Resolution of *tert*-Butyl Methyl Sulfoxide via Organometallic Lewis Acids and Chiral Amplification in Asymmetric Transformations of the Ruthenium Center in $[CpRu(CO)(PPh_3)]^+$ Adducts

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Summary: A method has been developed for the preparation of an optically pure sulfoxide from chiral sulfoxides obtained in moderate enantiomeric excess (ee) by catalytic asymmetric oxidation of dialkyl sulfides. Mutual resolution of the sulfoxide and chiral metal centers allows the preparation of optically pure sulfoxides and metal complexes. Treatment of racemic $[CpRu(CO)(PPh)_3(acetone)]^+$ with 32% ee (*R*)-*t*-BuMeSO produces an initial mixture with 20% diastereomeric excess (de) of (R_{Ru},S_S)- and (S_{Ru},S_S)-$[CpRu(CO)(PPh_3)(t\text{-BuMeSO})]^+$ diastereomers and their enantiomers. In solution this mixture epimerizes at the metal center to yield 32% ee (S_{Ru},S_S)-$[CpRu(CO)(PPh_3)(t\text{-BuMeSO})]^+$ with 94% de. The racemate is much less soluble than the pure enantiomer, so that initial precipitation yields a solid with near-zero optical activity. Recrystallization of the complex in the supernatant yields enantiomerically pure $(S_{Ru},S_S)[CpRu(CO)(PPh_3)(t\text{-BuMeSO})]SbF_6$. *This process allows isolation of both the enantiomerically pure sulfur center and metal center* starting from a sulfoxide obtained in only modest ee.

Optically active sulfoxides are recognized as versatile reagents for asymmetric synthesis,[1-4] and numerous approaches to their preparation have been developed in recent years.[3-6] Kagan et al. have developed an efficient asymmetric oxidation of prochiral sulfides to sulfoxides using a modified Sharpless epoxidation reagent. This reagent yields sulfoxides with varying degrees of enantiomeric enrichment depending upon the nature of the substrates.[7] Only in the limited cases where products were initially formed in high enantiomeric excess, however, could enantiomerically pure sulfoxides be obtained conveniently by means of fractional crystallization. An alternative method for further optical enrichment of these sulfoxide products would be desirable. For example, a sulfoxide which might ordinarily be a liquid may form a crystalline coordination complex which could permit its resolution via crystallization. Chiral transition-metal-complex-aided resolution of racemic sulfoxides are known in only a few cases, although the technique was first demonstrated in 1934.[8] In the course of our study of $[CpRu(CO)(PPh_3)]SbF_6$ as a Lewis acid[9] and our studies of asymmetric oxidation of sulfoxides,[10] we examined the coordination chemistry of sulfoxides with this moiety. We wished to investigate the potential for chiral recognition of the sulfoxide by the stereogenic ruthenium center. Our aim was to develop a means of resolving chiral sulfoxides of varying enantiomeric excess based on diastereomeric stabilities and the solubility difference of the racemates and enantiomers of the sulfoxide complexes. The resolution of *tert*-butyl methyl sulfoxide via complexation to a ruthenium Lewis acid and the asymmetric transformation of the metal center as a result of binding to the optically active sulfoxide will be discussed.

Experimental Section

All reactions of organometallic compounds were carried out under an atmosphere of nitrogen. Dichloromethane was distilled under nitrogen from calcium hydride. Other reagents and solvents were used as received.

Infrared spectra were obtained with a Nicolet 5SX FTIR spectrometer. ^1H NMR spectra were recorded on Bruker WM-250 and Yale 490 spectrometers. Chemical shifts are reported in parts per million downfield from tetramethylsilane using the residual proton resonance of the solvent for calibration. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

(Neomenthyl)$CpRu(CO)(PPh_3)I$[11] and the Lewis acid precursor $[CpRu(CO)(PPh_3)(acetone)]SbF_6$[9] was prepared according to the published procedures. The enantiomeric purity of *tert*-butyl methyl sulfoxide, was obtained from the *R*:*S* ratio determined by ^1H NMR spectroscopy at 490 MHz using the chiral Lewis acid $[NMCpRu(CO)(PPh_3)]SbF_6$ (NM = neomenthyl) as a shift reagent in $CDCl_3$. The shift reagent was generated in situ by treatment of $NMCpRu(CO)(PPh_3)I$[11] with $AgSbF_6$.

