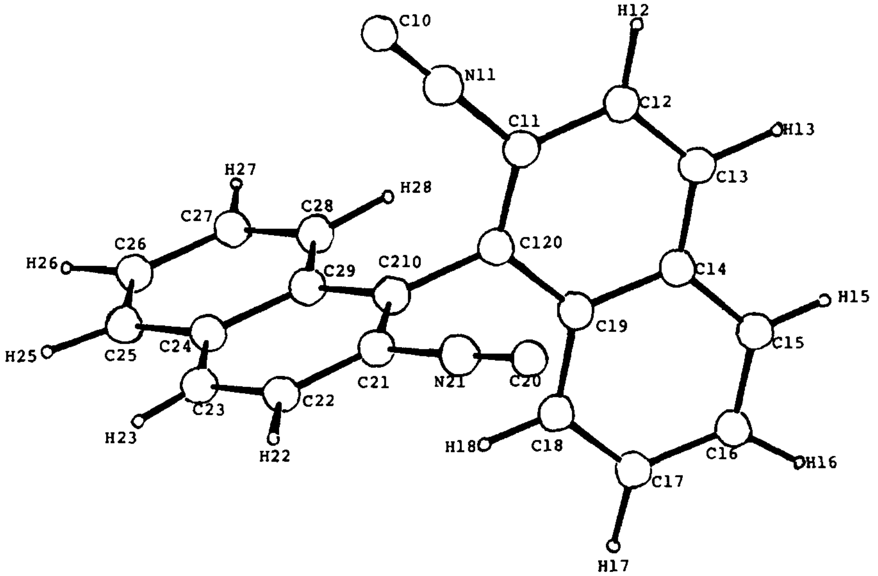

Fig. 2. Structure of 2,2' diisocyano-1,1'-binaphthyl (DIBN). Selected bond lengths (Å) and angles (°): C(10)–N(11), 1.157(9); C(20)–N(21), 1.156(8); C(120)–C(210), 1.497(6) Å, C(10)–N(11)–C(11), 176.9(6); C(20)–N(21)–C(21), 179.1(5)°.

tive one to the (*S*)-form. A similar trend has been observed in related compounds [5].

The molecule of [**1**(*R*)] exists in a *trans* configuration with an angle of 89.6° between the planes of the two naphthalene residues, lying in a perpendicular plane (Fig. 2)*. In binaphthyl, the naphthalene rings adopted a *cis* configuration with a dihedral angle of 68° [6] whereas two naphthalene rings in (*R*)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid dimethyl ester adopted a *trans* form with a dihedral angle of *ca.* 77° [7]. The C–N bond lengths are 1.157(9) and 1.156(8) Å and the C–N–C bond angles are linear, 176.9(6) and 179.1(5)°. The length of the sp^2–sp^2 single-bond linking two rings is 1.497(6) Å, being comparable to other related compounds [6, 8].

The compound [**1**(*R*)] reacted with $Pt_2Cl_4(PPh_3)_2$ to give a yellow $Pt_2Cl_4(PPh_3)_2$(*R*-DIBN) complex [**2**(*R*)].

The overall CD spectra of **2** shifted bathochromically in comparison with those of **1** (Fig. 3). The electronic spectrum is similar to that of $PtCl_2(PPh_3)$-$(2,6\text{-}Me_2C_6H_3NC)$, suggesting the square-planar structure around metal atoms. The CD spectrum of [**2**(*R*)] showed a new negative peak near 320 nm in addition to the peaks of the original ligand, due to an MLCT band. The CD spectrum of [**2**(*S*)] showed an asymmetrical curve to that of [**2**(*R*)]. The bromide [**3**(*R*)] and iodide [**4**(*R*)] complexes were obtained by metathesis of [**2**(*R*)] with KBr or KI. Their spectra showed similar patterns to the chloride complex **2**.

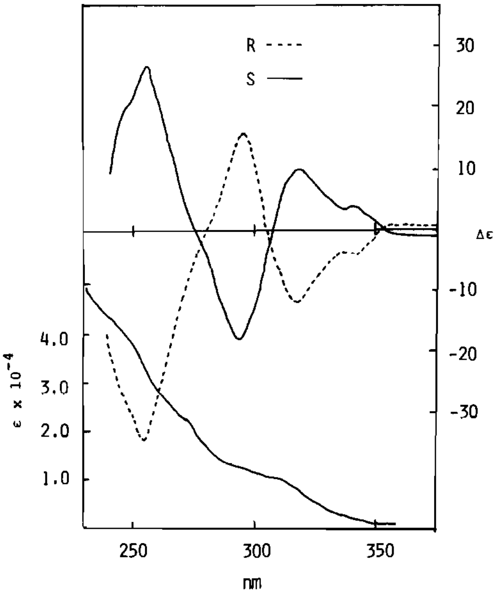

Fig. 3. Electronic and CD spectra of $Pt_2L_4(PPh_3)_2$(DIBN) in CH_2Cl_2.

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*Crystal Data: $C_{22}H_{12}N_2$, $M = 304.4$, monoclinic, space group $P2_1$, $a = 12.546(7)$, $b = 8.041(2)$, $c = 8.053(4)$ Å, $\beta = 92.19(4)°$, $U = 811.7(6)$ Å^{-3}, $Z = 4$. The intensities of 999 independent reflections were collected on a Rigaku four-circle diffractometer. The structure was solved via direct method (MULTAN) and refined by block-diagonal least-squares (BDLS) on the basis of 877 observed reflections [having $I \geqslant 3\sigma(I)$] to an R value of 3.92%. No attempt to determine the absolute configuration was made.

