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Communications

Synthesis of 1-[(R)-2'-hydroxy-1'-phenylethylamino]-7-[(R)-2''-hydroxy-1''-phenylethylimino]-1,3,5-cycloheptatriene (PGAT), a New Chiral Aminotroponimine Ligand and Its Nickel Complex

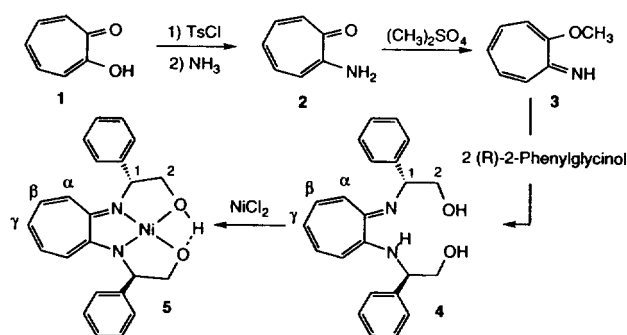
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Chiral metal complexes have been played an important role¹ in enantioselective reactions such as asymmetric hydrogenations² and Diels-Alder reactions.³ The chiral environment of the metal complex affects the transition state of the catalytic reaction to produce a chiral product from an achiral substrate. In order to achieve a good enantioselectivity in the reaction, the ligand structure has to have a good correlation with a substrate structure and a reagent to be used. Thus, many chiral metal complexes have been prepared for various enantioselective reactions.⁴

Aminotroponimines have been used as bis-chelating ligands for four coordinate metal complexes, which show interesting square planar/tetrahedral structural equilibrium dependent upon¹ the amine and imine group.⁵ A chiral aminotroponimine ligand was recently prepared and characterized.⁶ The copper complex of the ligand catalyzes enantioselective conjugate addition of Grignard reagents to enones which might be useful for the synthesis of chiral molecules.⁷ The enantioselectivity of the reaction, however, still needs to be optimized in order to be applied to the asymmetric synthesis. Thus, various chiral aminotroponimines are to be prepared and tested for the enantioselective reactions including enantioselective conjugate additions. Here, we report the synthesis of a new chiral ligand, 1-[(R)-2'-hydroxy-1'-phenylethylamino]-7-[(R)-2''-hydroxy-1''-phenylethylimino]-1,3,5-cycloheptatriene (PGAT, **4**) and its nickel complex (NiPGAT, **5**) which might be useful for asymmetric reactions and chiral recognition studies (Scheme 1).



Scheme 1. Synthesis of NiPGAT (**5**).

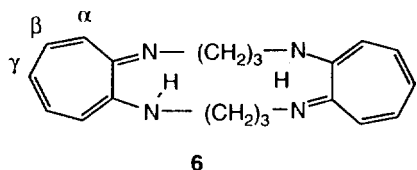
The tosyloxytropone (**3.62** mmol) prepared from the commercially available tropolone (**1**) was heated at reflux with 20% ammonia in methanol (10 mL) for 6 hours, solvent was evaporated, and the residue was chromatographed on silica gel (hexane-ethylacetate) to give aminotroponone⁸ (**2**, 3.08 mmol, 85% yield). The aminotroponone (3.08 mmol) in toluene (15 mL) was refluxed with dimethylsulfate (3.69 mmol) for 4 hours. The oily imine (**3**) separated from the solvent was dissolved in methanol, treated with (R)-2-phenylglycinol (6.77 mmol) and stirred for 2 days at room temperature. After purification by column chromatography, a yellow residue of the PGAT (**4**, 1.75 mmol, 57% yield) was obtained. The ¹H and ¹³C NMR spectra of the product was very similar to the general pattern of aminotroponimine derivatives.⁹ The molecule is symmetric with respect to C₂ axis as being evidenced from NMR spectrum. Mass spectrum of the compound confirmed the structure.¹⁰

Addition of ethanolic solution of NiCl₂ to PGAT in ethanol led to the immediate development of intense dark red color indicative of complex formation and gave a microcrystalline precipitate. ¹H NMR spectrum of the solid in CDCl₃ was similar to the non-metallated ligand.¹¹ All of the chemical shifts of the Ni complex were appeared in the diamagnetic region suggesting the energetically more favorable square planar structure of the complex,¹² and shielded except the ortho-proton of phenyl group. The shielding effect is contrast to the square planar complex of tropocoronand macrocycle (**6**) which showed deshielding effect upon the metallation

