

# Diastereoselective 1,2 Additions of Nucleophiles to Quinoline Complexes of the Chiral Rhenium Lewis Acid $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+$

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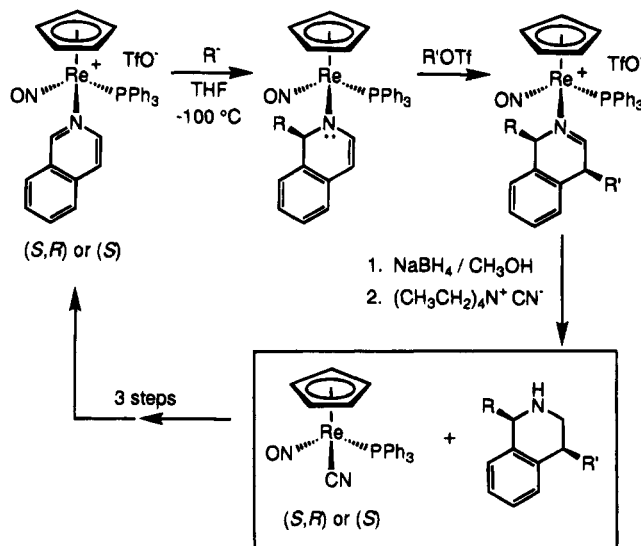
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The racemic or optically active quinoline complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NC}_9\text{H}_7)]^+\text{TfO}^-$  (**1**) and  $\text{RLi}$  ( $\text{R} =$  (a)  $\text{CH}_2\text{Si}(\text{CH}_3)_3$ , (b)  $\text{CH}_3$ , (c)  $\text{C}_6\text{H}_5$ ) rapidly react in THF at  $-80^\circ\text{C}$  to give the 1,2 addition products  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NCH}(\text{R})\text{CH}=\text{CHC}(\text{CH}_3)_4\text{C})$ , which contain new carbon stereocenters. Under optimum conditions, diastereoselectivities are  $\geq 92\%$ . Subsequent reactions with HOTf give mixtures of amine complexes (**3**) and alkene complexes (**4**) of the formulas  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NHCH}(\text{R})\text{CH}=\text{CHC}(\text{CH}_3)_4\text{C})]^+\text{TfO}^-$ . The latter dominate at equilibrium. The crystal structure of **4c** establishes the carbon configurations, which are consistent with  $\text{RLi}$  attack from a direction *anti* to the bulky  $\text{PPh}_3$  ligand in **1**. Reaction of (*S*)-**1** and  $(\text{CH}_3)_2\text{CHMgCl}$  at  $-80^\circ\text{C}$  gives the 1,4 addition product  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NCH}=\text{CHCH}(\text{CH}(\text{CH}_3)_2)\text{C}(\text{CH}_3)_4\text{C})$  as a 66:34 mixture of diastereomers. Reaction with HOTf gives the imine complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{N}=\text{CHCH}_2\text{CH}(\text{CH}(\text{CH}_3)_2)\text{C}(\text{CH}_3)_4\text{C})]^+\text{TfO}^-$ . Stereochemical features of the preceding compounds and transformations are analyzed in detail.

Chiral hydroquinoline moieties occur in a variety of natural products, drug candidates, and chiral auxiliaries.<sup>1,2</sup> However, there have been few prior efforts to effect enantioselective syntheses.<sup>3</sup> We wondered whether protocols could be developed starting from the parent compound quinoline, which is very inexpensive<sup>4</sup> and easily functionalized at nitrogen. In particular, we were attracted by the potential of chiral transition metal auxiliaries, which often activate unsaturated organic molecules or fragments toward nucleophilic or electrophilic additions.

We have recently shown that the chiral rhenium Lewis acid  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+$  (**I**) activates isoquinoline toward sequential diastereoselective nucleophilic and electrophilic additions, as summarized in Scheme 1.<sup>5</sup> Both 1-alkyl- and 1,4-dialkyl-1,2,3,4-tetrahydroisoquinolines can be isolated in high chemical yields and enantiomeric purities. The rhenium fragment is easily recycled with retention of configuration. We sought to determine if similar procedures could be

**Scheme 1. Diastereoselective Additions of Nucleophiles and Electrophiles to Isoquinoline Mediated by the Chiral Rhenium Lewis Acid I**



applied to related nitrogen heterocycles. Importantly, the quinoline complex of **I**,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NC}_9\text{H}_7)]^+\text{TfO}^-$  (**1**),<sup>6,7</sup> has been prepared in racemic and enantiomerically pure forms and characterized crystallographically.

In this paper, we report that **1** and selected alkyl-lithium reagents react to give 1,2 addition products with

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(2) Ito, K.; Katsuki, T. *Tetrahedron Lett.* **1993**, *34*, 2661.

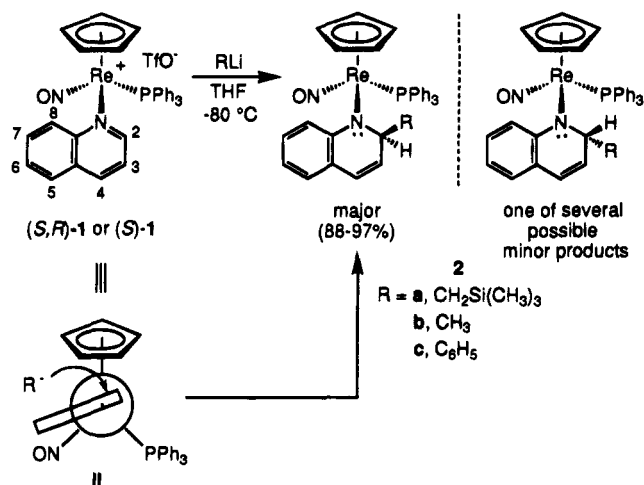
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(4) A recent catalog price: \$101.25/3 kg, or \$4.36/mol.

(5) Richter-Addo, G. B.; Knight, A. D.; Dewey, M. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 11863.

(6) Abbreviations: (a)  $\text{NC}_9\text{H}_7$  = quinoline; (b)  $\text{OTf}$  =  $\text{OSO}_2\text{CF}_3$ .

(7) Dewey, M. A.; Knight, D. A.; Arif, A. M.; Gladysz, J. A. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1992**, *47*, 1175.

**Scheme 2. Additions of Alkylolithium Reagents to Quinoline Complex 1**


$\geq 92\%$  diastereoselectivities. Subsequent protonation initiates novel, unanticipated rearrangements, leading to alkene complexes of the heterocyclic moiety. A crystal structure establishes the carbon configurations. The mechanism of asymmetric induction, and certain stereochemical features of the products, are analyzed in detail. In one related reaction, 1,4 addition occurs. However, the diastereoselectivity in this case is modest.

## Results

**1. Alkylolithium Additions to Coordinated Quinoline.** Yellow-orange THF solutions of the racemic or enantiomerically pure quinoline complexes **1** or  $(S)$ -**1**<sup>7</sup> were treated with alkyl- or aryllithium reagents RLi (1.0–1.5 equiv; R = (a)  $\text{CH}_2\text{Si}(\text{CH}_3)_3$ , (b)  $\text{CH}_3$ , (c)  $\text{C}_6\text{H}_5$ ) under a variety of conditions at  $-80\text{ }^\circ\text{C}$  (Scheme 2). The solutions turned deep red, characteristic of amido and enamido complexes of **I**,<sup>5,8</sup> and  $^{31}\text{P}$  NMR spectra were recorded. One major resonance (88–97%) and one to three minor resonances were observed. This, together with other data below, was taken as evidence for the diastereoselective generation of amido complexes ( $\eta^5\text{-C}_5\text{H}_5$ ) $\text{Re}(\text{NO})(\text{PPh}_3)(\text{NCH}(\text{R})\text{CH}=\text{CHC}(\text{CH}_3)_4)$  (**2**), which

contain new carbon and nitrogen stereocenters.<sup>9</sup> The dominant addition regiochemistry—1,2 as opposed to 1,4—was established as described below. Previous studies have shown that the nitrogens in amido complexes of **I** undergo rapid inversion ( $\Delta G^\ddagger$  ( $-102\text{ }^\circ\text{C}$ ) 7.8 kcal/mol for methyl exchange,  $-\text{N}(\text{CH}_3)_2$ ).<sup>8</sup>

Key details for each addition were as follows. When  $(S)$ -**1** and  $(\text{CH}_3)_3\text{SiCH}_2\text{Li}$  were combined in an NMR tube at  $-80\text{ }^\circ\text{C}$ , reaction was 95% complete after 10 min. Four new  $^{31}\text{P}$  resonances appeared at 23.3, 20.1, 19.4,

and 14.7 ppm (88:1:7:4;<sup>11</sup> probe temperature  $-100\text{ }^\circ\text{C}$ ).<sup>12</sup> The first was assigned to the major configurational diastereomer of **2a**. Configurational diastereomers of analogous isoquinoline addition products (Scheme 1) give chemical shifts that differ by 5–6 ppm.<sup>5</sup> Thus, the remaining resonances may correspond to other diastereomers, regioisomers, or other types of byproducts. When the probe was warmed to  $-20\text{ }^\circ\text{C}$ , only three resonances were detected (20.7, 18.9, 15.0 ppm; 86:9:5). When the probe was cooled to  $-100\text{ }^\circ\text{C}$ , four resonances were again observed (23.3, 20.2, 19.4, 14.7 ppm; 84:2:8:5).