Preparation of $[CpRu(CO)(PPh_3)(tert\text{-butyl methyl sulfoxide})]SbF_6$ (1). To a 5-mL CH_2Cl_2 solution of compound $[CpRu(CO)(PPh_3)(acetone)]SbF_6$ (1.25 g, 1.66 mmol) was added 1 equiv of 32% enantiomeric excess (ee) (*R*)-*tert*-butyl methyl sulfoxide. A slight lightening in the color of the solution was noted upon addition of the sulfoxide. After 20 min of stirring, an off-white crystalline precipitate was obtained upon addition of 30 mL of diethyl ether. The supernatant was decanted and the precipitate was dried in vacuo for 12 h. This yielded 1 (1.30 g, 1.60 mmol, 96%) as pale yellow, air-stable crystals. IR (CH_2Cl_2): ν(CO) 1996 cm^{-1} (s). ^1H NMR (CD_2Cl_2, 25 °C, 490 MHz): isomer 1A ($S_{Ru}S_S,R_{Ru}R_S$) δ 1.40 (s, 9 H, $(CH_3)_3CS$), 2.74 (s, 3 H, CH_3S), 5.26 (s, 5 H, HCp), 7.2-7.7 (m, 15 H, Ph_3P); isomer 1B ($S_{Ru}R_S,R_{Ru}S_S$) δ 1.33 (s, 9 H, $(CH_3)_3CS$), 2.33 (s, 3 H, CH_3S), 5.29 (s, 5 H, HCp), 7.3-7.6 (m, 15 H, Ph_3P). Anal. Calcd for

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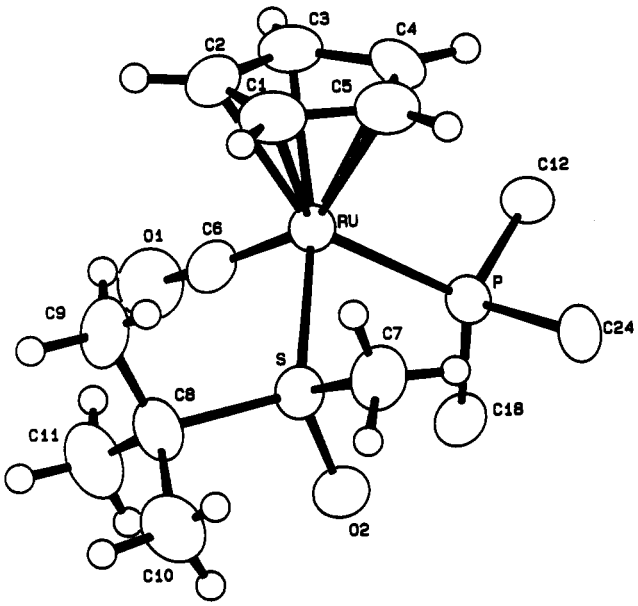

Figure 1. ORTEP drawing of the cation in [CpRu(CO)(PPh_3)(*t*-BuMeSO)]SbF_6·MeOH. Only the ipso carbon atoms of the phenyls are shown.

$C_{29}H_{32}O_2F_6PSRuSb$: C, 42.87; H, 3.97; S, 3.95. Found: C, 42.44; H, 3.87; S, 3.65. ^1H NMR analysis indicates that crystallization from CH_2Cl_2/Et_2O avoided the inclusion of solvent; whereas crystallization from CH_2Cl_2/MeOH resulted in solvent incorporation.

Preparation of (−)-(S_{Ru},S_S)-[CpRu(CO)(PPh_3)(*tert*-butyl methyl sulfoxide)]SbF_6, (S_{Ru},S_S)-1A, in High ee. The procedure above was followed, except that the reaction was allowed to stand for 24 h. This yielded a solution with 32% ee and 94% diastereomeric excess (de) (S_{Ru},S_S)-**1A**. Partial precipitation of the racemate with equal volume of Et_2O gave a supernatant with >90% ee (S_{Ru},S_S)-**1A**. Evaporation of this solution and recrystallization gave the product in high enantiomeric purity. $[\alpha]_D^{25}$ of the pure compound in CH_2Cl_2 is ~−102°. ^1H NMR spectroscopy indicated no incorporation of solvent in the crystals of the pure enantiomer.

Preparation of (R_S)-*tert*-Butyl Methyl Sulfoxide in High ee. (S_{Ru},S_S)-**1A** and 5 equiv of NaI were dissolved in acetone. The mixture was allowed to stir for 70 h, during which time the color of the mixture changed from pale yellow to orange. Completion of the reaction was verified by ^1H NMR analysis of the mixture. Solvent was removed from the reaction mixture using a rotary evaporator at room temperature. The residue was extracted with methylene chloride until it did not have an orange tinge. Upon removal of solvent from the combined extracts, (R_S)-*tert*-butyl methyl sulfoxide in high ee was obtained by high-vacuum transfer from the residue. CpRu(CO)(PPh_3)I in the residue from the vacuum transfer showed no significant rotation.

