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# Versatile Chiral Palladium(II) Complexes for Enantiomeric Purities of 1,2-Diamines

**Simon Y.M. Chooi, Pak-hing Leung*, Chin Chin Lim, K.F. Mok, G.H. Quek, K.Y. Sim and M.K. Tan**

**Department of Chemistry, National University of Singapore, Singapore 0511**

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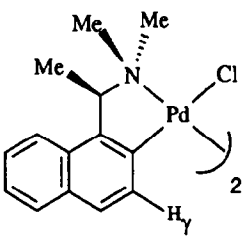
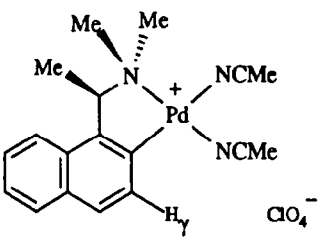
**Abstract:** An efficient NMR determination of the enantiomeric excess of $C_2$-symmetric 1,2-diamines can be achieved by coordination of the bidentates to the optically active forms of the diamagnetic [dimethyl(1-(2-naphthyl)ethyl)aminato-$C^2$,$N$]palladium(II) units.

Enantiomerically pure $C_2$-symmetric 1,2-diamines are extremely useful chiral auxiliaries for asymmetric catalysis[1]. In general, the optically active diamines are obtained from optical resolutions. Recently, several asymmetric syntheses of 1,2-diamines have been reported[2,3]. Except in rare instances[3a,4], however, the enantiomeric purities of these bidentate ligands have not been established; perhaps due to the difficulties associated with the formation of suitable diastereomers or the limitations of the chiral solvating and shift reagents[5]. Using the optically active forms of **1** and **2** as complexing agents, we report herein an efficient method for determining the e.e. of three $C_2$-symmetric 1,2-diamines **3a-c**.



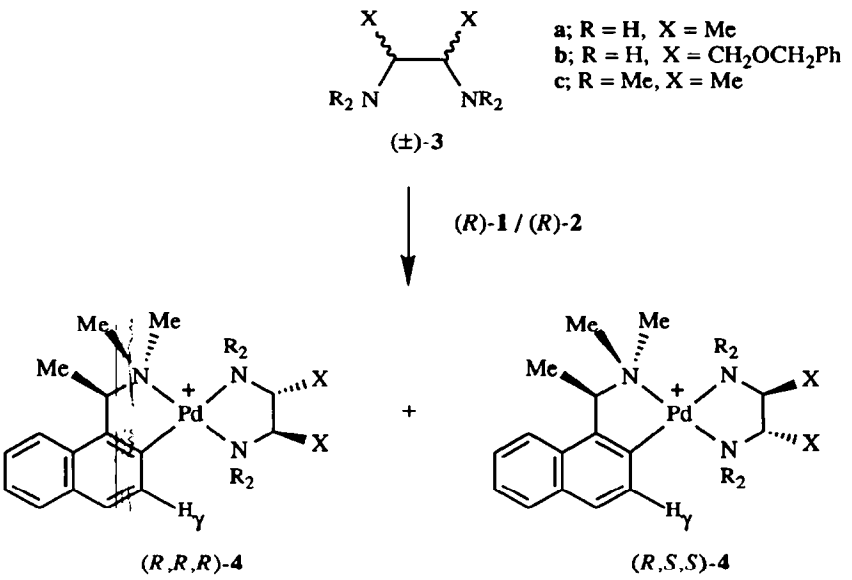

(*R*)-**1**




(*R*)-**2**

Both enantiomeric forms of the dimeric complex **1** are readily available[6]. The perchlorate salts **2** can be prepared by treating the corresponding enantiomeric forms of **1** with silver perchlorate in acetonitrile. Thus (*R*)-**2** can be crystallized as stable pale yellow needles from acetonitrile-diethyl ether in 85% isolated yield, $[\alpha]_D$ -104.4 (*c* 1.0, $CH_2Cl_2$).