Aliquots from preparative reactions of racemic **1** and  $(\text{CH}_3)_3\text{SiCH}_2\text{Li}$  ( $-80\text{ }^\circ\text{C}$ ) gave four analogous  $^{31}\text{P}$  resonances (23.1, 20.1, 19.4, 14.7 ppm; 92:1:4:3; probe temperature  $-100\text{ }^\circ\text{C}$ ). When the probe was warmed to  $-20\text{ }^\circ\text{C}$ , three resonances were again observed (20.7, 18.9, 15.0 ppm; 93:4:3). Since racemic **1** is much less soluble than  $(S)$ -**1**, these reactions were conducted under more dilute conditions. This would be one of several possible explanations for the slightly different product ratios.

When  $(S)$ -**1** and  $\text{CH}_3\text{Li}$  were combined in an NMR tube at  $-80\text{ }^\circ\text{C}$ , reaction was complete after 15 min. Four new  $^{31}\text{P}$  resonances appeared at 23.6, 17.3, 17.0, and 15.1 ppm (92:6:1:1; probe temperature  $-100\text{ }^\circ\text{C}$ ).<sup>12b</sup> The first was assigned to the major configurational diastereomer of **2b**. When the probe was warmed to  $-20\text{ }^\circ\text{C}$ , four resonances were still present (21.8, 17.6, 17.2, 15.5 ppm; 90:3:5:2). When the probe was warmed to  $20\text{ }^\circ\text{C}$ , only two resonances remained (20.7, 16.9 ppm; 93:7). When the probe was cooled to  $-100\text{ }^\circ\text{C}$ , four resonances were again observed (23.6, 17.3, 17.0, 15.1 ppm; 92:5:2:1).

An analogous preparative reaction was conducted with racemic **1**. Solvent was removed under oil pump vacuum as the sample was warmed. The residue was extracted with  $\text{THF-}d_8$  at  $-80\text{ }^\circ\text{C}$ . A  $^{31}\text{P}$  NMR spectrum ( $-20\text{ }^\circ\text{C}$ ) showed four resonances (21.8, 17.6, 17.2, 15.5 ppm; 94:1:4:1). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were consistent with the structure **2b**, as summarized in the Experimental Section. In particular, the  $^1\text{H}$   $\text{CH}_3$  resonance was markedly shielded ( $\delta$  0.45), suggesting close proximity to the  $\text{PPh}_3$  phenyl rings.

When  $(S)$ -**1** and  $\text{C}_6\text{H}_5\text{Li}$  were combined in an NMR tube at  $-80\text{ }^\circ\text{C}$ , reaction was complete after 10 min. Two new  $^{31}\text{P}$  resonances appeared at 17.6 and 14.5 ppm (11:89, probe temperature  $-100\text{ }^\circ\text{C}$ ). The second was assigned to the major configurational diastereomer of **2c**. When the probe was warmed to  $-50\text{ }^\circ\text{C}$ , two more resonances were detected (19.9, 18.2, 17.6, 15.4 ppm; 1:4:10:85). The relative areas of these peaks varied somewhat as the probe was cooled ( $-100\text{ }^\circ\text{C}$ ), warmed again ( $0\text{ }^\circ\text{C}$ ), and cooled ( $-100\text{ }^\circ\text{C}$ ). However, the upfield resonance was always dominant. Aliquots from preparative reactions utilizing racemic **1** ( $-80\text{ }^\circ\text{C}$ ) exhibited only the two major resonances (17.6 and 14.5 ppm, 3:97,  $-100\text{ }^\circ\text{C}$ ; 17.6 and 15.4 ppm, 3:97,  $-50\text{ }^\circ\text{C}$ ). Thus, under optimum conditions all of the preceding additions give

(11) All diastereomer ratios are normalized to 100, and error limits on each component are  $\pm 2$  (86:14 = (86  $\pm$  2):(14  $\pm$  2)).

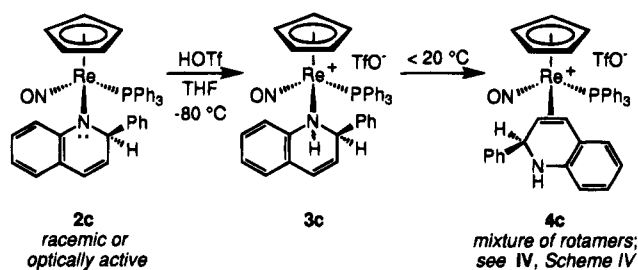
(12) (a) This experiment has been repeated several times. Sometimes small amounts of a transient were observed, at either  $-100\text{ }^\circ\text{C}$  (25.6 ppm, 1–5%), or  $-20\text{ }^\circ\text{C}$  (23.0, 5%). The former did not reappear when warmed samples were recooled. (b) A similar species appeared in some reactions of  $(S)$ -**1** and  $\text{CH}_3\text{Li}$  (25.1 ppm, 3%,  $-100\text{ }^\circ\text{C}$ ).

(8) Dewey, M. A.; Knight, D. A.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1992**, *125*, 815.

(9) Since the  $R/S$  designations of the  $\text{CH}=\text{CH}-\text{CHR}$  stereocenters in **2–4** vary with the R group ( $\text{CH}_2\text{Si}$ ,  $\text{C}_6\text{H}_5$  >  $\text{CH}=\text{CH}$  but  $\text{CH}=\text{CH}$  >  $\text{CH}_3$ ), the use of Cahn–Ingold–Prelog nomenclature is kept to a minimum in this paper. For **4c**, the rhenium configuration is specified first, followed by those of the  $\text{CH}=\text{CH}-\text{CHPh}$ ,  $\text{CH}=\text{CH}-\text{CHPh}$ , and  $\text{CH}=\text{CH}-\text{CHPh}$  carbons (order of Cahn–Ingold–Prelog priority). The  $R/S$  conventions for rhenium,<sup>5,7</sup> and =CHR stereocenters of alkene complexes of **I**,<sup>10</sup> have been described previously.

(10) (a) Pu, J.; Peng, T.-S.; Mayne, C. L.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2686. (b) Peng, T.-S.; Pu, J.; Gladysz, J. A. *Organometallics* **1994**, *13*, 929.

## Scheme 3. Protonation of Amido Complex 2c



only major configurational diastereomers depicted

greater than 92% selectivity for a single Re,C configurational diastereomer—a high level of 1,2 asymmetric induction.

**2. Protonation of Amido Complex 2c.** Previous studies have established that amido and enamido complexes of **I** epimerize at rhenium between room temperature and 60 °C.<sup>5,8,13</sup> The mechanism involves PPh<sub>3</sub> dissociation with anchimeric assistance of the nitrogen lone pair.<sup>14</sup> The exact rate is highly substrate-dependent. Thus, we sought to N-protonate the preceding compounds to the corresponding hydroquinoline complexes, which should be configurationally stable, even at elevated temperatures.<sup>5,15</sup> However, this concurrently generates a nonlabile nitrogen stereocenter, potentially doubling the number of diastereomers and thereby complicating product analysis.

The amido complex **2c** was generated as described above for (*S*)-**1** in an NMR tube (17.7, 14.5 ppm; 11:89) and treated with triflic acid (HOTf; 2 equiv) at -80 °C, as shown in Scheme 3. A <sup>31</sup>P spectrum (-60 °C) showed eight new resonances (12:2:2:9:23:23:27:2). The first four had chemical shifts that were plausible for amine complexes of **I** (**3c**; 19.7, 18.8, 18.0, 15.0 ppm).<sup>5,15</sup> The second four, which were dominant, were in an upfield region typical of alkene complexes of **I** (**4c**; 8.9, 6.8, 6.6, 4.5 ppm).<sup>10</sup> The probe was slowly warmed to 20 °C. After 15 min, only three resonances remained, with one in the alkene region greatly dominating (19.3, 18.5, 7.7 ppm; 13:2:85).

