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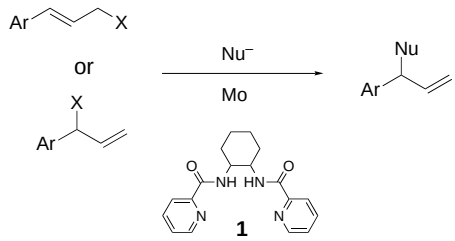
[28] Additional interaction of an NH_3^+ group with the phenyl group of the neighboring guest moiety by cation – π interactions might also contribute to the observed cooperativity. However, it seems likely that solvent molecules in the first solvation shell play an important role in these interactions, because modeling studies indicate that direct contact between two complexed acid molecules is rather unlikely.

Designed Ligands as Probes for the Catalytic Binding Mode in Mo-Catalyzed Asymmetric Allylic Alkylation**

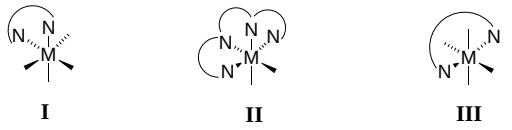
Barry M. Trost,* Kalindi Dogra, Iwao Hachiya, Takashi Emura, David L. Hughes,* Shane Krska, Robert A. Reamer, Michael Palucki, Nobuyoshi Yasuda, and Paul J. Reider

Asymmetric allylic alkylation has been developing significantly over the past several years.[1] Among the metals capable of effecting such reactions are palladium,[2] molybdenum,[3] and tungsten.[4] In contrast to these metals, in which the chirality of some substrates, notably vinylcarbinols of the type shown in Equation (1), is lost, iridium,[5] rhodium,[6] and ruthenium[7] normally retain the optical purity of such starting substrates. In spite of these many studies, very little is known about the structure of the active complex in the catalytic cycle. The case of Mo is quite intriguing. The catalyst system based on ligand **1**[8] has shown extraordinary levels of regio- and enantioselectivity, even at elevated temperatures (80 – 100 °C) [Eq. (1)].[3a] Furthermore, the reactions were qualitatively significantly faster than in the previously reported achiral reactions.[9] How such a seemingly flat system is able to provide such high selectivities has stimulated the development of an understanding of its binding mode. Although the direct characterization of π-allyl – metal complexes is certainly desirable, the relevance of these isolable/observable complexes to the catalytic cycle is not assured. Herein we adopted an indirect probe of the question of the binding of this ligand to Mo during the catalytic cycle which has led to a totally unexpected result.

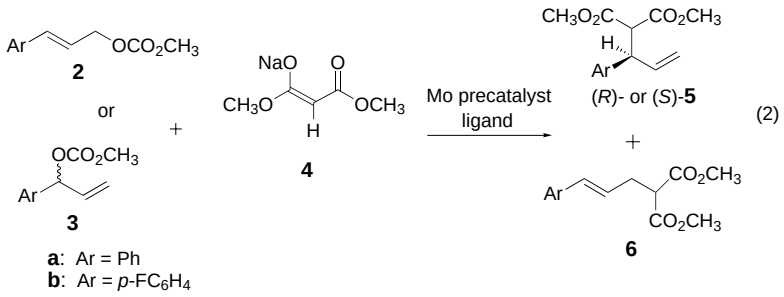


(1)

In the original design, three binding modes **I**—**III** for these octahedral metals were considered. Conceptually, it was postulated that binding mode **I**, while the most common,



would have less probability of inducing high enantiomeric excesses in asymmetric allylic alkylations than **II** and **III**. The reaction depicted in Equation (2) was employed to evaluate



(2)

the ligands. Several ligands were evaluated, and their effectiveness compared with that of **1** as the standard ligand (Table 1, entries 1, 2, and 12).

