

Synthesis, resolution and rates of racemisation of 1-(2'-methyl-3'-indenyl)-2-naphthylamine and -2-naphthol

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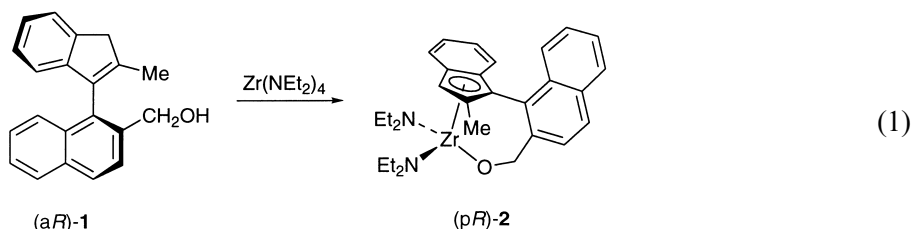
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Abstract

Axially chiral ligands 1-(2'-methyl-3'-indenyl)-2-naphthylamine **7** and -2-naphthol **8** have been prepared in three and four steps, respectively, from 2-nitro-1-naphthol. Following resolution by chiral HPLC, the absolute configurations were assigned by circular dichroism as (a*R*)-(–)-**7** and (a*R*)-(+)-**8**. The enantiomers of both ligands have significant thermal stability, with half-lives for racemisation of 73 h at 144°C and 220 h at 110°C, for **7** and **8**, respectively. © 2000 Elsevier Science Ltd. All rights reserved.

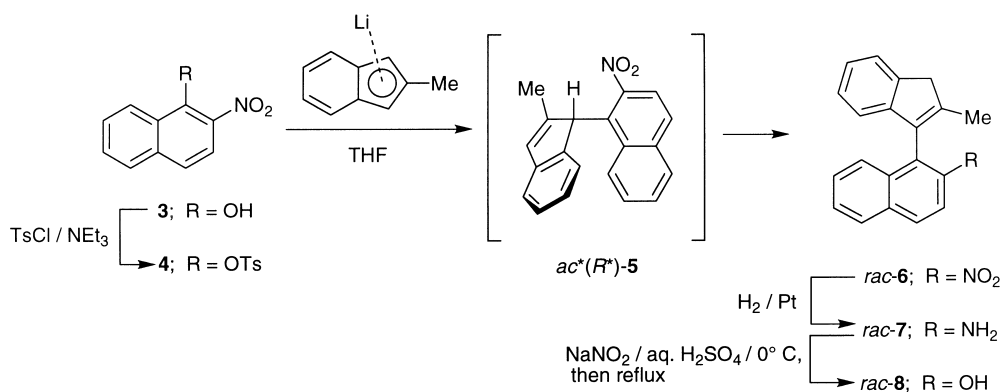
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Planar chiral cyclopentadienylmetal complexes offer enormous potential as stereoselective catalysts, but obtaining them in stereochemically pure form is often problematic.¹ We have recently demonstrated that a unique ligand design—axially chiral chelating cyclopentadienyl ligands—has the ability to allow the enantiospecific synthesis of planar chiral cyclopentadienylmetal complexes containing pendant donor atoms² or a second cyclopentadienyl moiety.³ In the former case, the reaction of axially chiral (a*R*)-1-(2'-methyl-3'-indenyl)naphthalene-2-methanol, (a*R*)-**1**, with Zr(NEt₂)₄ was shown to enantiospecifically provide planar chiral complex (p*R*)-**2** (Eq. (1)).² In extending this chemistry, particularly attractive targets were ligands in which the second metal coordination site is directly attached to the aromatic bridge, since metal complexes of such ligands would be expected to show a higher level of stereorrigidity. In this Letter we report the facile synthesis of two such ligands, containing pendant nitrogen and oxygen donor atoms, and the determination of the absolute configurations and rates of racemisation of their enantiomers.

