1,1′-Bi-isoquinoline: a Chiral Bidentate *N*-Donor Ligand with C_2-symmetry; Formation of Optically Active Complexes with High Chiral Recognition

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1,1′-Bi-isoquinoline was co-ordinated with two enantiomers of a chiral palladium complex forming optically active binuclear Pd complexes, and high chiral recognition between the complexing partners was observed during the complexation.

Chiral bidentate ligands with C_2-symmetry play an important role in homogeneous catalytic asymmetric reactions.[1–4] Typically, such ligands are diphosphines or diols; *N*-donors have received limited attention despite the fact that 2,2′-bipyridine has long been an important ligand in homogeneous catalytic reactions. We now report our preliminary study on 1,1′-bi-isoquinoline.

1,1′-Bi-isoquinoline (**1**) was prepared by homocoupling of 1-bromo-isoquinoline catalysed with $NiCl_2$–PPh_3–Zn[5] in 85% yield.† Crawford[6] failed to resolve the optically active tartaric acid salt of this compound as a result of the rapid mutarotation of the salt in solution ($t_{\frac{1}{2}}$ only 1.3 ± 0.3 min). Accordingly, we attempted to fix the configuration of the bi-isoquinoline by metal co-ordination. Thus, the chiral complexes (*R*)-(−)-(**2**) and (*S*)-(+)-(**3**) were treated wth 1,1′-bi-isoquinoline affording the new complexes (**4**) and (**5**), respectively. The corresponding complexes (**6**) and (**7**) were also prepared from 2,2′-bipyridine for comparison. All the complexes were obtained in >90% yield.‡

The specific rotation of (**4**) is $[\alpha]_D^{10}$ + 30.7° (*c* 0.43, MeOH) while that of (**5**) has almost the same absolute value but the opposite sign, $[\alpha]_D^{10}$ −31.6° (*c* 0.25, MeOH). Complexes (**4**) and (**5**) have identical ^{1}H n.m.r. spectra [δ 3.39 (q, benzylic H) and 0.44 (d, benzylic Me)]. Further crystallization of (**4**) and

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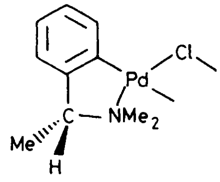
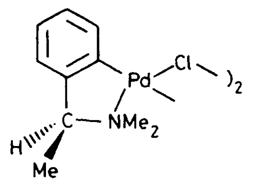
† (**1**) has been prepared by F. H. Case (*J. Org. Chem.*, 1952, **17**, 471) and by A. J. Clarke, S. McNamara, and O. Meth-Cohn (*Tetrahedron Lett.*, 1974, 2373), in rather low yield.

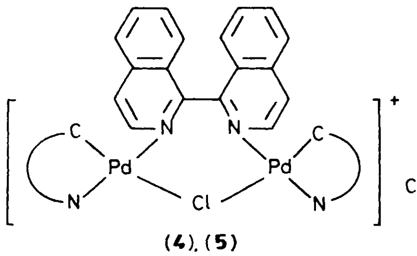
‡ All new compounds had satisfactory spectroscopic properties and elemental analysis data (*cf.* H. Akimoto, T. Shiori, Y. Iitaka, and S. Yamada, *Tetrahedron Lett.*, 1968, 97).



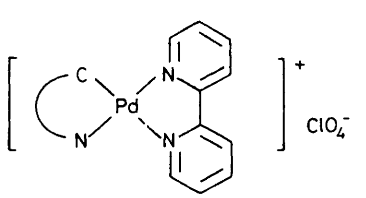
(R)-(−)-(2)



(S)-(+)-(3)



(4), (5)



(6), (7)

(4),(6) C͡N = (R)- and (5),(7) C͡N = (S)-N,N-dimethyl-α-phenylethylamine

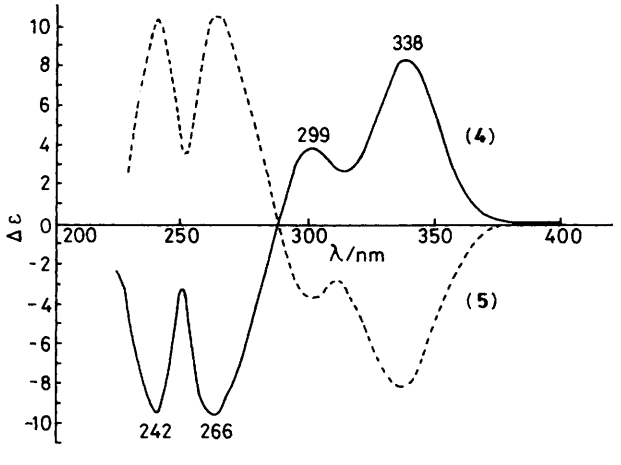


Figure 1. C.d. curves for complexes (**4**) and (**5**).