The diastereomeric complexes **4a-b** can be prepared as their chloride salts in quantitative yields from the reaction between (*R*)-**1** and the appropriate forms of the diamines **3a-b**[7] in dichloromethane (Scheme 1). Interestingly, no reaction was observed between (*R*)-**1** and both enantiomers of **3c**, presumably due to stereo-electronic reasons. In contrast, a pair of internally




Scheme 1

diastereomeric perchlorate salts were obtained instantly when (±)-**3c** was treated with (*R*)-**2**. Both diastereomers of **4a** are not soluble in dichloromethane and are precipitated immediately from the reaction solution. Complexes **4b-c** are soluble in organic solvents. In each preparation, the $^1$H NMR spectrum of the crude product was recorded prior to recrystallization to avoid separation of diastereomers. Selected NMR data and optical rotation values of **4a-c** are given in Table I. Both diastereomeric complexes of each 1,2-diamine are of $C_1$ symmetry and are clearly discriminated by $^1$H NMR spectroscopy. A study of the proportions of both diastereomers present for a particular diamine under a given set of conditions will therefore provide an estimate of the enantiomeric purities of the bidentate ligand. It is obvious that the non-equivalent methyl groups in both chelate rings of the complexes are useful spectroscopic handles. In the present series of compounds, all the NMe resonances occurred as sharp singlets. The non-equivalent CMe groups in all the diastereomeric complexes are observed as individual simple doublets. Additionally, the chemical shift of the γ naphthylene proton ($H_\gamma$) adjacent to the metalated carbon of the five membered organometallic ring is of considerable assistance in making enantiomeric purity assignments. This aromatic proton is protruding into the stereochemical environment of the neighbouring 1,2-diaminoethane ring. For example, the resonance signals of ($H_\gamma$) in the pair of diastereomers (*R*,*R*,*R*)-**4a** and (*R*,*S*,*S*)-**4a** are clearly identified as doublets at δ 7.18 and 7.12 respectively (Figure 1). The chemical shift of ($H_\gamma$) is of particular importance in **4b** since the diamine does not carry any NMR sensitive methyl substituent. While the NMe signals are diagnostic of enantiomeric purities, the ($H_\gamma$) signals in both diastereomers of **4c** are, however, not discernible within the broad manifold of aromatic resonances.

Table 1. Selected spectroscopic properties of **4a-c**.

| Complexes | $[\alpha]_D$[a] | $^1$H NMR[b] | | |
|---|---|---|---|---|
| | | δ CMe[c] | δ NMe[d] | δ $H_\gamma$[c] |
| (*R*,*R*,*R*)-**4a**[e] | -53.4 | 1.26 (6.3), 1.28 (6.1), 1.79 (6.3) | 2.77, 2.82 | 7.18 (8.3) |
| (*R*,*S*,*S*)-**4a**[e] | -115.4 | 1.22 (6.2), 1.26 (6.2), 1.78 (6.4) | 2.74, 2.80 | 7.12 (8.3) |
| (*R*,*R*,*R*)-**4b** | -41.5 | 1.79 (6.3) | 2.88[f] | 7.13 (8.4) |
| (*R*,*S*,*S*)-**4b** | -106.7 | 1.77 (6.2) | 2.88, 2.94 | 6.93 (8.3) |
| (*R*,*R*,*R*)-**4c** | -87.0 | 1.09 (6.8), 1.12 (6.7), 2.07 (6.3) | 2.66, 2.72, 2.74 2.77, 2.79, 3.14 | ¶ |
| (*R*,*S*,*S*)-**4c** | -164.5 | 1.07 (6.4), 1.08 (6.4), 2.12 (6.2) | 2.59[f], 2.73, 2.83 2.86, 2.95 | ¶ |

[a] Measured in $CH_2Cl_2$ unless otherwise stated. [b] All the 300 MHz NMR spectra were recorded in $CDCl_3$, unless otherwise stated. [c] Resonance signals appeared as doublets ($^3J_{H-H}$ values are given in parentheses). [d] Sharp singlets. [e] $[\alpha]_D$ measured in $H_2O$. NMR spectra recorded in $D_2O$. [f] Two NMe resonances occurred at the same chemical shift. ¶ Signals not discernible.