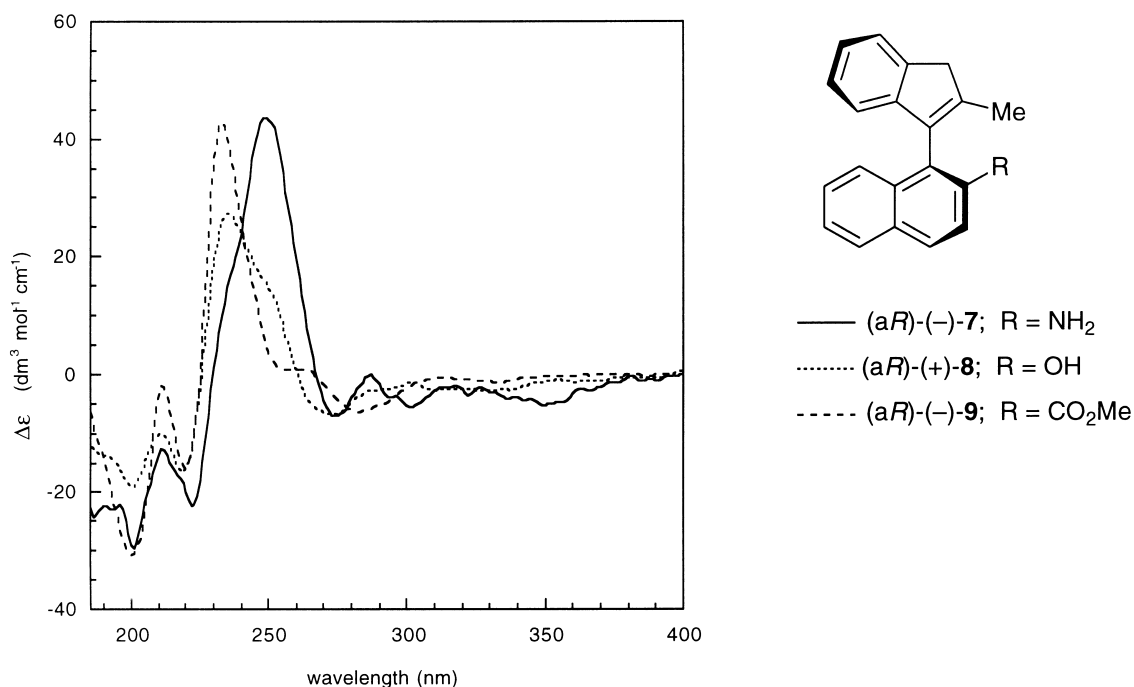


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The preparation of the ligand *rac*-1-(2'-methyl-3'-indenyl)-2-naphthylamine, *rac*-7, was achieved in just three steps from commercially available 2-nitro-1-naphthol **3**, as outlined in Scheme 1. The naphthol **3** was first converted to the tosylate **4** (1 equiv. TsCl, 1.1 equiv. triethylamine, CH₂Cl₂, rt, 12 h) in 85% yield. Slow addition over 2 h of a THF solution of the tosylate **4** to a solution of 2-methylindenyllithium (1.5 equiv., generated by treatment of 2-methylindene with BuLi) in THF at -20°C, followed by a further 1 h at -20°C, provided *rac*-1-(2'-methyl-1'-indenyl)-2-nitronaphthalene as a single stable rotamer, *ac**(*R**)-**5**, in 40% yield. Allowing the reaction to warm to rt, then stirring for an additional 12 h, led to in situ base-catalysed isomerisation of *ac**(*R**)-**5** to *rac*-1-(2'-methyl-3'-indenyl)-2-nitronaphthalene, *rac*-**6**, also isolated in 40% yield. Finally, reduction



Scheme 1.

Figure 1. CD spectra (acetonitrile) of (a*R*)-(-)-**7**, (a*R*)-(+)-**8** and (a*R*)-(-)-**9**

of *rac*-**6** in EtOAc solution with hydrogen at atmospheric pressure over a platinum catalyst (Adam's catalyst or Pt on C) during 12 h, provided *rac*-**7** in 90% yield. Conversion of *rac*-**7** to *rac*-1-(2'-methyl-3'-indenyl)-2-naphthol, *rac*-**8**, was achieved by diazotization with sodium nitrite in 50% aqueous sulfuric acid at 0°C, followed by heating at reflux overnight, in 45% yield.

Resolution of the ligands *rac*-**7** and *rac*-**8** was achieved by semi-preparative chiral HPLC using a Pirkle Type-1A column [ionically-bound (*R*)-*N*-(3,5-dinitrobenzoyl)phenylglycine].⁴ In the case of **7** only the enantiomer eluting first was obtained in enantiomerically pure form, while both enantiomers of **8** could be obtained in enantiomerically pure form. The enantiomer of **7** eluting first had $[\alpha]_D -53.5$ (*c* 1.45, toluene), while the enantiomer of **8** eluting first had $[\alpha]_D +165$ (*c* 0.64, toluene). Comparison of the CD spectra of the two enantiomers with that of methyl (*aR*)-1-(2'-methyl-3'-indenyl)naphthalene-2-carboxylate, (*aR*)-(-)-**9** (the absolute configuration of which has been previously determined),⁵ indicates that both have (*aR*) absolute configurations (Fig. 1).

The rates of racemisation of the resolved ligands were determined by monitoring the ee of the ligands by chiral HPLC;⁶ in the case of **7** the half-life for racemisation for a solution in xylenes at reflux (144°C) was 73 h; in the case of **8** the half-life for racemisation for a solution in toluene at reflux (110°C—the ligand decomposed in refluxing xylenes) was 220 h. Thus, both ligands have useful stability towards thermal racemisation. The preparation of transition metal complexes using these new ligands will be reported in due course.

References

1. Halterman, R. L. *Chem. Rev.* **1992**, 92, 965, and references cited therein.
2. Baker, R. W.; Wallace, B. J. *Chem. Commun.* **1999**, 1405.
3. Baker, R. W.; Wallace, B. J.; Turner, P. J. *Chem. Soc., Dalton Trans.* **2000**, 431.
4. A 10×250 mm column (Pirkle Type-1A, Regis) was used with 1% 2-propanol/hexanes as eluent at a flow rate of 3.0 ml min⁻¹, detection 280 nm; *t*_R: 19.2 min for (*aR*)-**7** and 21.6 min for (*aS*)-**7**, 18.6 min for (*aR*)-**8** and 25.3 min for (*aS*)-**8**.
5. Baker, R. W.; Reek, J. N. H.; Wallace, B. J. *Tetrahedron Lett.* **1998**, 39, 6573.
6. A 4.6×250 mm column (Pirkle Type-1A, Regis) was used with 1% 2-propanol/hexane as eluent at a flow rate of 1.0 ml min⁻¹, detection 254 nm, *t*_R: 6.0 min for (*aR*)-**7** and 6.6 min for (*aS*)-**7**, 11.4 min for (*aR*)-**8** and 12.9 min for (*aS*)-**8**.