TABLE II. Positional and Thermal Parameters for the Complex 4(*R*)[a]

Atom	x	y	z	B_{eq}
Pt	−1060(1)	−4650(0)	−2496(1)	3.5(0.1)
I1	712(2)	−4410(5)	−1246(3)	7.0(0.2)
I2	−1054(2)	−5964(4)	−3692(3)	6.2(0.2)
P1	−2569(7)	−4978(9)	−3410(8)	3.6(0.6)
Atom	x	y	z	B
C10	−99(3)	−359(3)	−160(3)	3.7(0.8)
N10	−101(2)	−291(4)	−117(3)	5.0(0.8)
C11	−111(3)	−198(4)	−68(3)	3.8(0.8)
C12	−193(3)	−207(4)	−84(3)	4.7(0.9)
C13	−201(3)	−108(4)	−38(3)	4.1(0.9)
C14	−137(3)	−23(4)	24(3)	4.6(0.9)
C15	−150(3)	74(5)	70(3)	7.0(1.3)
C16	−84(3)	161(4)	123(3)	4.3(0.9)
C17	−6(3)	169(5)	141(3)	5.5(1.0)
C18	16(3)	74(6)	104(4)	7.5(1.3)
C19	−52(3)	−22(4)	43(3)	4.7(0.9)
C20	−38(2)	−114(4)	−4(3)	3.5(0.7)
C111	−311(3)	−351(4)	−348(3)	4.1(0.8)
C112	−380(3)	−360(4)	−345(3)	4.8(0.9)
C113	−424(4)	−251(6)	−351(4)	7.8(1.4)
C114	−396(3)	−135(5)	−359(4)	6.6(1.2)
C115	−326(4)	−122(6)	−367(4)	8.2(1.5)
C116	−279(3)	−244(5)	−358(3)	5.5(1.0)
C121	−273(3)	−620(5)	−278(3)	5.2(1.0)
C122	−359(3)	−680(5)	−336(4)	6.5(1.2)
C123	−364(4)	−768(5)	−275(4)	7.5(1.3)
C124	−288(5)	−788(8)	−185(5)	11.3(2.1)
C125	−206(4)	−717(6)	−124(4)	7.5(1.4)
C126	−200(4)	−648(5)	−183(4)	6.8(1.3)
C131	−329(3)	−551(5)	−469(3)	5.3(1.1)
C132	−331(3)	−678(5)	−490(3)	5.5(1.0)
C133	−382(4)	−719(6)	−582(4)	8.6(1.6)
C134	−421(4)	−641(6)	−656(4)	7.7(1.4)
C135	−421(5)	−509(7)	−641(5)	11.0(2.2)
C136	−366(3)	−462(8)	−537(3)	6.5(1.0)

[a] Positional parameters [from Pt to P1] are multiplied by 10^4 and hydrogen atoms, by 10^3.

In an X-ray analysis of [4(*R*)], (Fig. 4), the Pt——Pt contact is *ca.* 10 Å, having no interaction*.

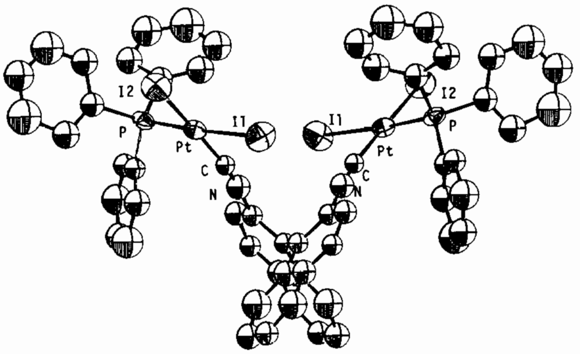

Fig. 4. Structure of $Pt_2I_4(PPh_3)_2(DIBN)$. Selected bond lengths (Å) and angles (°): Pt–I(10), 2.630(3); Pt–I(2), 2.614(6); Pt–P(1), 2.81(12); Pt–C(10), 1.92(5); C(10)–N(10), 1.10(7) Å; I(1)–Pt–I(2), 91.2(2); I(1)–Pt–P(1), 172.3(4); I(1)–Pt–C(10), 85.0(12); I(2)–Pt–P(1), 92.(2); I(2)–Pt–C(10), 174.9(16); Pt–C(10)–N(10), 172.6(32); C(10)–N(10)–C(11), 175.5(34)°.

Positional and thermal parameters for [4(*R*)] are shown in Table II. The napthalene rings adopt a *cis* configuration with a dihedral angle of 73°.

From the EHMO calculation, potential energy differences estimated as a function of dihedral angles of free ligand were calculated to be only *ca.* 0.04 eV between molecules with dihedral angles of 90° and 75°, showing them to be interconvertible. Thus, the contraction of the dihedral angle between two naphthalene rings in [4(*R*)] by *ca.* 17° for that of free [1(*R*)] may be responsible for steric strain, arising from coordination to the metals.

Asymmetric hydrosilylation of α-methylstyrene catalysed by 4(*R*) is now in progress.

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*Crystal data: $C_{58}H_{42}N_2P_2I_4Pt_2$, $M = 1726.7$, monoclinic, space group $C2$, $a = 19.973(11)$ $b = 10.573(6)$, $c = 18.459(12)$ Å, $\beta = 132.38(4)°$. $U = 2881.3(35)$ Å^{-3}, $Z = 2$. The intensities of 1602 independent reflections were collected. The structure was solved via a heavy atom method and refined by BDLS on the basis of 1428 observed reflections [having $I \geqslant 3\sigma(I)$] to an R value of 6.05%. The absolute configuration was determined as in Fig. 4.