Crystallographic Studies. A solution of **1A** and **1B** was allowed to equilibrate to a de of 94%. Precipitation and recrystallization from methanol/CH_2Cl_2 yielded crystals of racemic **A**. A crystal (0.15 × 0.15 × 0.21 mm) was mounted in a capillary, and data were collected on a Rigaku AFC5S diffractometer using Cu Kα radiation. The position of the Ru atom was determined from the Patterson map and the remaining non-hydrogen atoms were found in subsequent difference Fourier analyses using the TEXSAN structure determination package. The structure determination followed procedures outlined elsewhere,[12] and the results are given in full in the supplementary material but are summarized in Tables I and II. The principal purpose here was to establish the relative configuration of the ruthenium and sulfur centers. A disordered MeOH solvent prevented a really high quality structure determination. The bond lengths for the S–methyl and S–oxygen (1.79 and 1.48 Å, respectively) firmly established the identity of the groups bound to sulfur and consequently the relative configuration at sulfur.

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Table I. Crystallographic Data for [CpRu(CO)(PPh_3)(*t*-BuMeSO)]SbF_6·MeOH

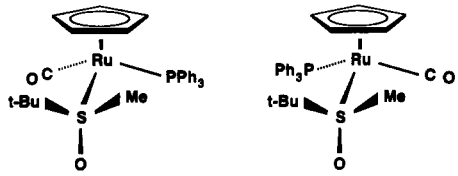
$SbRuSPF_6O_2C_{29}H_{32}·CH_4O$	fw 844.46
a = 11.243 (4) Å	space group $P\bar{1}$ (No. 2)
b = 14.135 (2) Å	T = 23 °C
c = 10.434 (3) Å	ρ = 1.714 g/cm^3
α = 91.55 (1)°	μ = 121.68 cm^{-1}
β = 94.53 (3)°	R = 0.047
γ = 97.87 (2)°	R_w = 0.059
V = 1636.3 (8) Å^3	
Z = 2	

Table II. Positional Parameters and *B*(eq) Values for [CpRu(CO)(PPh_3)(*t*-BuMeSO)]SbF_6·MeOH

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ru	0.72861 (6)	0.70258 (5)	0.84061 (7)	2.77 (3)
S	0.8951 (2)	0.8084 (2)	0.7936 (2)	3.2 (1)
P	0.7292 (2)	0.7874 (2)	1.0377 (2)	2.7 (1)
O(1)	0.5375 (7)	0.8038 (6)	0.7061 (8)	5.5 (4)
O(2)	0.9073 (6)	0.9059 (5)	0.8518 (6)	3.9 (3)
C(1)	0.792 (1)	0.5693 (7)	0.761 (1)	4.4 (5)
C(2)	0.669 (1)	0.5673 (7)	0.721 (1)	4.4 (5)
C(3)	0.603 (1)	0.5653 (7)	0.832 (1)	3.8 (4)
C(4)	0.684 (1)	0.5641 (7)	0.940 (1)	4.3 (5)
C(5)	0.802 (1)	0.5674 (7)	0.896 (1)	4.4 (5)
C(6)	0.611 (1)	0.7685 (8)	0.757 (1)	3.9 (4)
C(7)	1.0280 (9)	0.7591 (8)	0.848 (1)	4.0 (5)
C(8)	0.914 (1)	0.8251 (8)	0.619 (1)	4.3 (5)
C(9)	0.901 (1)	0.7296 (9)	0.547 (1)	5.6 (6)
C(10)	1.039 (1)	0.883 (1)	0.612 (1)	5.9 (6)
C(11)	0.817 (1)	0.881 (1)	0.574 (1)	5.8 (6)
C(12)	0.6098 (8)	0.7336 (6)	1.1343 (9)	2.9 (4)
C(13)	0.628 (1)	0.7234 (8)	1.267 (1)	4.1 (5)
C(14)	0.530 (1)	0.6926 (9)	1.336 (1)	5.2 (6)
C(15)	0.418 (1)	0.6738 (8)	1.278 (1)	4.8 (6)
C(16)	0.3973 (9)	0.6833 (7)	1.147 (1)	4.4 (5)
C(17)	0.494 (1)	0.7117 (7)	1.075 (1)	3.6 (4)
C(18)	0.7034 (8)	0.9127 (7)	1.0491 (9)	3.0 (4)
C(19)	0.700 (1)	0.9537 (7)	1.172 (1)	4.0 (5)
C(20)	0.677 (1)	1.0471 (8)	1.186 (1)	4.7 (5)
C(21)	0.655 (1)	1.0994 (8)	1.077 (1)	4.8 (5)
C(22)	0.657 (1)	1.0577 (7)	0.956 (1)	4.5 (5)
C(23)	0.6818 (9)	0.9656 (7)	0.941 (1)	3.5 (4)
C(24)	0.8724 (8)	0.7847 (7)	1.1346 (8)	3.0 (4)
C(25)	0.899 (1)	0.6980 (7)	1.1797 (9)	3.6 (4)
C(26)	1.010 (1)	0.6925 (8)	1.240 (1)	4.4 (5)
C(27)	1.095 (1)	0.772 (1)	1.254 (1)	4.6 (5)
C(28)	1.070 (1)	0.8584 (9)	1.209 (1)	4.5 (5)
C(29)	0.9576 (9)	0.8666 (7)	1.150 (1)	3.5 (4)
Sb	0.75548 (6)	0.41810 (5)	0.35105 (7)	3.94 (3)
F(1)	0.9075 (6)	0.4405 (5)	0.2907 (8)	7.6 (4)
F(2)	0.6009 (6)	0.3967 (6)	0.4082 (7)	7.0 (4)
F(3)	0.700 (1)	0.465 (1)	0.207 (1)	18 (1)
F(4)	0.739 (1)	0.3032 (8)	0.285 (2)	25 (1)
F(5)	0.768 (1)	0.5390 (8)	0.410 (2)	17 (1)
F(6)	0.813 (1)	0.386 (1)	0.507 (1)	19 (1)
O(3)	0.450 (1)	0.9552 (9)	0.443 (1)	10.6 (8)
C(30)	0.359 (1)	0.917 (1)	0.447 (1)	5.7 (7)