Workup of a preparative reaction of racemic **2c** gave **4c** as a diastereomerically and analytically pure powder in 76% yield. Many alkene complexes of **I** have been characterized previously,<sup>10</sup> and **4c** displayed commensurate IR and NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) properties, as summarized in the Experimental Section. More importantly, **4c** crystallized, and the crystal structure was determined as outlined in Table 1 and described in the Experimental Section. The result, depicted in Figure 1, shows that rhenium has migrated from nitrogen to the non-benzenoid C=C linkage of the hydroquinoline—and the CH=CH face *trans* to the allylic CHPh substituent. Figure 1 also shows that isolated **4c** is a *RSRS,SRSR* diastereomer.<sup>9</sup> As analyzed in the Discussion, the configuration of the CHPh carbon is consistent

Table 1. Summary of Crystallographic Data for (*RSRS,SRSR*)-**4c**

mol formula	C <sub>43</sub> H <sub>41</sub> F <sub>3</sub> N <sub>2</sub> O <sub>5</sub> PReS
fw	972.05
cryst syst	monoclinic
space group	P2 <sub>1</sub> /c
cell dimens	
<i>a</i> , Å	13.799(4)
<i>b</i> , Å	14.438(4)
<i>c</i> , Å	20.732(7)
β, deg	108.25(2)
<i>V</i> , Å <sup>3</sup>	3922.73
<i>Z</i>	4
temp of collcn, °C	-125
<i>d</i> <sub>calc</sub> , g/cm <sup>3</sup>	1.65 (-125 °C)
<i>d</i> <sub>obs</sub> , g/cm <sup>3</sup> (CCl <sub>4</sub> /CH <sub>2</sub> Cl <sub>2</sub> )	1.54 (22 °C)
cryst dimens, mm	0.37 × 0.25 × 0.12
diffractometer	Enraf-Nonius CAD-4
radiation (λ, Å)	Mo K <sub>α</sub> (0.709 30)
data collcn method	θ-2θ
scan speed, deg/min	variable
no. of reflns measd	6702
range/indices ( <i>h,k,l</i> )	0, 15; 0, 16; -22, 22
scan range	0.8 + 0.34 tan θ
2θ limit, deg	4.0-48.0
std refln check	1 X-ray h
total no. of unique data	6129
no. of obsd data, <i>I</i> > 3σ( <i>I</i> )	5143
abs coefficient, cm <sup>-1</sup>	32.9
min trans, %	87.98
max trans, %	99.81
no. of variables	506
goodness of fit	1.5021
$R = \frac{\sum   F_o  -  F_c  }{\sum  F_o }$	0.0397
$R_w = \frac{[\sum w( F_o  -  F_c )^2 / \sum w  F_o ^2]^{1/2}}{\sum w  F_o ^2}$	0.0466
Δσ(max)	0.004
Δρ(max), e/Å <sup>3</sup>	1.244 (1.46 Å from Re)

with the transition state model for allyllithium addition shown at the bottom of Scheme 2 (II). Atomic coordinates and selected bond lengths, bond angles, and torsion angles are given in Tables 2 and 3.<sup>16</sup>

A CH<sub>2</sub>Cl<sub>2</sub> solution of crystalline (*RSRS,SRSR*)-**4c** was kept at room temperature. After 2 days, a <sup>31</sup>P NMR spectrum showed a 98:2 mixture of (*RSRS,SRSR*)-**4c** (6.8 ppm) and a new species (22.6 ppm). After 7 days, the ratio stabilized at 95:5, presumably an equilibrium value. Although the new resonance has a plausible chemical shift for a diastereomer of amine complex **3c**, it was not observed in the original reaction of **2c** and HOTf. The allylic and vinylic protons in alkene complexes of **I** are easily abstracted by *t*-BuO<sup>-</sup>K<sup>+</sup>,<sup>17,18</sup> and proton transfer equilibria involving the trivalent nitrogen in (*RSRS,SRSR*)-**4c** can be envisioned. The limited data do not distinguish these possibilities.

When samples of (*RSRS,SRSR*)-**4c** were cooled, NMR spectra showed the decoalescence of two isomers. For example, CD<sub>2</sub>Cl<sub>2</sub>, THF, and CD<sub>3</sub>NO<sub>2</sub> solutions gave 79:21, 80:20, and 53:47 mixtures, respectively, at -80, -100, and -30 °C. These were attributed to *ac/sc* Re-(C=C) rotamers (III, IV; Scheme 4),<sup>19</sup> as observed previously for unsymmetrically substituted *cis* and *trans*

(16) The structural properties of alkene complexes of **I** have been extensively analyzed.<sup>10</sup> In this context, we also calculated the "slippage value" (1%), the angles of the Re-C24-C25 or Re-C=C plane with the Re-P and Re-NO bonds (2°, 97°), and the angles of the C25-C26 and C24-C32 bonds with the plane perpendicular to the Re-C24-C25 plane (20.7°, 27.5°; "bend back" angles).

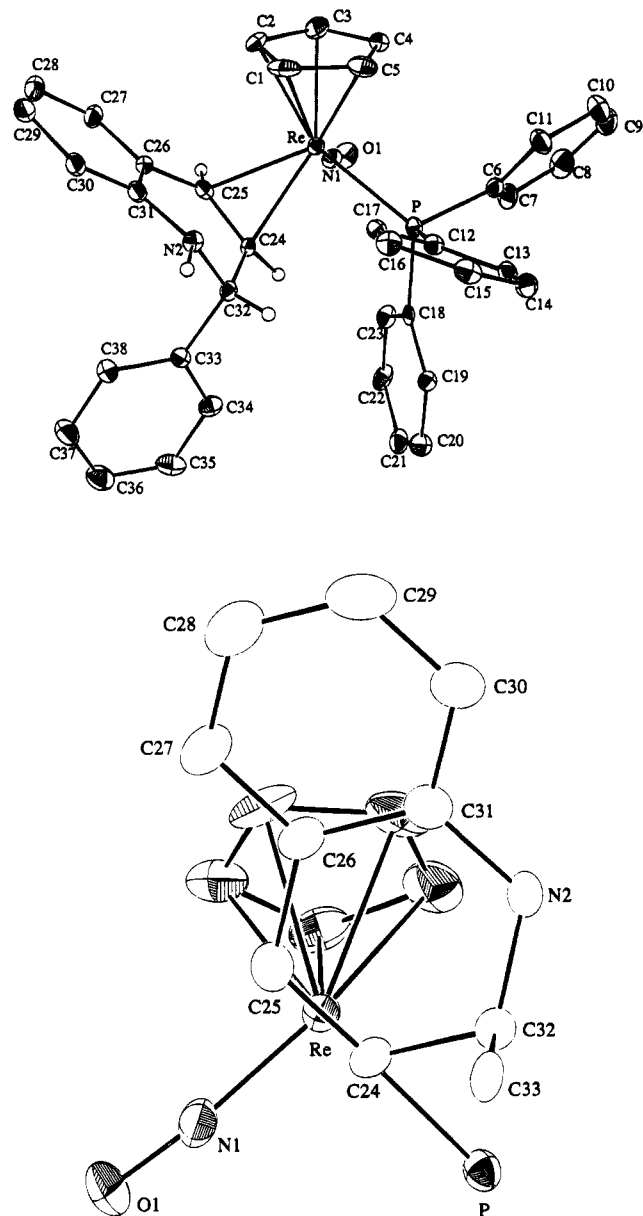
(17) Bodner, G. S.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *Organometallics* **1989**, *8*, 2399; **1990**, *9*, 1191.

(18) (a) Peng, T.-S.; Gladysz, J. A. *Organometallics* **1990**, *9*, 2884. (b) Peng, T.-S.; Gladysz, J. A. Submitted for publication.

(13) (a) Dewey, M. A.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1351. (b) See also: Saura-Llamas, I.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 2136.

(14) When THF solutions of **2b** were kept for 1 h at room temperature, the ratios of the 20.7 and 16.9 <sup>31</sup>P resonances changed very slightly (93:7 to 90:10). Concurrently, 5-8% of PPh<sub>3</sub> formed (-4.8 ppm).

(15) Dewey, M. A.; Knight, D. A.; Klein, D. P.; Arif, A. M.; Gladysz, J. A. *Inorg. Chem.* **1991**, *30*, 4995.



**Figure 1.** Structure of the cation of *(RSRS,SRSR)*-**4c**: (top) numbering diagram; (bottom) Newman type projection with phenyl rings omitted.

alkene complexes of **I**. The *ac* rotamer was assigned from the shielded cyclopentadienyl  $^1\text{H}$  resonance, which has been shown to be diagnostic of a phenyl  $\text{C}=\text{C}$  substituent in the position shown in **III** ( $\Delta\delta$  0.32).<sup>10</sup> Thus, the dominant rotamer in solution is the one that crystallizes. Further, the four  $^{31}\text{P}$  resonances noted for **4c** at low temperature (8.9–4.5 ppm) would be consistent with *ac/sc* rotamers of two configurational diastereomers—the latter potentially differing in the  $\text{CH}=\text{CH}$  diastereoface bound to rhenium, as discussed below.

