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Communication

Heterochiral Triangulo Nickel Complex as Evidence of a Large Positive Nonlinear Effect in Catalysis

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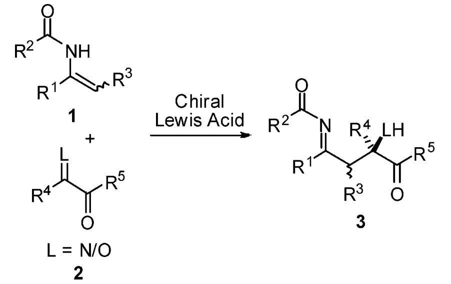
A novel triangulo complex was generated by heating, in vacuo, a racemic C_2-symmetric octahedral nickel(II) diamine complex. The trinuclear species was identified by single-crystal X-ray diffraction, which revealed a 2:1 ligand stereochemistry relationship in each unit. This solid-state structure evidences the hypothesis that a 1:2 stereochemical relationship lies at the heart of the strong positive nonlinear effect observed in enecarbamate aldol-like reactions catalyzed by nickel(II) diamine complexes.

The Lewis acid catalyzed nucleophilic addition of enecarbamates and enamides (**1**) to aldehyde, ketone, and imine electrophiles (**2**) has been exploited by us in aldol-like reactions to give compounds of the general formula **3** with some success (Scheme 1).[1−5]

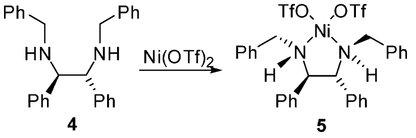
During these studies, we noted a strong positive nonlinear effect for low enantiomeric excess (ee) diamine ligand **4** (Scheme 2) in combination with nickel(II) triflate. Through a series of metal versus ligand loading experiments, we speculated that a 2:1 stereochemical relationship lies at the heart of the deactivated species.[4]

In this Communication, we present crystal structure evidence for the formation of a related heterochiral trinuclear complex that displays the predicted 2:1 ligand enantiomer ratio and the catalytic activity is probed.

Scheme 1. General Asymmetric Lewis Acid Catalyzed Reaction of Eneamide/carbamate (**1**) with a Chelating Electrophile



Scheme 2. Preparation of Catalytically Active Nickel Triflate Species



A racemic bis(aquo)nickel(II) triflate complex of **4** was previously reported (from easy to prepare **7a**), and the X-ray structure was obtained.[4] *Chiral relay*[6] from the stereogenic benzyl positions to the *chiral by coordination*[7−9] N atoms was completely efficient. Relay of stereochemical information to nitrogen is presumed in many cases; the reports of Pelz et al. demonstrate the important role that nitrogen's chirality plays in asymmetric transformations mediated by diamine complexes.[7,10]

Prompted by the ease of synthesis of the nickel(II) bromide complex [**7a**; X-ray diffraction (XRD); Figure 1], preparation of the nickel(II) iodide complex was attempted under the same conditions (Scheme 3).[4,11,12]

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(1) Matsubara, R.; Vital, P.; Nakamura, Y.; Kiyohara, H.; Kobayashi, S. *Tetrahedron* **2004**, *60*, 9769−9784.

(2) Matsubara, R.; Nakamura, Y.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3258−3260.

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(4) Fossey, J. S.; Matsubara, R.; Vital, P.; Kobayashi, S. *Org. Biomol. Chem.* **2005**, *3*, 2910−2913.

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(6) Bull, S. D.; Davies, S. G.; Epstein, S. W.; Leech, M. A.; Ouzman, J. V. A. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2321−2330.

(7) Pelz, K. A.; White, P. S.; Gagné, M. R. *Organometallics* **2004**, *23*, 3210−3217.

(8) Pelz et al. detailed the first example of chiral only at nitrogen coordination complexes displaying stable central chirality in the absence of other forms of stereocontrol (coordinational chirality); these workers showed that coordinationally chiral nitrogen could impart asymmetry in catalysis and elegantly demonstrated the survival of stereochemical information. Johansson et al. have more recently examined potential chirality by coordination diamine complexes of Co, Ni, Cu, and Zn.

(9) Johansson, A.; Wingstrand, E.; Håkansson, M. *Inorg. Chim. Acta* **2005**, *358*, 3293−3302.

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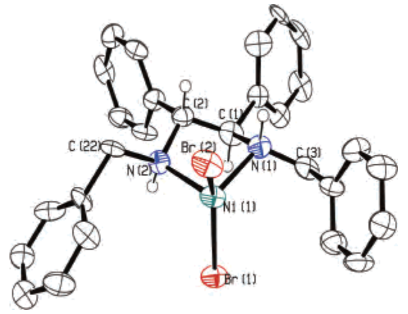


Figure 1. Representation of the crystal structure of **7a**.

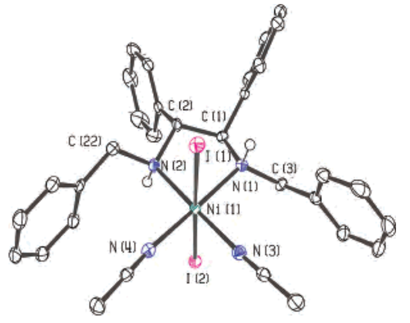
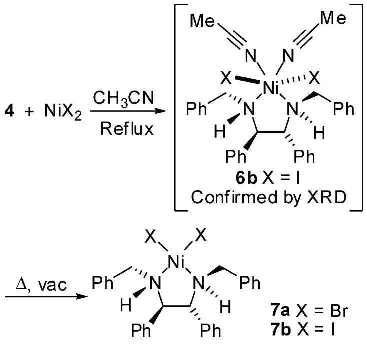


Figure 2. Representation of the crystal structure of **6b**.