Table 1. ¹H NMR Data for ligand **4**, **6** and its Ni(II) complex

Compound	α	β	γ	C1	C2 (ppm)
4	6.29	6.66	6.16	4.75	3.96
5	5.77	6.47	6.04	2.83	3.79 (<i>trans</i>) 3.86 (<i>cis</i>)
Trop (6)	6.24	6.78	6.12		
NiTrop	6.31	6.83	6.16		

of the macrocycle.⁹

**6**

Interestingly, as shown in the Table 1, the shielding effect of Ni on the hydrogen resonances of the cycloheptatriene ring is related to the distance from the Ni atom showing the large upfield shift of α hydrogen of **5**. In the case of hydrogens on C1 and C2 carbons, the effect on C1 hydrogen is quite significant when compared to C2 hydrogens, suggesting that the distances from Ni to C1 and C2 may not be equal and the Ni atom is more tightly bounded to two nitrogen site than two oxygen site. The square planar structure of the complex can also be confirmed from the inequivalent resonances of two geminal C2 hydrogens which are identical in the non metallated ligand. The two hydrogen resonances, *cis* and *trans* to phenyl group at C1 are distinguishable based on coupling constants.¹³

The NiPGAT (**5**) showed a complexation with amino acids in solution. In U-tube comprising three layers of water (phenylalanine)/chloroform (NiPGAT)/water, the NiPGAT in CHCl₃ actively transfers phenylalanine from one water layer to another water layer. We are currently investigating the selective transfer of D- or L-form of amino acid through NiPGAT in chloroform which can be applied in the separation of D- and L-form of amino acids from a racemic mixtures.

In conclusion, we have prepared a new chiral aminotroponeimine ligand (**4**) and its nickel complex (**5**). The ligand and metal complex were identified based on various spectroscopic data. Their applications to asymmetric reactions are being under study in our laboratory.

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10. Spectral data of PGAT (**4**): UV-VIS (EtOH): λ_{max} (logε) 242 (4.14), 348 (3.84), 359 (3.83), 400 (3.74) nm; IR (KBr): 3300 (broad), 3028, 2864, 1678, 1590, 1274, 1040, 730, 700 cm⁻¹; ¹H NMR (400.13 MHz, CDCl₃): δ 3.52-3.46 (3H, s, broad), 3.96 (4H, d, J=4.4 Hz), 4.75 (2H, t, J=5.6 Hz), 6.16 (1H, t, J=10.4 Hz), 6.29 (2H, d, J=10.1 Hz), 6.66 (2H, t, J=10.2 Hz), 7.26-7.60 (10H, m) ppm; ¹³C NMR (CDCl₃): δ 62.3, 67.3, 126.8, 127.3, 127.7, 128.6, 128.8, 132.0, 153.5 ppm; MS (EI) m/z (%) 360 (28, M⁺), 329 (100), 223 (30), 209 (100), 165 (15), 131 (55), 116 (29), 103 (53), 91 (45), 79 (23), 77 (22); HRMS calcd for C₂₃H₂₄N₂O₂ 360.1838, found 360.1830.
11. Spectral data of NiPGAT (**5**): UV-VIS (CHCl₃): λ_{max} (logε) 505 (3.72), 438 (3.81), 312 (3.97), 270 (4.29) nm; IR (KBr): 724, 1132, 1229, 1516, 1581, 2871, 3022, 3400 cm⁻¹; ¹H NMR (400.13 MHz, CDCl₃): δ 2.83 (2H, d, J=9.6 Hz), 3.79 (2H, dd, J=9.6 & 5.6 Hz), 3.86 (2H, d, J=4.8 Hz), 5.77 (2H, d, J=11.2 Hz), 6.04 (1H, t, J=9.6 Hz), 6.47 (2H, dd, 9.6 & 11.2 Hz), 7.27 (2H, t, J=7.2 Hz), 7.40 (4H, t, J=7.2 Hz), 7.25-7.41 (1H, br.), 7.79 (4H, d, J=7.2 Hz) ppm; ¹³C NMR (CDCl₃): δ 63.9, 75.6, 114.3, 118.3, 126.9, 128.5, 131.6, 141.1, 164.0 ppm; Anal. Calcd for C₂₃H₂₂N₂O₂Ni: C, 66.23; H, 5.32; N, 6.72. Found: C, 65.18; H, 5.21; N, 6.47.
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Oxidative Demercuration of Cyclohexylmercury Cyanides

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Introduction of various nucleophiles to carbon-carbon double bond using soft acid is an important tool for functionali-