(19) (a) In synclinal (*sc*)  $\text{Re}-(\text{C}^{\text{---}}\text{C})$  rotamers of alkene complexes of **I**, the highest priority substituents on rhenium ( $\eta^5\text{-C}_5\text{H}_5$ ) and the  $\text{C}^{\text{---}}\text{C}$  centroid ( $=\text{CHC}-(\text{N})(\text{C})(\text{H}) > =\text{CHC}(\text{C})(\text{C})(\text{C})$ ) define  $60 \pm 30^\circ$  torsion angles. In anticlinal (*ac*) rotamers, the highest priority substituents define  $120 \pm 30^\circ$  torsion angles. The torsion angles in the idealized rotamers **III** and **IV**—which maximize overlap of the d orbital HOMO of the Lewis acid **I** and the  $\text{C}=\text{C}$   $\pi^*$  acceptor orbitals—are 45 and  $135^\circ$  (Scheme 4).

**Table 2.** Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Located Atoms of *(RSRS,SRSR)*-**4c**<sup>a</sup>

atom	x	y	z	B ( $\text{\AA}^2$ )
Re	0.97762(2)	0.26878(2)	0.12945(1)	1.421(5)
S	0.2260(2)	0.3867(2)	-0.0052(1)	2.51(4)
P	0.8498(1)	0.1568(1)	0.3502(9)	1.47(4)
F1	0.2748(5)	0.5606(4)	0.0147(3)	4.2(1)
F2	0.3902(4)	0.4765(5)	-0.0042(3)	5.6(1)
F3	0.3646(5)	0.4704(4)	0.0922(3)	4.9(2)
O1	0.9210(4)	0.2615(4)	-0.0191(3)	2.9(1)
O2	0.2903(5)	0.4009(5)	-0.0771(3)	3.8(2)
O3	0.1518(5)	0.4027(6)	0.0278(4)	5.5(2)
O4	0.2859(6)	0.3047(5)	0.0156(4)	5.8(2)
O5	0.4718(5)	0.5341(5)	0.3851(4)	5.0(2)
N1	0.9477(4)	0.2557(4)	0.0414(3)	2.0(1)
N2	1.1574(4)	0.1569(4)	0.2785(3)	1.7(1)
C1	1.0215(8)	0.3611(6)	0.2230(4)	3.1(2)
C2	1.0553(6)	0.4047(6)	0.1718(5)	2.9(2)
C3	0.9653(6)	0.4241(6)	0.1172(4)	2.8(2)
C4	0.8818(6)	0.3952(6)	0.1346(4)	2.3(2)
C5	0.9152(7)	0.3575(6)	0.2005(4)	2.8(2)
C6	0.7257(5)	0.2008(5)	0.0843(4)	1.8(2)
C7	0.6916(5)	0.1893(6)	0.0144(4)	2.6(2)
C8	0.6000(7)	0.2292(8)	-0.0252(4)	3.5(2)
C9	0.5427(6)	0.2798(7)	0.0046(5)	3.7(2)
C10	0.5749(6)	0.2924(7)	0.0734(5)	3.5(2)
C11	0.6662(6)	0.2536(6)	0.1141(4)	2.6(2)
C12	0.8396(5)	0.1349(5)	0.2189(3)	1.6(1)
C13	0.7499(5)	0.0970(5)	0.2264(4)	1.8(2)
C14	0.7439(6)	0.0842(6)	0.2915(4)	2.1(2)
C15	0.8252(6)	0.1064(6)	0.3485(4)	2.1(2)
C16	0.9150(6)	0.1421(6)	0.3413(5)	2.0(2)
C17	0.9200(5)	0.1575(5)	0.2766(3)	1.6(1)
C18	0.8593(5)	0.0433(5)	0.0983(4)	1.6(1)
C19	0.8443(5)	-0.0384(5)	0.1293(4)	1.7(1)
C20	0.8543(6)	-0.1229(6)	0.1007(4)	2.3(2)
C21	0.8763(6)	-0.1280(6)	0.0405(4)	2.4(2)
C22	0.8893(6)	-0.0466(6)	0.0090(4)	2.5(2)
C23	0.8822(6)	0.0379(6)	0.0375(4)	2.1(2)
C24	1.0829(4)	0.1447(5)	0.1562(4)	1.5(1)
C25	1.1407(5)	0.2215(5)	0.1475(3)	1.7(1)
C26	1.2217(5)	0.2566(5)	0.2079(4)	1.7(1)
C27	1.2909(6)	0.3236(6)	0.2019(4)	2.3(2)
C28	1.3643(6)	0.3585(6)	0.2589(5)	2.8(2)
C29	1.3686(6)	0.3251(6)	0.3227(4)	2.8(2)
C30	1.3032(5)	0.2559(5)	0.3299(4)	2.0(2)
C31	1.2291(5)	0.2213(5)	0.2722(4)	1.8(1)
C32	1.1140(5)	0.0929(5)	0.2227(3)	1.6(1)
C33	1.1852(5)	0.0136(5)	0.2181(3)	1.7(1)
C34	1.1496(6)	-0.0547(6)	0.1683(4)	2.1(2)
C35	1.2116(7)	-0.1279(6)	0.1632(4)	2.9(2)
C36	1.3098(7)	-0.1339(7)	0.2072(5)	3.2(2)
C37	1.3455(6)	-0.0678(7)	0.2567(5)	3.2(2)
C38	1.2838(6)	0.0056(6)	0.2630(4)	2.4(2)
C39	0.3176(6)	0.4772(6)	0.0256(4)	2.9(2)
C40	0.6124(7)	0.5719(8)	0.4822(6)	4.4(3)
C41	0.5502(7)	0.5728(7)	0.4070(5)	3.6(2)
C42	0.5989(7)	0.6263(8)	0.3623(5)	4.0(2)
C43	0.5302(7)	0.6378(8)	0.2902(5)	4.3(2)
H21	0.0410	0.3945	0.6152	5.0*
H22	0.1445	0.2500	0.0996	5.0*
H28	0.0625	0.4375	0.7324	5.0*
H29	1.0778	-0.0503	0.1358	5.0*

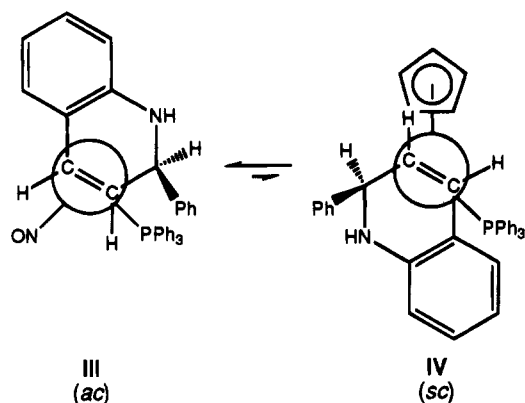
<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $(4/3)[a^2U(1,1) + b^2U(2,2) + c^2U(3,3) + ab(\cos \gamma)U(1,2) + ac(\cos \beta)U(1,3) + bc(\cos \alpha)U(2,3)]$ . Starred atoms were located but not refined.

**3. Protonation of Amido Complexes 2a,b.** Since one diastereomer greatly dominates in all of the reactions in Scheme 2, a uniform addition stereochemistry would be logical (e.g., **II**). However, the  $^{31}\text{P}$  NMR chemical shift of the major diastereomer of **2c** (14.5 ppm) is considerably upfield of those of **2a,b** (23.3–20.7 ppm). We provisionally attribute this to a shielding effect of the phenyl substituent in **2c**, complementary to that noted above for the  $\text{CH}_3$   $^1\text{H}$  resonance at **2b**. Therefore,

**Table 3.** Key Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in (RSRS,RSRS)-4c<sup>a</sup>

Re—P	2.422(2)	Re—N1	1.750(5)
Re—C1	2.272(7)	Re—C2	2.276(7)
Re—C3	2.258(7)	Re—C4	2.276(7)
Re—C5	2.311(7)	Re—C24	2.264(6)
Re—C25	2.268(6)	P—C6	1.820(6)
P—C12	1.816(6)	P—C18	1.829(6)
O1—N1	1.194(6)	C24—C25	1.410(9)
C25—C26	1.483(8)	C24—C32	1.508(8)
P—Re—N1	92.3(2)	P—Re—C24	83.2(2)
P—Re—C25	119.4(2)	N1—Re—C24	95.4(2)
N1—Re—C25	92.1(2)	C24—Re—C25	36.3(2)
Re—P—C6	107.9(2)	Re—P—C12	116.0(2)
Re—P—C18	115.5(2)	Re—N1—O1	169.1(5)
Re—C24—C25	72.0(3)	Re—C24—C32	126.4(4)
Re—C25—C24	71.7(3)	Re—C25—C26	118.9(4)
C24—C25—C26	117.9(5)	C25—C24—C32	119.8(5)
C32—C24—C25—H22			-157.3
H21—C24—C25—C26			162.0
C32—C24—C25—C26			8.6(1)
H21—C24—C25—H22			-4.0

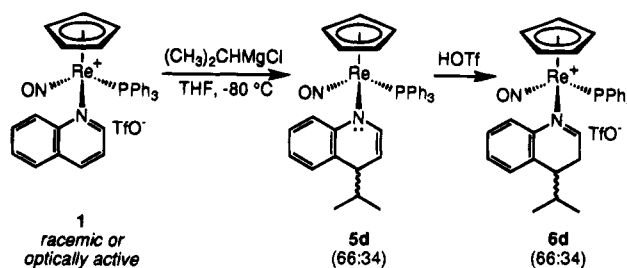
<sup>a</sup> Since hydrogen atom positions were not refined, estimated standard deviations are not given for the corresponding metrical parameters.