Scheme 3. Nickel(II) Bromide and Iodide Complexes of Diamine **4**



When nickel(II) iodide was employed in the complexation reaction with ligand **4**, compound **6b** was obtained in quantitative yield. In the case of racemic **4**, crystals suitable for XRD analysis were obtained for the intermediate **6b** and a *triangulo* structure for **7b** was identified by XRD analysis (see Figures 2 and 3, respectively).

The bis(acetonitrile) complex **6b** was dried in vacuo at 85 °C until constant mass (correlating to acetonitrile loss), with a concomitant color change from green to dark brown.

This material was recrystallized from nonanhydrous CH_2Cl_2/hexane, a stable trinuclear species containing two μ^3-O atoms and an I_3^- counterion was confirmed by XRD analysis (Figure 3). Related *triangulo* structures have been reported for Ni(tmeda) complexes by Handley et al., who also commented upon an equilibrium between monomeric and trimeric solution structures.[13] Sacconi et al. noted that similar achiral nickel(II) bromide and iodide ethylenediamines were particularly sensitive to water and deduced a pseudotetrahedral geometry at nickel.[14] Polynuclear nickel(II) and copper(II) oxime complexes containing μ^3-O atoms were also reported in context to their magnetic properties.[15]

XRD data obtained from **7b** (racemic **4**) initially appeared to show a high level of disorder. Further inspection revealed a trinuclear species, depicted in Figure 3. The asymmetric unit in this structure consists of half of a cation and half of an anion. The remaining portion of the cation is generated by a 2-fold crystallographic rotation axis on which I(1) and Ni(2) are located. In the anion, the central iodine [I(2)] is similarly located at a special position, in this instance an inversion center.

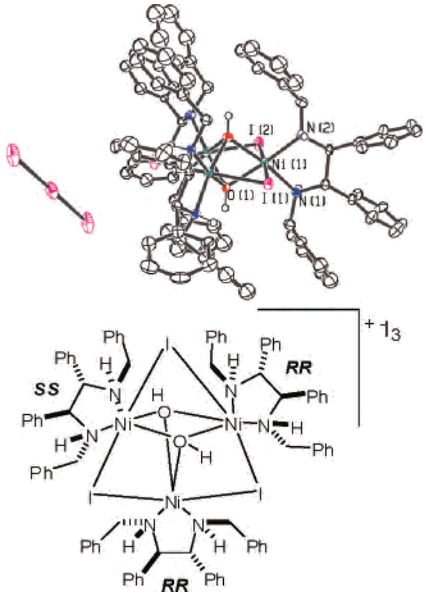


Figure 3. Representation of the crystal structure of **7b** prepared from racemic ligand **4**.

That this *triangulo* structure contains a 2:1 ratio of enantiomers of ligand **4** is strong corroboratory evidence for a trinuclear species forming in catalysis with a low-ee ligand, resulting in an effective high ee of the *active* catalyst in solution.[16] In our hands, attempts to prepare analogous trinuclear complexes from single enantiomer ligand **4** failed, also suggesting that the heterochiral complexes are more favored.

Both single enantiomer and racemic nickel(II) bromide and iodide complexes were evaluated as asymmetric catalysts for enecarbamate addition to a ketone (Scheme 4). The reaction to **3a** proceeded in moderate yield catalyzed by (*RR*)-**7a** and (*RR*)-**7b** (78% and 48%, respectively), whereas complexes prepared from a racemic ligand failed to catalyze the reaction under the same conditions. While the ee obtained was not

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(11) Racemic nickel(II) bromide complex **7a** was obtained in up to 98% crude yield as a single enantiomer; recrystallized material was stable to ambient conditions, handled in air, and stored in a desiccator.

(12) We found that racemic complexes provided better quality crystals; XRD data in this report were obtained from analogously prepared racemic complexes.

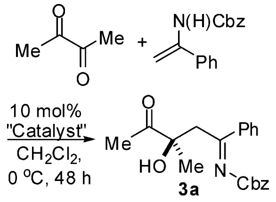
(13) Handley, D. A.; Hitchcock, P. B.; Leigh, G. J. *Inorg. Chim. Acta* **2001**, *314*, 1−13.

(14) Sacconi, L.; Bertini, I.; Mani, F. *Inorg. Chem.* **1967**, *6*, 262−267.

(15) Jiang, Y.-B.; Kou, H.-Z.; Wang, R.-J.; Cui, A.-L.; Ribas, J. *Inorg. Chem.* **2005**, *44*, 709−715.

(16) In a previous report,[4] we suggested that the origin of the large positive nonlinear effect that we observed for the same reaction with a differently derived catalyst might be due to heterochiral interactions at one metal or between more than one metal and speculated a 2:1 heterochiral interaction might be important.

Scheme 4. Nickel(II) Bromide and Iodide Catalyzed Enecarbamate Addition to a Ketone To Afford **3a**



"Catalyst"	Yield (%)	e.e.*(%)
(*RR*) **7a**	78%	26%
(*RR*) **7b**	48%	29%
(*rac*) **7a**	No reaction	
(*rac*) **7b**	No reaction	

**Determined after hydrolysis of imine*

high (<30%), that asymmetric induction from the nickel halide complexes is observed was gratifying and is being further investigated in our laboratories. That racemic complexes **7a** and **7b** do not catalyze the reaction provides evidence for a common mode of heterochiral interaction, leading to deactivation in this and our previously reported nickel(II) triflate diamine complex catalyzed reaction.

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Supporting Information Available: Synthetic procedures, lists of key X-ray data, and CIF files for ORTEP plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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