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Synthesis and Isolation of Diastereomers of Optically Active Cyclomercurated Ferrocenylimines

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Abstract: Asymmetric cyclomercuration of chiral ferrocenylimines (+)-(R)-**2** and (-)-(S)-**2** with mercuric acetate and subsequent treatment by lithium chloride gave a mixture of diastereomeric cyclomercurated ferrocenylimines. The four enantiomeric pure compounds with both planar and central chirality were isolated from the two mixtures by the thin layer chromatography.

Keywords: Chiral ferrocenylimines, asymmetric cyclomercuration.

Introduction

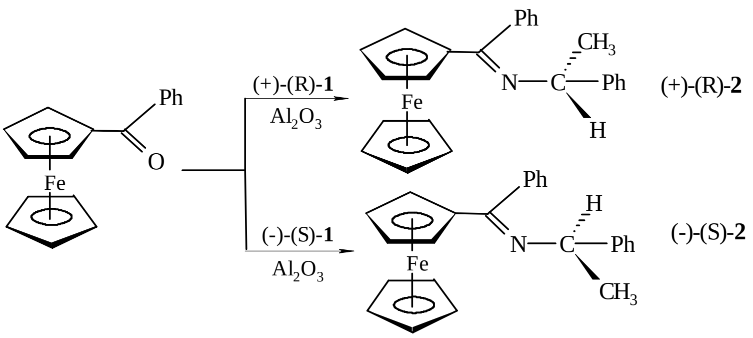
Organomercurials have been used extensively in organic synthesis and synthesis of other organometallics due to their ability to accommodate practically all the important organic functional groups and their ease in undergoing transmetallation for syntheses of transition metal organometallics which are very useful in organic synthesis. Recently, we reported the synthesis of optically active 1,2-disubstituted cyclomercurated ferrocenylimines by transmetallation reaction of planar chiral cyclopalladated ferrocenylimines with metallic mercury[1]. But to the best of our knowledge, up to now no report has dealt with the direct mercuration of chiral ferrocenylimines. Synthesis and isolation of this kind of compounds are very important for understanding the stereochemistry of the related reactions. In this paper we report the direct *ortho*-mercuration of chiral ferrocenylimines.

Results and Discussion

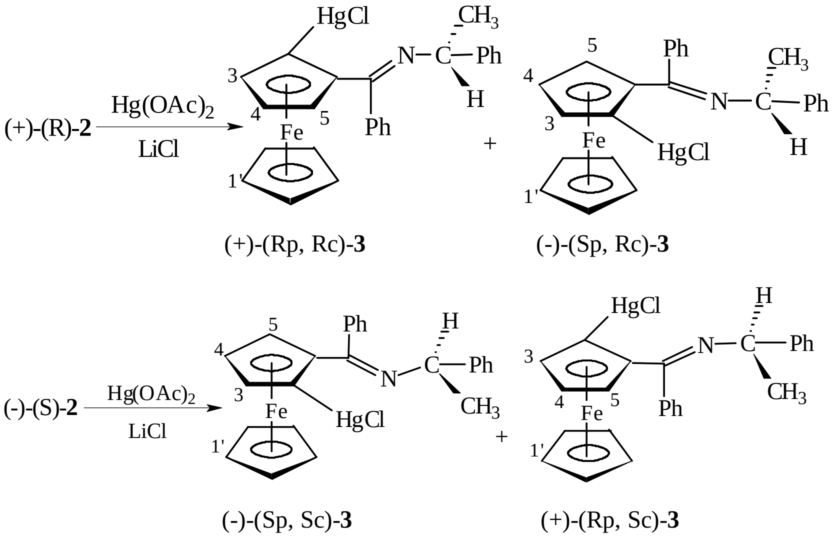
Synthesis of Chiral Ferrocenylimines

Ferrocenylimines R-**2** and S-**2** were prepared by condensation of benzoylferrocene with (+)-(R)-α–phenylethylamine [(+)–(R)-**1**] and (-)-(S)-α–phenylethylamine [(–)–(S)–**1**] respectively, in dry toluene in the presence of freshly activated Al_2O_3 (**Scheme 1**). The products R-**2** and S-**2** were characterized by elemental analysis, IR and ^{1}H NMR spectra[2].