In initial studies, one of the two picolinamide units was replaced with a nicotinamide group (see **7**). Surprisingly, the regio- and enantioselectivities were slightly better than with the standard ligand **1**, although the reactions were slower (Table 1, entry 3). Since it seemed that the nitrogen atom of the nicotinamide group could not participate in the binding, the simple benzamide ligand **8** was examined. In agreement with the above hypothesis, the reaction of ligand **8** with the achiral substrate **2** (Table 1, entry 4) gave the same results as the reaction of ligand **7** with **2** (Table 1, entry 3). Interestingly, better selectivities were obtained in the reaction of ligand **8** with chiral racemic substrate **3** (Table 1, entry 5) than in the

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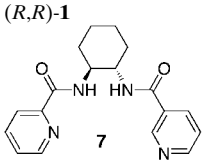
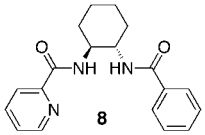
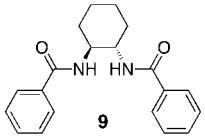
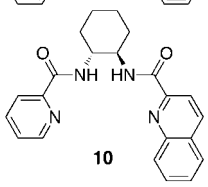
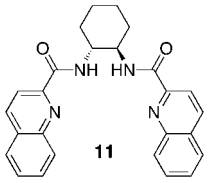
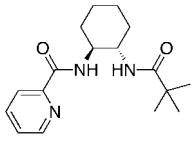
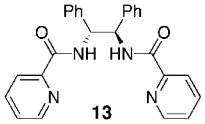
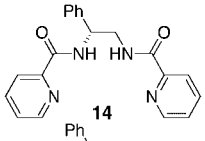
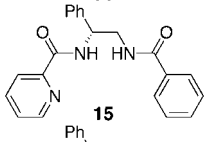
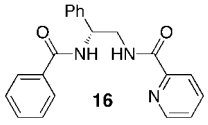
Table 1. Ligand effects in the Mo-catalyzed asymmetric allylic alkylation with sodium dimethyl malonate.

Entry	Ligand	Substrate	Yield	**5/6**	% *ee*
1a	(*S*,*S*)-**1**	**2a**	95	35	97 (*R*)
1b	(*R*,*R*)-**1**	**2a**	90	28	99 (*S*)
2a	(*S*,*S*)-**1**	**3a**	93	25	87 (*R*)
2b[b]	(*R*,*R*)-**1**	**3a**	70	13	92 (*S*)
3	 **7**	**2a**	93	46	99 (*R*)
4	 **8**	**2a**	90	60	99 (*R*)
5		**3a**	90	53	92 (*R*)
6	 **9**	**2a**	35	1	24 (*R*)
7[b]	 **10**	**2a**	29	19	98 (*S*)
8[b]	 **11**	**2a**	traces	–	–
9	 **12**	**2a**	95	30	98 (*R*)
10		**3a**	88	28	88 (*R*)
11	 **13**	**2a**	95	19	99 (*S*)
12	(*R*,*R*)-**1**	**2b**	93	13	96 (*S*)
13		**2b**	84	10	94 (*S*)
14	 **14**	**2b**	92	6	91 (*S*)
15	 **15**	**2b**	43	9	77 (*S*)
16	 **16**	**2b**	72	8	90 (*S*)

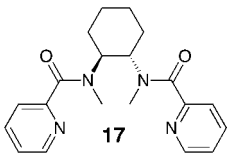
[a] $(C_7H_8)Mo(CO)_3$ was employed as the precatalyst in all reactions, unless otherwise indicated. The reactions were performed by adding sodium hydride (2 equiv) and dimethyl malonate (2.1 equiv) to a solution of allyl substrate (1 equiv) in THF (0.1M). [b] $(CH_3CH_2CN)_3Mo(CO)_3$ was used as precatalyst.

reaction of standard ligand **1** with **3** (Table 1, entry 2). Removal of both pyridine nitrogen atoms (e.g. bisbenzamide **9**) led to a very poor ligand in terms of rate and selectivity (Table 1, entry 6).