**Scheme 4.** Re—(C=C) Rotamers of (RSRS,RSRS)-4c

Solvent	Temperature	Ratio
CD <sub>2</sub> Cl <sub>2</sub>	-80 °C	79 : 21
THF	-100 °C	80 : 20
CD <sub>3</sub> NO <sub>2</sub>	-30 °C	53 : 47

reactions of **2a,b** and HOTf analogous to that in Scheme 3 were conducted so that additional comparisons could be made.

Thus, racemic **2a** was treated with HOTf at 0 °C. A <sup>31</sup>P NMR spectrum of an aliquot showed five new resonances (5:4:4:41:46). The first four had chemical shifts plausible for hydroquinoline complex **3a** (20.0, 18.9, 17.9, 14.6 ppm). The fifth was in the upfield region that would be expected for alkene complex **4a** (8.1 ppm). The probe was warmed to 20 °C. After 15 min, only three resonances remained, with the upfield one greatly dominating (19.6, 17.8, 8.0 ppm; 4:5:91). Workup gave an 80% yield of a 91:5:4 mixture of **4a** and two diastereomers of **3a**, as assigned from the NMR and IR data in the Experimental Section. All attempts to separate these isomers, or obtain enriched samples, failed. Hence, they may be in facile equilibrium. Consistent with this formulation, the mixture gave a correct microanalysis. When THF solutions were cooled, <sup>31</sup>P NMR spectra showed the docoalescence of **4a** to two isomers (7.7, 5.8 ppm, 59:41, -100 °C), presumably *ac/sc* rotamers, as in Scheme 4.

**Scheme 5.** 1,4 Addition to Quinoline Complex 1

Complex **2b** was generated from (*S*)-**1** in an NMR tube at -80 °C and treated with HOTf at -20 °C. A <sup>31</sup>P NMR spectrum showed six new resonances (2:10:4:32:39:13). The first four had chemical shifts plausible for hydroquinoline complex **3b** (20.5, 19.6, 18.7, 14.9 ppm). Thus, **2a-c** all protonate to give mixtures of hydroquinoline complexes with very similar chemical shift patterns (14.6–15.0 ppm usually dominant). The other two resonances were in the region that would be expected for alkene complex **4b** (8.0, 5.8 ppm). The probe was warmed to 20 °C. After 30 min, only three resonances remained (19.4, 18.6, 7.9 ppm; 33:4:63). In contrast to the above examples, an appreciable amount of one downfield resonance persisted at room temperature, suggesting a less biased **4b/3b** equilibrium. All attempts to separate **4b** and **3b** were unsuccessful.

**4. Other Reactions.** Exploratory reactions of **1** or (*S*)-**1** and other alkylolithium reagents (CH<sub>3</sub>CH<sub>2</sub>Li, (CH<sub>3</sub>)<sub>2</sub>CHLi, (CH<sub>3</sub>)<sub>3</sub>CLi) gave a multitude of products, as assayed by <sup>31</sup>P NMR. However, when (*S*)-**1** and the Grignard reagent (CH<sub>3</sub>)<sub>2</sub>CHMgCl were combined in an NMR tube in THF at -80 °C, a 66:34 mixture of two species formed (**5d**; 17.5, 14.2 ppm). When the probe was warmed to 25 °C, the ratio remained unchanged. In a separate experiment, a sample was kept at 50 °C for 12 h. A <sup>31</sup>P NMR spectrum showed a 44:56 mixture, suggestive of two equilibrating diastereomers of an amido or enamido complex.<sup>5,13</sup>

A THF solution of **5d** was treated with HOTf at -20 °C. A <sup>31</sup>P NMR spectrum showed a 66:34 mixture of two new complexes (**6d**; 18.7, 16.5 ppm).<sup>20</sup> Preparative reactions starting with racemic **1** gave 67:33 mixtures in 71–75% yields.<sup>20</sup> However, spectroscopic features (Experimental Section) paralleled those of *imine*, rather than amine or alkene, complexes of **I**.<sup>5,21</sup> In particular, the <sup>1</sup>H and <sup>13</sup>C NMR spectra exhibited characteristic downfield CH=N resonances (δ 8.56–8.43; 186.4/183.5 ppm). Hence, **6d** was assigned as the diastereomeric imine complex [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(N=CHCH<sub>2</sub>-CH(CH(CH<sub>3</sub>)<sub>2</sub>)C(CH<sub>3</sub>)<sub>4</sub>C)]<sup>+</sup>TfO<sup>-</sup>, as shown in Scheme 5.

Accordingly, **5d** was assigned as the 1,4 addition product (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(NCH=CHCH(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>4</sub>C). Related enamido complexes have been previously shown to react with HOTf to give imine complexes.<sup>5,21c</sup>

(20) Although **6d** is "homogeneous" by <sup>1</sup>H NMR, <sup>31</sup>P NMR spectra show small amounts of a third species (18.0 ppm, CDCl<sub>3</sub>; 4%) that was not removed under a variety of workup conditions.

(21) (a) Knight, D. A.; Dewey, M. A.; Stark, G. A.; Bennett, B. K.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4523. (b) Cantrell, W. R., Jr.; Richter-Addo, G. B.; Gladysz, J. A. *J. Organomet. Chem.* **1994**, *472*, 195. (c) Johnson, T. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1994**, *13*, 3182.

Thus, the more hindered secondary alkyl nucleophile  $(\text{CH}_3)_2\text{CHMgCl}$  attacks the less congested C4 position of the quinoline ligand.<sup>22</sup> Some of the minor byproducts noted in the alkyllithium reactions in Scheme 2 could similarly be derived from 1,4 addition. The major diastereomers of **5d** and **6d** are *provisionally* assigned *SR,RS* and *SS,RR* configurations, respectively,<sup>9</sup> on the assumption that attack opposite to the  $\text{PPh}_3$  ligand (see II, Scheme 2) should be slightly favored.

The cuprate  $(\text{CH}_3)_2\text{CuLi}$  reacts with monosubstituted alkene complexes of **I** to give neutral alkyl complexes derived from methyl group additions.<sup>23</sup> However, analogous reactions with *(RSRS,SRSR)*-**4c** gave only the methyl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_3)$ . NMR monitoring showed several transients, but all converted to the methyl complex. Finally, *(RSRS,SRSR)*-**4c** and *t*-BuO<sup>-</sup>K<sup>+</sup> were combined in THF at  $-80^\circ\text{C}$ . Although several interesting NH or CH deprotonations can be envisioned,<sup>17,18</sup> <sup>31</sup>P NMR spectra showed that four species formed (25.8, 19.5, 16.8, 14.7 ppm; 50:9:10:31; probe temperature  $-100^\circ\text{C}$ ). The three upfield resonances were close to those assigned to isomers of **2c** above.

## Discussion

**1. Additions to Coordinated Quinoline.** Nucleophiles have been previously found to add to C2 and C4 of free quinoline.<sup>24</sup> However, the cationic rhenium complex **1** and other N-derivatized quinolines are considerably more reactive. Other types of metal-coordinated quinolines also undergo various addition reactions.<sup>25</sup> However, to our knowledge there are no prior examples that involve direct attack of an exogenous agent upon a stable  $\sigma$  complex. Importantly, the chiral Lewis acid **I** renders the  $\pi$  faces of quinoline diastereotopic. Accordingly, for the alkyl- or aryllithium additions in Scheme 2, one configuration of the new carbon stereocenter greatly dominates.