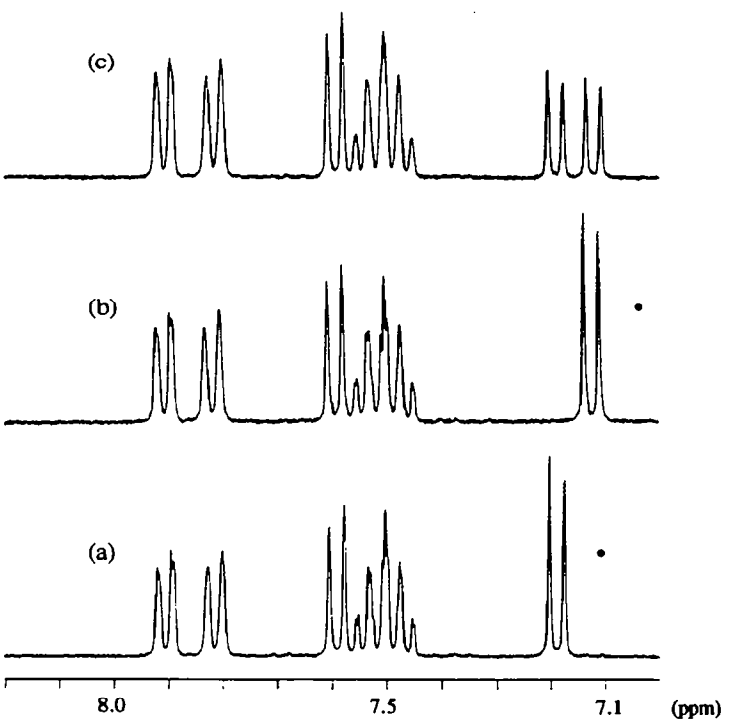



Figure 1. The aromatic region of the 300 MHz $^1$H NMR spectra of (a) (*R*,*R*,*R*)-**4a**, (b) (*R*,*S*,*S*)-**4a** and (c) a 1:1 diastereomeric mixture of **4a** in $D_2O$. •: $H_\gamma$ signal.

It is worth noting that enantiomerically pure (*R*)-**1** could be recovered quantitatively from **4a-c** by treating the cations with dilute hydrochloric acid[6]. The 1,2-diamines were then recovered without loss of optical activities from the ammonium salts simply by neutralization. As intimated earlier, the use of the diamagnetic complexes **1** and **2** is an efficient method for the confirmation of the e.e. for $C_2$ symmetric diamines regardless of the absence of good NMR handles in the bidentate ligands. Due to the high molecular weights of the chiral complexing agents, only small quantities of diamines are required for the NMR determinations. It should be noted, however, that it is often more convenient to prepare a particular pair of diastereomers by using both enantiomeric forms of **1** or **2** than by preparing the optical antipodes of the diamines. Details concerning the prochiral methyl-methyl interactions in **4c** will be reported in a further paper.

**References and Notes**

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3. For examples, see: (a) Davies, S.G.; Mortlock, A.A. *Tetrahedron: Asymmetry* **1991**, *2*, 1001; (b) Oi, R.; Sharpless, K.B. *Tetrahedron Lett.* **1991**, *32*, 999; (c) Benalil, A.; Carboni, B.; Vaultier, M. *Tetrahedron 1991*, *38*, 8177.
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6. Enantiomerically pure **1** can be prepared in 95% using the appropriate forms of (1-ethyl-α-naphthyl)amine as starting materials. Both antipodes of the amine ligand are available commerically in their pure forms. For details, see: Kerr, P.G.; Leung, P.H.; Wild, S.B. *J. Am. Chem. Soc.* **1987**, *109*, 4321 and references cited therein.
7. Both enantiomers of **3a** were prepared as previously described[2]. Enantiomerically pure **3b** and **3c** were prepared from the antipodes of tartaric acid and 2,3-diaminobutane respectively; (*S*,*S*)-**3b**: $[\alpha]_D$ +12.1, chloroform; (*S*,*S*)-**3c**: $[\alpha]_D$ +4.6, benzene, +7.4, toluene. Experimental details will be published in a further paper.

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