Steric factors also play a role in the effectiveness of a ligand. When a picolinamide unit of **1** is replaced by one or two quinoline analogues (**10** (Table 1, entry 7) and **11** (Table 1, entry 8), respectively), much lower reaction rates were observed, although ligand **10** was highly enantioselective. A similar observation was recently reported by Moberg and coworkers who used the methyl-2-picolinamide ligand.[3c,d] When a pivalamide group (see **12**) was used instead of a picolinamide group, good selectivities were still observed (Table 1, entries 9 and 10) but with a further decrease in rate (fourfold slower than the reaction with the standard ligand **1**). A ligand with a different backbone (e.g. stilbenediamine **13**) gave comparable results as **1** (Table 1, entry 11), with a decrease in the branched/linear (**5/6**) ratio.

Substrate **2b** showed similar behavior with the standard ligand **1** (Table 1, entry 12). The stilbenediamine ligand **13** gave slightly poorer selectivity (Table 1, entry 13). Removing the symmetry in the chiral backbone (see **14**) led to a reaction that was twice as fast, but with diminished regio- and enantioselectivity (Table 1, entry 14). The effect of the position of the picolinamide and the benzamide groups in the unsymmetrical ligand was investigated (**15** (Table 1, entry 15) vs. **16** (Table 1, entry 16)). As anticipated, different results in terms of rate, regioselectivity, and enantioselectivity were observed. Interestingly, ligand **16** gave significantly better results than ligand **15**.[10]

The role of the secondary amides was probed by using ligands **17** and **18**. The former generated a catalyst that was 200-fold less active than **1** and gave very poor enantioselectivities; the latter did not lead to any observable reaction.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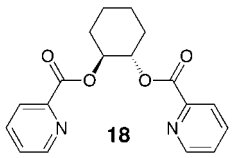
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These observations led us to suspect that the secondary amide ligands were deprotonated under the basic conditions of the reaction. This suspicion was supported by deprotonating the ligand with tritylllithium and then forming the catalyst. The results of the reaction of substrate **2a** were identical to those of Table 1, entry 1 within experimental error.

The ligand study provides the first picture of the type of coordination involved. Contrary to our initial working hypothesis, bidentate coordination of the two pyridine nitrogen atoms of ligand **1** is clearly not involved. This conclusion also contradicts the recent structural studies of bisoxazolidine chiral ligands for Mo.[11] The efficiency of ligands **8** and **12** indicates that only one pyridyl nitrogen atom of ligand **1** is involved. Furthermore, either the dianion or the monoanion of the two secondary amides appears to be involved. Scheme 1 depicts several reasonable potential monoanionic complexes.

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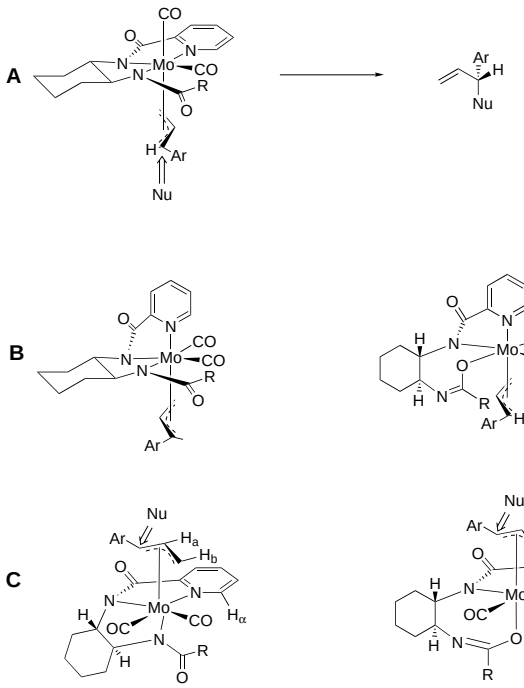
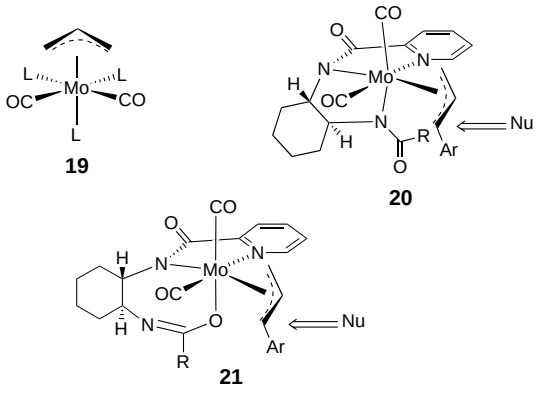