Crystalline **1** exhibits the rhenium–nitrogen conformation shown in Newman projection **II** in Scheme 2.<sup>7</sup> The interstice between the small nitrosyl and medium-sized cyclopentadienyl ligand is the most spacious, and can best accommodate the quinoline CH group in the *peri* position 8, which must abut the metal fragment. Indeed, quinoline is much less reactive toward the triflate complex of **I** than *isoquinoline*, which cannot give an analogous steric interaction.<sup>7</sup> Furthermore, attempts to prepare an 8-methylquinoline complex of **I** have been unsuccessful.<sup>7</sup> Hence, **II** is likely the only rhenium–nitrogen rotamer present in significant quantities in solution.

The stereochemistry of the dominant diastereomer of addition products **2a–c** is consistent with nucleophilic attack upon **II** from a direction opposite to the bulky  $\text{PPh}_3$  ligand, as sketched in Scheme 2. A similar transition state model accounts for the major diaster-

eomers formed in 1,2-additions to the *isoquinoline* complex of **I** (Scheme 1). Unfortunately, the generality of Scheme 2 does not appear to be as high as Scheme 1. In particular, some nucleophiles give complex product mixtures, and at least one gives 1,4 addition (Scheme 5). In the latter case, the lower diastereoselectivity is consistent with attack at a site further removed from the chiral rhenium environment.

**2. Isomerization Reactions.** A variety of isomerization processes complicated this study. First, due to the potential for configurational lability or irreversible  $\text{PPh}_3$  dissociation,<sup>5,8,14</sup> addition products **2a,c** and **5d** were characterized only by <sup>31</sup>P NMR at low temperatures. Second, attempted N protonation of **2a–c** to hydroquinoline complexes **3a–c** gave instead mixtures containing mainly linkage isomers, alkene complexes **4a–c** (Scheme 3). Cyanide ion displaces amine ligands from **I** at room temperature (Scheme 1),<sup>5,7,15</sup> but alkene ligands can normally be detached only at  $\geq 75^\circ\text{C}$ .<sup>26</sup> Thus, free hydroquinolines cannot easily be generated from these precursors, at least by presently known methodology.

Similar linkage isomerizations occur with adducts of **I** and keto–alkenes.<sup>27</sup> In these cases, O=C ligated complexes, which are usually favored kinetically, convert to C=C ligated complexes at temperatures ranging from 0 to  $100^\circ\text{C}$ . Deuterium labeling experiments show that rearrangements can be largely nondissociative, even in nonconjugated cases.<sup>27b,c</sup> Surprisingly, alkenes can also exchange the C=C face bound to **I** without dissociation, and coordinated styrene does not exchange with styrene-*d*<sub>3</sub> at temperatures as high as  $150^\circ\text{C}$ .<sup>28</sup> Hence, we favor a nondissociative isomerization of **3** to **4**, involving either a concerted through-space migration of rhenium from nitrogen to the CH=CH moiety or one that is mediated by the  $\pi$  cloud of the benzenoid ring.

The isomerization of **3** to **4** shows that at least some *cis*-disubstituted alkenes are thermodynamically stronger Lewis bases toward **I** than secondary arylamines. We sought to probe the generality of this trend.<sup>29</sup> The allylamine complex of **I** appears to rearrange to an alkene complex at  $110^\circ\text{C}$  in  $\text{CHCl}_2\text{CHCl}_2$ . However, we are unable to purify the dark product, which gives broad <sup>1</sup>H NMR peaks. Attempts to prepare a tertiary *N,N*-dimethylallylamine complex of **I** give an alkene complex directly. Reaction of the *N,N*-diallylamido complex of **I** and  $\text{CH}_3\text{OTf}$  at  $-80^\circ\text{C}$  gives an amine complex, as assayed by <sup>31</sup>P NMR. Isomerization to an alkene complex occurs upon warming. Interestingly, Harman has shown that the d<sup>6</sup> osmium fragment  $[\text{Os}(\text{NH}_3)_5]^{2+}$ , which is a stronger  $\pi$  base than **I**, binds aniline through an arene C=C linkage.<sup>30</sup> With **I**, only an N-coordinated aniline complex is detected.<sup>15</sup> This suggests that metal fragments that are weaker  $\pi$  donors may be less likely to give rearrangements of amine to alkene complexes.

(22) A reviewer has suggested that the softer nucleophilicity of Grignard reagents may be the controlling factor in 1,4-addition. See: (a) Yamaguchi, R.; Nakazono, Y.; Kawanisi, M. *Tetrahedron Lett.* **1983**, *24*, 1801. (b) Yamaguchi, R.; Nakazono, Y.; Mastuki, T.; Hata, E.; Kawanisi, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 215.

(23) Peng, T.-S.; Gladysz, J. A. *Tetrahedron Lett.* **1990**, *31*, 4417.

(24) *Quinolines*; Jones, G., Ed.; Wiley: New York, 1977; Part I, pp 30–42.

(25) (a) Baralt, E.; Smith, S. J.; Hurwitz, J.; Horváth, I. T.; Fish, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5187. (b) Sánchez-Delgado, R. A.; Rondón, D.; Andriollo, A.; Herrera, V.; Martín, G.; Chaudret, B. *Organometallics* **1993**, *12*, 4291.

(26) Bodner, G. S.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1191.

(27) (a) Wang, Y.; Agbossou, F.; Dalton, D. M.; Liu, Y.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2699. (b) Fairfax, E. J. M.S. Thesis, University of Utah, 1993. (c) Holden, M. Unpublished results, University of Utah, 1994.

(28) Peng, T.-S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 4174.

(29) Stark, G. A.; Cagle, P. C.; Meyer, O. Unpublished results, University of Utah, 1994.

(30) Gonzalez, J.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1993**, *115*, 8857 and references therein.

Several stereochemical nuances of Scheme 3 deserve emphasis. First, the N protonation of **2a-c** will set the rhenium as either *trans* or *cis* to the CH=CH-CHR substituent in **3a-c**. The *trans* isomer should be more stable and dominate. The crystal structure of (*RSRS*,-*SRSR*)-**4c** (Figure 1) shows that a *trans* relationship is maintained after isomerization.<sup>31</sup> An analogous rearrangement of the *cis* isomer would give (*RRSS*,*SSRR*)-**4c**, in which rhenium is bound to the opposite CH=CH diastereoface—a possibility for one of the minor isomers.<sup>32</sup> The rhenium could then migrate to the opposite CH=CH face, relieving steric interactions with the *cis* phenyl group and giving (*RSRS*,*SRSR*)-**4c**. Other disubstituted alkene complexes of **I** that have appreciable ground state strain (e.g., the less stable adduct of *trans*-stilbene)<sup>10b</sup> undergo similar isomerizations at room temperature.<sup>33</sup>

The *cis*-2-butene complex of **I** also exhibits a rotameric equilibrium similar to that in Scheme 4.<sup>10a</sup> In contrast, however, the rotamer corresponding to **IV** is slightly more stable. Detailed studies with a variety of *trans*, *cis*, and geminally disubstituted alkene complexes of **I** have established the relative steric environments of the four C=C positions.<sup>10b</sup> The -CHPh and benzenoid C=C substituents in **IV** occupy the *least* and *most* congested positions, respectively. Apparently, they are more readily accommodated in the sterically intermediate positions in **III**.

**3. Conclusions.** To our knowledge, the rhenium Lewis acid **I** constitutes the first chiral auxiliary capable of controlling carbon configurations in nucleophilic additions to C2 of quinoline. Although diastereoselectivities of  $\geq 92\%$  have been realized, several limitations will preclude practical application in enantioselective organic synthesis. Nonetheless, this study establishes the potential of chiral transition metal auxiliaries for the elaboration of quinolines, and it can be anticipated that other metal fragments will eventually be identified that avoid the preceding complications. In particular, the possibility that one auxiliary can be used for the sequential introduction of multiple stereocenters (Scheme 1) should be noted. Additional studies of nucleophilic and electrophilic additions to adducts of **I** and unsaturated nitrogen heterocycles are in progress.<sup>34</sup>

## Experimental Section

**General Data.** General procedures were given in an earlier paper.<sup>5</sup> Solvents were used as received except for CH<sub>2</sub>Cl<sub>2</sub>

(31) In principle, protonation might be reversible on the time scale of isomerization, thereby allowing **3a-c** with *trans* or *cis* rhenium and CHR substituents to convert to opposite isomers of **4a-c**. It would also be of interest to know the configurations of the isomers of **3a-c** that appear not to isomerize or remain at equilibrium with **4a-c**. However, these assignments cannot be made from our present data.