(**5**) did not result in a change in the specific rotations or in the ^{1}H n.m.r. spectra, and complexes recovered from the mother liquors also showed no changes.

This suggests that both (**4**) and (**5**) might be single diastereoisomers with high optical purity and that they might be enantiomers. This is further supported by c.d. studies. Figure 1 shows the c.d. curves of (**4**) and (**5**), which are mirror images.

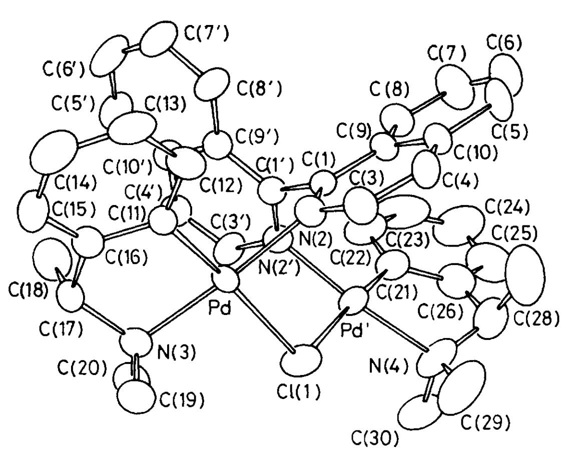


Figure 2. ORTEP plot of the cation of complex (**4**).

The structures of the binuclear Pd complexes (**4**) and (**5**) as well as their absolute configurations were confirmed by X-ray crystallographic studies. Figure 2 shows the structure of (**4**).§

Therefore, the absolute configuration is (R,R,R)¶ for (**4**), and (S,S,S,) for (**5**). Almost complete chiral recognition between the complexing partners had occurred during the formation of (**4**) and (**5**). It is evident from the ORTEP view and from a Corey–Pauling–Koltun molecular model that 1,1′-bi-isoquinoline with the R-configuration is compatible only with (R)-(−)-(**2**); in (S)-(+)-(**3**) there will be steric repulsion between the (R)-1,1′-bi-isoquinoline moiety and the methyl group on the chiral centre of (S)-(+)-(**3**). Therefore, during the complexation of (R)-(−)-(**2**) with the racemic (**1**), efficient kinetic resolution operated. In combination with the rapid mutarotation of (**1**), complete chiral recognition eventually resulted. That is, (R)-(−)-(**2**) complexes with the racemic (**1**) to afford (R,R,R)-(**4**), and (S)-(+)-(**3**) to afford (S,S,S)-(**5**) exclusively.

The two isoquinoline moieties in (**4**) and (**5**) are almost perpendicular to each other (88.3°). Thus, the 1,1′-bi-iso-

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§ *Crystal data:* (R,R,R)-$C_{38}H_{40}O_4N_4Cl_2Pd_2 \cdot MeOH$ (**4**), M = 932.6, orthorhombic, space group $P2_12_12_1$, a = 11.082(1), b = 16.668(1), c = 21.593(2) Å, U = 3988(1) Å^3, Z = 4, D_c = 1.50 g cm^{-3}, $F(000)$ = 1888, $\mu(\mathrm{Cu}\text{-}K_\alpha)$ = 88.25 cm^{-1} (λ = 1.54178 Å), crystal dimensions 0.30 × 0.23 × 0.17 mm. The intensities of 4066 unique reflections were collected on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by the heavy atom method and refined by full-matrix least-squares including all H-atoms in calculated positions. For 3673 observed reflections [$|F_o| > 6\sigma(|F_o|)$] for the final value of R is 0.032 (R_w = 0.036) for absorption-corrected data; under identical conditions refinement based on the assumed enantiomer gave an R value of 0.053. Therefore the subsequent calculations were based on the first model. The final difference electron density map showed a maximum of 0.48 e Å^{-3} and a minimum of −0.66 e Å^{-3}. The absolute configuration of complex (**4**) was determined by the anomalous scattering technique.[7] The coincidence of the observed and calculated structure factors of 30 Bijvoet pairs indicated that the absolute configuration is R,R,R.

The structure of the enantiomer (S,S,S)-$C_{38}H_{40}O_4N_4Cl_2Pd_2 \cdot MeOH$ (**5**), was also determined: orthorhombic, space group $P2_12_12_1$, a = 11.079(3), b = 16.668(1), c = 21.593(2) Å, crystal dimensions 0.80 × 0.60 × 0.23 mm. 4051 reflections, 3809 unique; R = 0.076 (R_w = 0.085) for absorption corrected data. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ The absolute configuration of 1,1′-bi-isoquinoline is defined in accordance with that of 1,1′-binaphthyls (*cf.*, H. Akimoto, T. Shioiri, Y. Iitaka, and S. Yamada, *Tetrahedron Lett.*, 1968, 97).

quinoline prefers to form binuclear Pd complexes in order to retain the square planar Pd^{II} configuration while 2,2′-bipyridine forms a mononuclear square planar Pd^{II} complex.

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