Scheme 1



Scheme 2



Cyclomercuration of Ferrocenylimines R-2 and S-2

Cyclomercuration of R-**2** with mercuric acetate and subsequent treatment by lithium chloride at room temperature gave a mixture of diastereomeric cyclomercurated products (Rp, Rc)-**3** and (Sp, Rc)-**3**. Asymmetric cyclomercuration of S-**2** by the same procedure gave a pair of diastereomers (Sp, Sc)-**3** and (Rp, Sc)-**3** (**Scheme 2**). The four enantiomeric pure compounds were isolated from the two mixtures by silica gel plate developed by methylene dichloride and petroleum ether (60-90°C), since the diastereomers (Rp, Rc)-**3** and (Sp, Sc)-**3** exhibited a higher R_f value than those of the diastereomers (Sp, Rc)-**3** and (Rp, Sc)-**3**, respectively. All of the compounds **3** were characterized by elemental analysis, IR and ^{1}H NMR spectra[3]. The structures and absolute configurations of the four stereoisomers of compounds **3** were determined by X-ray diffraction. **Figure 1** and **Figure 2** indicate the absolute configurations of (Rp, Rc)-**3** and (Sp, Sc)-**3**, respectively. The details of the structures and absolute configurations of all the cyclomercurated complexes and related stereochemistry will be reported in full paper.

Figure 1 Perspective view of complex (Rp, Rc)-**3**. Selected bond distances (Å) and angles (°) are: Hg(1)-N(1), 2.774; Hg(1)-C(1), 2.017; C(1)-Hg(1)-Cl(1), 175.9(2); Hg(1)-C(1)-C(2), 119.7(7); C(1)-C(2)-C(11), 124.8(8); C(2)-C(11)-N(1), 117.8(7)

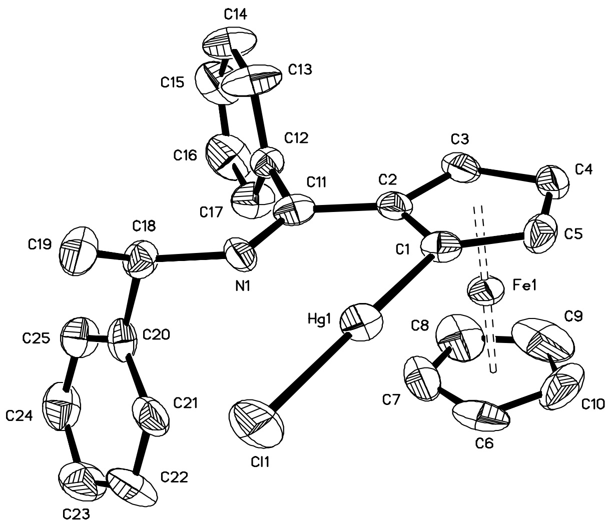
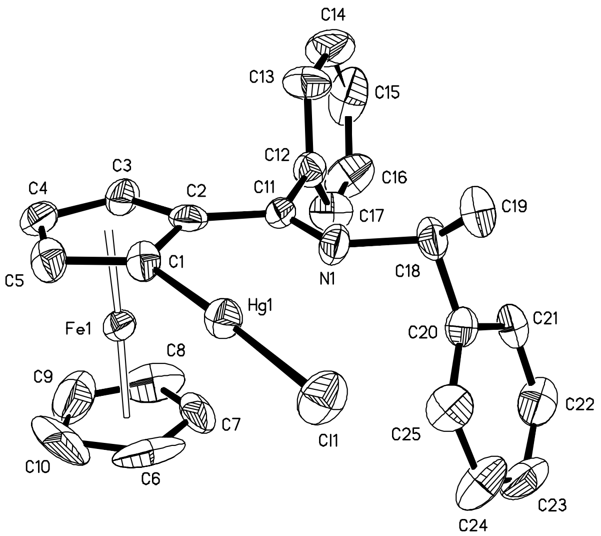


Figure 2 Perspective view of complex (Sp, Sc)-**3**. Selected bond distances (Å) and angles (°) are: Hg(1)-N(1), 2.741; Hg(1)-C(1), 2.051; C(1)-Hg(1)-Cl(1), 176.7(4); Hg(1)-C(1)-C(2), 118.7(11); C(1)-C(2)-C(11), 123.0(14); C(2)-C(11)-N(1), 112.2(2)