(32) (a) Note that CH=CH-CHR configurations in **4a-c** are fixed relative to each other (one inversion would generate a *trans*-cyclohexene), reducing the number of possible diastereomers. (b) Of the four <sup>31</sup>P signals attributed to **4c**, two are due to Re-(C=C) rotamers of the same configurational diastereomer (Scheme 4). Thus, at least one additional configurational diastereomer must be generated. (c) The reactions of **2a,b** and HOTf are conducted and analyzed at higher temperatures (0 and -20 °C) than that of **2c** and HOTf (-80 to -60 °C). This may explain the lower number of isomers of **4a,b** detected.

(33) Other isomerization mechanisms are in theory possible. For example, loss of a CH=CH-CHR proton from **4a-c** would give a  $\sigma$ -allyl complex that could reprotonate from the opposite direction.<sup>26</sup> However, we have no evidence for such a process, which would alter the relative rhenium and CH=CH-CHR carbon configurations set in Scheme 2.

(34) Johnson, T. J.; Alvey, L. J.; Mayne, C. L.; Arif, A. M.; Gladysz, J. A. Manuscript in preparation.

(distilled from CaH<sub>2</sub>), THF (distilled from K/benzophenone), and THF-*d*<sub>8</sub> (vacuum transferred from CaH<sub>2</sub>). Reagents were used as received from Aldrich, and RLi and RMgCl solutions were standardized before use.<sup>35</sup>

**Reactions of [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(NC<sub>6</sub>H<sub>7</sub>)]<sup>+</sup>TfO<sup>-</sup> (**1**) and (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Li.<sup>6</sup> A.** A 5-mm NMR tube was charged with (*S*)-**1** (0.022 g, 0.027 mmol)<sup>7</sup> and capped with a septum. Then THF (0.8 mL) was added, and the tube was cooled to -80 °C (ether/CO<sub>2</sub>). Then (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Li (0.037 mL, 0.027 mmol, 0.73 M in pentane) was added. The tube was transferred to a -100 °C NMR probe, and <sup>31</sup>P spectra were recorded. Then HOTf (0.004 mL, 0.05 mmol) was added (-80 °C), and the probe was slowly warmed. Data: see text.

**B.** A Schlenk flask was charged with **1** (0.362 g, 0.444 mmol),<sup>7</sup> THF (100 mL), and a stir bar and cooled to -80 °C. Then (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Li (0.666 mL, 0.666 mmol, 1.0 M in pentane) was added dropwise with stirring. After 0.5 h, the flask was transferred to a 0 °C bath. After 0.5 h, HOTf (0.059 mL, 0.66 mmol) was added dropwise with stirring, and the cold bath was removed. After 1 h, solvent was removed under oil pump vacuum. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (ca. 30 mL) and charcoal was added. The mixture was stirred (0.5 h) and filtered through Celite. Solvent was removed from the filtrate by rotary evaporation. The dark oily residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>/hexane (50:50) and slowly concentrated by oil pump vacuum. The resulting yellow precipitate was collected by filtration, washed with pentane, and dried under oil pump vacuum to give [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(NHCH(CH<sub>2</sub>-

Si(CH<sub>3</sub>)<sub>3</sub>)CH=CHC(CH<sub>3</sub>)<sub>4</sub>C)]<sup>+</sup>TfO<sup>-</sup> (0.322 g, 0.354 mmol, 80%)

as a 9:1 mixture of **3a** (NH ligated, two diastereomers) and **4a** (C=C ligated), mp 134-135 °C dec. Anal. Calcd for C<sub>37</sub>H<sub>39</sub>F<sub>3</sub>N<sub>2</sub>O<sub>4</sub>PrReSSi: C, 48.83; H, 4.32. Found: C, 48.83; H, 4.35. IR (cm<sup>-1</sup>, KBr):  $\nu_{\text{NO}}$  1721 (vs).

NMR (CDCl<sub>3</sub>):<sup>36</sup> <sup>1</sup>H ( $\delta$ ) 7.68-7.28 (m, PPh<sub>3</sub>), 6.96-6.74 (m, C<sub>6</sub>H<sub>4</sub>), 5.56 (s, C<sub>5</sub>H<sub>5</sub>), 4.98-4.77, 4.44-4.29, 4.02-3.78 (3m, 1H each, CH=CH, NH), 3.77-3.67 (m, CHN),<sup>37</sup> 1.23-1.12 (dd, *J* = 11.3, 14.6 Hz, CHH'CHN), 0.48-0.32 (m, CHH'CHN), -0.06 (s, Si(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} (ppm) 141.9, 141.8, 123.7, 123.0, 118.7, 115.9 (6s, C<sub>6</sub>H<sub>4</sub>) 133.3 (d, *J* = 7.5, *o*-PPh), 132.3 (s, *p*-PPh), 129.5 (d, *J* = 10.9, *m*-PPh), 128.7 (d, *J* = 58.8, *i*-PPh), 99.3 (s, C<sub>5</sub>H<sub>5</sub>), 63.7 (br s, CHN), 51.7, 49.4 (2s, CH=CH), 26.6 (s, CHH'CH), -1.1 (s, Si(CH<sub>3</sub>)<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} (ppm) 19.2, 17.2, 6.9 (5:4:91; **3a/3a/4a**).

**Reactions of **1** and CH<sub>3</sub>Li.** A. Complex (*S*)-**1** (0.019 g, 0.023 mmol), THF (0.8 mL), and CH<sub>3</sub>Li (0.037 mL, 0.023 mmol, 0.62 M in ether) were combined in an NMR tube as described in procedure A for (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Li above. The probe was warmed from -100 to -20 °C. Then HOTf (0.004 mL, 0.05 mmol) was added, and the probe was further warmed. Data: see text.

**B.** Complex **1** (0.096 g, 0.12 mmol), THF (20 mL), and CH<sub>3</sub>Li (0.12 mL, 0.12 mmol, 0.97 M in ether) were combined as described in procedure B for (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Li above. After 15 min, the cold bath was removed and an oil pump vacuum applied. The residue was dried under vacuum (1 h) and cooled to -80 °C, and THF-*d*<sub>8</sub> was added by vacuum transfer. The product, ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)( $\dot{\text{N}}\text{CH}(\text{CH}_2)_3\text{CH}=\text{CHC}(\text{CH}_3)_4\text{C}$ )

(**2b**), was extracted via cannula into a -80 °C NMR tube.

NMR (THF-*d*<sub>8</sub>, -20 °C): <sup>1</sup>H ( $\delta$ ) 7.74-7.12 (m, PPh<sub>3</sub>), 6.99, 6.73, 6.47, 6.04, 5.90, 4.18, 4.06 (d/t/d/t/d/m/m, *J* = 8.1/7.5/7.1/

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(36) NMR spectra were recorded at ambient probe temperature unless noted and referenced as follows: <sup>1</sup>H ( $\delta$ ), Si(CH<sub>3</sub>)<sub>4</sub> (0.00), CHDCl<sub>2</sub> (5.32), or THF-*d*<sub>7</sub> (1.73); <sup>13</sup>C (ppm), CDCl<sub>3</sub> (77.0), CD<sub>2</sub>Cl<sub>2</sub> (53.8), or THF-*d*<sub>8</sub> (67.4); <sup>31</sup>P (ppm), external 85% H<sub>3</sub>PO<sub>4</sub> (0.00). All coupling constants (*J*) are in hertz.

(37) This assignment was established by a COSY <sup>1</sup>H NMR experiment.



7.0/8.9/7.3/6.1, 1H each, C<sub>6</sub>H<sub>4</sub>, CH=CHCH), 5.41 (s, C<sub>5</sub>H<sub>5</sub>), 0.45 (d, *J* = 5.8, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} (ppm) 157.4, 151.9, 127.7, 126.5, 123.7, 123.6, 119.3, 112.2 (8s, C<sub>6</sub>H<sub>4</sub>, C=C), 131.0 (d, *J* = 1.8, *p*-PPh), 129.4 (d, *J* = 10.1, *o*-PPh), 124.6 (d, *J* = 10.6, *m*-PPh), 92.4 (s, C<sub>5</sub>H<sub>5</sub>), 68.2 (s, CHN), 26.4 (s, CH<sub>3</sub>);<sup>38</sup> <sup>31</sup>P{<sup>1</sup>H} (ppm) 21.8, 17.6, 17.2, 15.5 (4s, 94:1:4:1).

**Reactions of 1 and C<sub>6</sub>H<sub>5</sub>Li.** **A.** Complex (*S*)-1 (0.020 g, 0.024 mmol), THF (0.80 mL), C<sub>6</sub>H<sub>5</sub>Li (0.014 mL, 0.024 mmol, 1.8 M in 70:30 cyclohexane/ether), and HOTf (0.004 mL, 0.05 mmol) were combined in an NMR tube as described in procedure A for (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Li above. Data: see text.