Scheme 1. Possible binding modes of the ligands.

NMR spectroscopic studies of the π-allyl complex formed from ligand **8**, [Mo(CO)$_4$(norbornadiene)], and linear carbonate **2** in [D$_8$]THF reveal a monoanionic complex as the major species in solution. In the ^{15}N NMR spectrum of this complex, the amide nitrogen atoms give rise to signals at $\delta = 130$ and 175 ppm and the pyridine nitrogen atom results in a signal at $\delta = 263$ ppm; for the free ligand, signals are found at $\delta = 118$, 119, and 304 ppm, respectively. The $\delta = 175$ ppm resonance of one of the amide nitrogen atoms, the absence of a signal for one NH proton in the ^{1}H NMR spectrum, as well as proton coupling data clearly indicate that one amide is deprotonated in the complex. The other amide is still protonated, but the downfield shifts of the signal for the nitrogen atom in the ^{15}N NMR spectrum and of the signal for the NH proton in ^{1}H NMR spectrum relative to the uncomplexed ligand suggest that this amide is also involved in coordination to Mo in the complex. The complex shows NOE interactions between H$_a$ and H$_b$ of the allyl moiety (see Scheme 1, **C**), and the picoline hydrogen (H$_\alpha$) at C6, which effectively rules out structures **A** and **B** in Scheme 1 since the π-allyl moiety is too far removed from the pyridine ring in these structures to give rise to NOE interactions. Furthermore, the other two protons of the allyl moiety (not shown for clarity) show NOE interactions with each other and correlations to both CO groups.

Theoretical calculations on allyl (dicarbonyl) molybdenum complexes suggest a strong bias for structures like **19**.[12] Structures **20** and **21** meet this requirement, fit all the other data, and also rationalize the regio- and enantioselectivities. The ligands studied to date reveal that one binding position does involve both nitrogen atoms of a picolinamide unit; the binding of the remote amide then provides the additional rigidification required for the high chiral recognition and reactivity. The presence of good donor ligands (anionic amides) and acceptor ligands (CO) provides a good balance for alkene coordination (which is facilitated by acceptor ligands) and for ionization (which is facilitated by donor ligands). Although further studies are clearly required to establish the structure of the catalytically active species, the current results implicate an unusual coordination mode and reveal that the ligands have much broader potential than originally suggested. Furthermore, monopicolinamide ligands (e.g. **8** and **12**) are the best ligands for maximum regio- and enantioselectivity with the chiral racemic substrates, although at the expense of rate. The ability to design new ligands for octahedral complexes has now been greatly expanded.