The IR spectra of C=N bond showed absorption at *ca.*1608cm^{-1} for (Rp, Rc)-**3** and (Sp, Sc)-**3**, and at *ca.* 1603cm^{-1} for (Sp, Rc)-**3** and (Rp, Sc)-**3**, which are shifted to lower energy from *ca.* 4 to 9cm^{-1} in comparison with the unmercurated parent compounds **2** (the C=N absorption for **2** appear at *ca.* 1612cm^{-1}), indicating the presence of intramolecular N→Hg coordination [4]. The IR spectra of compounds **2** and **3** showed absorption at *ca*. 1000 and 1100cm^{-1}, indicative of an unsubstituted Cp ring [5]. It is noted that the ^{1}H NMR spectra of two pairs of diastereomers **3** are obviously quite different from each other. The chemical shifts for unsubstituted cyclopentadienyl protons and methylidyne protons of enantiomers (Rp, Rc)-**3** and (Sp, Sc)-**3** are 4.00 and 4.61ppm, respectively, but those of (Sp, Rc)-**3** and (Rp, Sc)-**3** are 4.22 and 4.68ppm, respectively. The chemical shifts for methylidyne proton shifted downfield by 0.18ppm in enantiomers (Rp, Rc)-**3** and (Sp, Sc)-**3**, and by 0.25ppm in enantiomers (Sp, Rc)-**3** and (Rp, Sc)-**3**, compared with the starting materials **2**, due to intramolecular N→Hg coordination. Moreover, the signals of substituted cyclopentadienyl protons H-3, H-4 and H-5 in (Rp, Rc)-**3** and (Sp, Sc)-**3** are 4.40, 4.43 and 4.04ppm, respectively and those in (Sp, Rc)-**3** and (Rp, Sc)-**3** are 4.38, 4.47 and 4.00ppm, respectively.

Acknowledgments

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References and Notes

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2. Characterization data for (+)-R-**2**, red oil, yield 96%, $[\alpha]_D^{22}$ = +151.63 (c, 0.6, CH_2Cl_2); ^{1}H NMR (selected data) δ 4.29, 4.34 (4H, substituted Cp-ring); 4.12 (5H, unsubstituted Cp-ring); 4.43 (1H, *CH*); 1.42 (3H, CH_3). Anal. Calcd for $C_{25}H_{23}NFe$: C, 76.34; H, 5.89; N, 3.56. Found: C, 76.67; H, 6.03; N, 3.44. For (-)-S-**2**, red oil, yield 90%, $[\alpha]_D^{22}$ = -150.30 (c, 0.8, CH_2Cl_2); ^{1}HNMR (selected data) δ4.28, 4.34 (4H, substituted Cp-ring); 4.12 (5H, unsubstituted Cp-ring); 4.43 (1H, *CH*); 1.42 (3H, CH_3). Found: C, 76.12; H, 6.08; N, 3.56.
3. Selected data for (+)-(Rp, Rc)-**3**: mp. 132-133°C, $[\alpha]_D^{22}$ =+493.0 (c, 1.06, CH_2Cl_2); IR (KBr pellet): 3081, 3023, 2978, 2921, 1608, 1594, 1494, 1431, 1104, 1000, 770, 699; ^{1}H NMR (Selected data): δ 4.40 (1H, H-3), 4.43 (1H, H-4), 4.04 (1H, H-5), 4.00 (5H, H-1'), 4.61 (1H, *CH*), 1.52 (3H, CH_3); Anal. Calcd for $C_{25}H_{22}ClFeHgN$: C, 47.78; H, 3.53; N, 2.23. Found: C, 47.78; H, 3.57; N, 2.20. For (-)-(Sp, Rc)-**3**: mp. 102-103°C, $[\alpha]_D^{22}$ = -661.4 (c, 1.01, CH_2Cl_2). IR (KBr pellet): 3081, 3024, 2957, 2923, 1603, 1592, 1491, 1430, 1106, 1001, 771, 702; ^{1}HNMR (Selected data): δ 4.38 (1H, H-3), 4.46 (1H, H-4), 4.00 (1H, H-5), 4.22 (5H, H-1'), 4.68 (1H, *CH*), 1.61 (3H, CH_3); Found: C, 47.66; H, 3.38; N, 2.15. For (-)-(Sp, Sc)-**3:** mp. 132-133°C, $[\alpha]_D^{22}$ = –493.5 (c, 1.07, CH_2Cl_2). IR (KBr pellet): 3080, 3023, 2978, 2921, 1608, 1595, 1492, 1431, 1104, 1000, 770, 700; ^{1}HNMR (Selected data): δ 4.40 (1H, H-3), 4.43 (1H, H-4), 4.03 (1H, H-5), 4.00 (5H, H-1'), 4.61 (1H, *CH*), 1.52 (3H, CH_3); Found: C, 47.94; H, 3.55; N, 2.27. For (+)-(Rp, Sc)-**3:** mp. 102-103°C, $[\alpha]_D^{22}$ =+660.1 (c, 1.06, CH_2Cl_2); IR (KBr pellet): 3080, 3028, 2963, 2922, 1603, 1591, 1492, 1431, 1104, 1000, 769, 703; ^{1}HNMR (Selected data): δ 4.38 (1H, H-3), 4.47 (1H, H-4), 4.00 (1H, H-5), 4.22 (5H, H-1'), 4.68 (1H, *CH*), 1.61 (3H, CH_3); Found: C, 47.81; H, 3.64; N, 2.43.
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