**B.** Complex 1 (0.698 g, 0.849 mmol), THF (40 mL), C<sub>6</sub>H<sub>5</sub>Li (0.696 mL, 0.849 mmol, 1.22 M in 70:30 cyclohexane/ether), and HOTf (0.098 mL, 1.1 mmol) were combined as described in procedure B for (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Li above. After 1 h, solvent was removed by oil pump vacuum. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (ca. 30 mL) and charcoal was added. The mixture was stirred (15 min) and filtered through Celite. The filtrate was concentrated by rotary evaporation to ca. 2 mL and added dropwise to rapidly stirring ether (100 mL). A yellow precipitate formed, which was collected by filtration, washed with pentane, and dried under oil pump vacuum to give [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)-Re(NO)(PPh<sub>3</sub>)(NHCH(C<sub>6</sub>H<sub>5</sub>)CH=CHC(CH<sub>3</sub>)<sub>4</sub>C)]<sup>+</sup>TfO<sup>-</sup> (**4c**, C=C

ligated; 0.579 g, 0.644 mmol, 76%), mp 134–135 °C dec. Anal. Calcd for C<sub>39</sub>H<sub>33</sub>F<sub>3</sub>N<sub>2</sub>O<sub>4</sub>PR<sub>3</sub>S: C, 52.05; H, 3.70. Found: C, 51.94; H, 3.72. IR (cm<sup>-1</sup>, KBr): ν<sub>NO</sub> 1722 (vs).

NMR (CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H (δ) 7.73–7.25 (m, PPh<sub>3</sub>), 7.18–6.91 (m, C<sub>6</sub>H<sub>5</sub>), 6.85–6.58 (m, C<sub>6</sub>H<sub>4</sub>), 5.58 (s, C<sub>5</sub>H<sub>5</sub>), 5.12–4.86, 4.78–4.61, 4.67–4.48, 4.35–4.19 (4m, 1H each, CH=CHCHNH); <sup>13</sup>C{<sup>1</sup>H} (ppm) 145.6, 142.4, 129.4, 129.2, 129.1, 128.3, 127.5, 125.8, 118.9, 114.8 (10s, *CPh* and C<sub>6</sub>H<sub>4</sub>), 133.4 (d, *J* = 8.8, *o*-PPh), 132.3 (s, *p*-PPh), 129.6 (d, *J* = 11.4, *m*-PPh), 129.2 (d, *J* = 56.6, *i*-PPh), 99.7 (s, C<sub>6</sub>H<sub>5</sub>), 57.8, 49.0 (2s, CH=CH);<sup>39</sup> <sup>31</sup>P{<sup>1</sup>H} (ppm) 6.8 (s).

NMR (low temperature, partial, *ac/sc*): <sup>1</sup>H (δ, -80 °C, CD<sub>2</sub>Cl<sub>2</sub>) 5.43/5.75 (2s, C<sub>5</sub>H<sub>5</sub>, 79:21), CH=CHCHNH at 5.20/4.98 (2d, *J* = 9.1/7.3), 5.10/4.88 (m/d, *J* = 10.0), 4.41/4.38 (2m), 3.89/3.96 (2 pseudo t, *J* = 9.5/9.0); <sup>13</sup>C{<sup>1</sup>H} (ppm, -80 °C, CD<sub>2</sub>Cl<sub>2</sub>) 100.1/97.1 (2s, C<sub>5</sub>H<sub>5</sub>), 59.8/60.0 (2d, *J* = 5.9, =CH syn to PPh<sub>3</sub><sup>10</sup>), 55.6/49.7, 45.5/49.3 (4s, =CH anti to PPh<sub>3</sub>, CHN); <sup>31</sup>P{<sup>1</sup>H} (ppm) 8.8/9.3 (2s, 79:21, -80 °C, CD<sub>2</sub>Cl<sub>2</sub>), 8.5/8.9 (2s, 80:20, -100 °C, THF), 8.5/8.8 (2s, 53:47, -30 °C, CD<sub>3</sub>NO<sub>2</sub>).

**Reaction of 1 and (CH<sub>3</sub>)<sub>2</sub>CHMgCl.** Complex 1 (0.166 g, 0.202 mmol), THF (80 mL), (CH<sub>3</sub>)<sub>2</sub>CHMgCl (0.101 mL, 0.202 mmol, 2.0 M in ether), and HOTf (0.036 mL, 0.40 mmol) were combined as described in procedure B for (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Li above. After 1 h, solvent was removed by oil pump vacuum. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and charcoal was added. The mixture was stirred (15 min), filtered through Celite, and concentrated to ca. 5 mL by rotary evaporation. Hexane (100 mL) was added. A yellow powder formed, which

(38) The *i*-PPh <sup>13</sup>C resonance was not observed, and minor C<sub>6</sub>H<sub>5</sub> <sup>1</sup>H and <sup>13</sup>C resonances were present at δ 5.18 (4%) and 93.0 ppm.

(39) The CHN <sup>13</sup>C resonance was not observed at room temperature.

was collected by filtration, washed with pentane, and dried under oil pump vacuum to give [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)-(N=CHCH<sub>2</sub>CH(CH(CH<sub>3</sub>)<sub>2</sub>)C(CH<sub>3</sub>)<sub>4</sub>C)]<sup>+</sup>TfO<sup>-</sup> (**6d**; 0.124 g, 0.143 mmol, 71%) as a 67:33 diastereomer mixture, mp 169–171 °C dec.<sup>20</sup> IR (cm<sup>-1</sup>, KBr): ν<sub>NO</sub> 1695 (vs).

NMR: <sup>1</sup>H (δ, CDCl<sub>3</sub>, major + minor diastereomer unless noted) 8.56–8.43 (m, CH=N), 7.97 (d, *J* = 7.8, 1H of C<sub>6</sub>H<sub>4</sub>), 7.86 (d, *J* = 7.8, 1H of C<sub>6</sub>H<sub>4</sub>), 7.59–7.12 (m, PPh<sub>3</sub>), 7.59–7.05 (m, 2H of C<sub>6</sub>H<sub>4</sub>), 5.63 (s, C<sub>5</sub>H<sub>5</sub>), 3.17–2.98/2.67–2.48 (2m, (CH<sub>3</sub>)<sub>2</sub>CHCH, minor/major), 2.27–2.10/1.81–1.60 (2m, *CHH'*-CH=N, major/minor), 1.38–1.20 (m, (CH<sub>3</sub>)<sub>2</sub>CH), 0.82/0.63, 0.71/0.58 (4d, *J* = 6.6, (CH<sub>3</sub>)<sub>2</sub>CH, major/minor); <sup>13</sup>C{<sup>1</sup>H} (ppm, CD<sub>2</sub>Cl<sub>2</sub>, major/minor) 186.4/183.5 (2s br, CH=N), 133.8/133.6 (2d, *J* = 10.8/10.7, *o*-PPh), 131.7/131.9 (2d, *J* = 2.2/2.3, *p*-PPh), 131.2/131.2 (d, *J* = 55.3, *i*-PPh), 129.6/129.7 (2d, *J* = 11.1/10.5, *m*-PPh), 145.9/144.6, 133.6/132.9, 133.0/130.5, 129.2/129.4, 127.7/128.6, 126.1/124.9 (12s, C<sub>6</sub>H<sub>4</sub>), 121.1/121.1 (q, *J*<sub>CF</sub> = 321.0, CF<sub>3</sub>), 92.8/93.3 (2s, C<sub>5</sub>H<sub>5</sub>), 40.0/31.9, 36.4/28.4 (4s, CHCHCN), 27.2/23.0 (2s, CHCH<sub>3</sub>), 20.8/21.5, 16.6/14.2 (4s, CH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} (ppm, CDCl<sub>3</sub>) 19.1/17.0 (2s, 67:33).

**Crystallography.** Yellow prisms of (*RSRS,SRSR*)-**4c**<sup>9</sup> were grown from layered 2-butanone/hexane. Data were collected as outlined in Table 1. Cell constants were obtained for 30 reflections with 10° < 2θ < 20°. The space group was determined from systematic absences (*h*0*l*, *h* + *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1) and subsequent least squares refinement. Lorentz, polarization, and empirical absorption (*ψ* scans) corrections were applied. The structure was solved by standard heavy-atom techniques with the SDP-VAX package.<sup>40</sup> Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the alkene ligand were located. The positions of the remaining hydrogen atoms were calculated. All hydrogen positions were added to the final structure calculations but were not refined. Scattering factors, and Δ*f*' and Δ*f*'' values, were taken from the literature.<sup>41</sup>

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**Supplementary Material Available:** Anisotropic thermal parameters for (*RSRS,SRSR*)-**4c** (2 pages). Ordering information is given on any current masthead page.

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