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Creation of a Unique Self-Supported Pattern of Radially Aligned Semiconductor Ag_2S Nanorods**

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Novel technologies based on nanoscale machines and devices will bring us a new world.[1] The key to realizing this nanotech world is to devise simple and efficient methods to create patterns of well-arranged nanocrystallites.[2] Recent research on metal and semiconductor nanostructures is expanding rapidly into the assembly of nanoparticles in two- (2D) and three-dimensional (3D) ordered superstructures.[3] A range of methods, including solvent evaporation of hydrophobic colloids,[4] molecular cross-linking in colloidal aggregates,[5] and biotemplate-directed synthesis,[6] have been reported, and they usually require the synthesis of initial nanoparticles with uniform size. One-dimensional (1D) nanostructures are of particular interest because of their potential in fundamental research and industrial applications.[7] The synthesis of nanorod arrays, especially the creation of aligned nanorods with novel patterns on surfaces, is considered to be a definitive step towards the fabrication of advanced electronic and opto-electronic nanodevices.[8] However, due to the anisotropic structure of nanorods, the oriented growth of nanorods on surfaces is difficult and usually requires solid templates, such as porous alumina,[9] polymer nanotubes,[10] and patterned catalysts,[11] to control the directional growth. Mostly substrates such as silicon wafers, Al_2O_3 membranes, and polycrystal glass plates are used to sustain nanorod growth.[12] The development of simple, mild, and effective methods for creating novel assemblies of 1D metal or semiconductor nanostructures on heterogeneous substrates, or even on self-generated homogeneous substrates, is of importance to nanotechnology and remains a key research challenge.

Here we demonstrate a room-temperature solution-growth method to synthesize of a self-supported pattern of radial semiconductor Ag_2S nanorod arrays with only $AgNO_3$, thiourea (Tu), and NaOH as the reagents. To the best of our knowledge, this is the first self-supported growth of Ag_2S nanorods. The reaction between $AgNO_3$ and Tu to form an unstable Ag-Tu complex has been well studied.[13] Our strategy is based on the experimental finding that basic conditions accelerate the decomposition of Tu.[14] We induce the reaction of $AgNO_3$ and Tu under basic conditions to control the decomposition rate of the complex and hence the nucleation and growth rates of crystalline Ag_2S. This synthetic process is very simple and mild, free of any templates (either membranes or surfactants), and provides a novel method for low-temperature homogeneous growth of 1D nanostructures and their simultaneous assembly into patterns.

The formation of the crystalline Ag_2S phase was established from X-ray diffraction (XRD) pattern (Figure 1). All peaks can be indexed to monoclinic Ag_2S with lattice constants comparable to the values of JCPDS card 14-72, and no impurities can be detected in this pattern, which indicates that crystalline Ag_2S is formed from solution at room temperature.

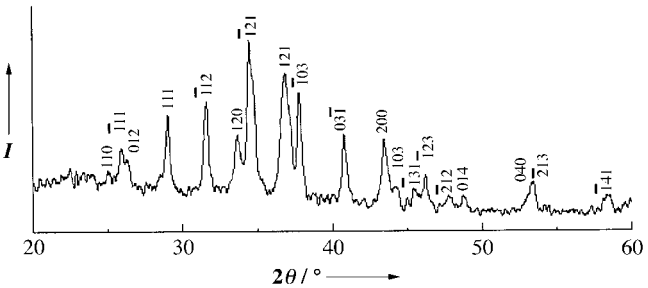

Figure 1. XRD pattern of the Ag_2S nanorod arrays.

The product morphology and chemical composition were determined by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Figure 2 shows the unusual structure of radially aligned Ag_2S nanorods grown on a flakelike substance. The flakes usually have an irregular morphology with size up to dozens of micrometers, on which a large number of Ag_2S nanorods grow radially from one center. The nanorods have nonuniform diameters in the range of 50 to 200 nm and lengths of up to several micrometers. The Ag_2S nanorods at the radial center are slightly wider and longer than those at the edge. The EDS spectra (not shown) of the Ag_2S nanorods and flakes show strong silver and sulfur signals with Ag:S ratios of 2.00:1.03 and 2.04:1.00, respectively, which indicate stoichiometric relations between Ag and S in both the nanorods and the flakelike material. These results clearly indicate the formation of a distinctive radial pattern of aligned Ag_2S nanorods on self-provided Ag_2S flakes.

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