Results and Discussion

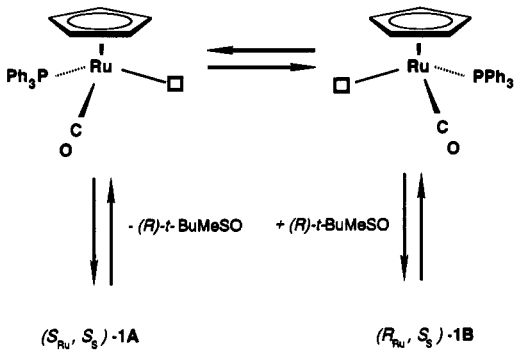
The Lewis acid–base adduct [CpRu(CO)(PPh_3)(*tert*-butyl methyl sulfoxide)]SbF_6 (**1**) was obtained by addition of *tert*-butyl methyl sulfoxide to a solution of [CpRu(CO)(PPh_3)(acetone)]SbF_6 in CH_2Cl_2. The ^1H NMR spectrum of the initial product showed two distinct species owing to the formation of the two diastereomers, **1A** and **1B**, as expected for a complex containing both a stereogenic ruthenium and sulfur center. *Both the enantiomers shown and their mirror images, the* (R_{Ru},R_S) *and* (S_{Ru},R_S), *are present.* A **1A** to **1B** ratio of 60:40 was formed initially. Upon standing in solution, however, isomer **1B** was observed to gradually convert to **1A** with an approximate half-life of 4 h. An equilibrium ratio of 97:3 was measured



(S_{Ru}, S_S)-1A (R_{Ru}, S_S)-1B

for 1A:1B after allowing the solution to stand for 2 days. The stereochemistry of racemic 1A was determined by an X-ray crystallographic measurement (vide infra) and the enantiomer with a S_{Ru},S_S configuration is shown in Figure 1. *(n.b. The chirality descriptor for the sulfoxide changes upon binding to the metal; a (R_S)-sulfur center in t-BuMeSO becomes (S_S) upon coordination to Ru.)*

The conformation found in the solid and presumably that in solution minimizes interaction between the *tert*-butyl group and the phosphine.[13] This *tert*-butyl methyl sulfoxide complex is ideal both in terms of its large diastereomeric ratio at equilibrium and relatively facile epimerization at the Ru center. The equilibrium de can be attributed to the large steric difference of the two alkyl groups, and an enhanced epimerization rate can be attributed to a weakened M–S bond from the interaction of the bulky *tert*-butyl group.[14] A dynamic chiral recognition process drives the asymmetric transformation of the stereogenic ruthenium center:



(S_{Ru}, S_S)-1A (R_{Ru}, S_S)-1B

The driving force is preferential complexation of a specific enantiomer of *t*-BuMeSO by a particular enantiomer of the CpRu(CO)(PPh_3) Lewis acid. When the sulfoxide dissociates, the coordinatively unsaturated CpRu(PPh_3)(CO) fragment has limited chiral stability and racemizes relatively rapidly. Thus, a given hand of sulfoxide can select the most thermodynamically compatible configuration of the stereogenic ruthenium center. *Therefore, if the sulfoxide were enantiomerically pure, practically **all** of the ruthenium centers would be converted to one configuration.*

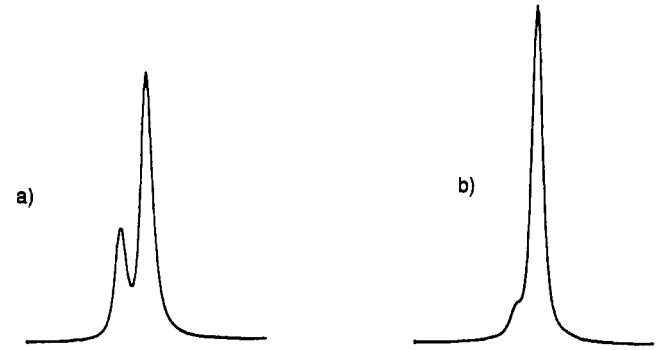


Figure 2. δ 2.72 and 2.73 resonances of NMCpRu(CO)(PPh_3)(*t*-BuMeSO)SbF_6 obtained from (a) the starting enriched sulfoxide and (b) the sulfoxide recovered from the complex in solution after one precipitation of racemate.

Resolution of *tert*-Butyl Methyl Sulfoxide. Nonracemic *t*-BuMeSO with an enrichment in the (*R*)-enantiomer was prepared by oxidizing *t*-BuMeS using the Kagan modification of the Sharpless reagent, Ti(O-*i*-Pr)$_4$/H_2O/TBHP/DIPT, as shown in eq 1.[7b] A 32%

$$t\text{-BuMeS} \xrightarrow[t\text{-BuOOH/(+)-DIPT}]{\text{Ti(O-}i\text{-Pr)}_4/H_2O} (S)\text{-}t\text{-BuMeSO} + (R)\text{-}t\text{-BuMeSO} \quad (1)$$

enantiomeric excess of the (*R*)-product was determined by ^{1}H NMR spectroscopy at 490 MHz using a convenient chiral shift reagent (vide infra). The Lewis acid–base adduct [CpRu(CO)(PPh_3)(*t*-BuMeSO)]SbF_6 was obtained by addition of the nonracemic sulfoxide to a solution of racemic [CpRu(CO)(PPh_3)(acetone)]SbF_6 in CH_2Cl_2. The optical rotation of the reaction mixture was monitored after mixing the reactants. A significant increase ($\sim$1000%) in the magnitude of α was observed as the acetone was displaced by the sulfoxide. ^{1}H NMR analysis confirmed that the conversion to the sulfoxide complex was essentially complete in 20 min.

If this solution was treated with an equal volume of diethyl ether to precipitate a portion of the sulfoxide complex, the precipitate showed little optical activity. This suggested that the precipitate was a mixture of racemates of 1A and 1B. In the original solution each of the diastereomers was present as a nonracemic mixture of enantiomers, (R_{Ru},R_S; S_{Ru},S_S)-1A and (R_{Ru},S_S; S_{Ru},R_S)-1B, with the (S_S)-enantiomers in excess. Precipitation of the racemates resulted in enrichment of the solution in the complexes containing the bound sulfoxide with the S_S configuration, namely (S_{Ru},S_S)-1A and (R_{Ru},S_S)-1B. Subsequent stepwise precipitations from the enriched supernatant until the precipitates showed significant optical activity, provided a solution containing (S_{Ru},S_S)-1A and (R_{Ru},S_S)-1B in high enantiomeric excess. This A/B mixture of diastereomers could be decomposed to yield high ee *t*-BuMeSO (vide infra). Alternatively, such a solution could be allowed to stand for 24 h and epimerize to a 97:3 mixture of 1A and 1B diastereomers, which effectively provides a solution of relatively pure (S_{Ru},S_S)-1A. Evaporation of the solution and recrystallization of the solid yield pure (S_{Ru},S_S)-1A.

tert-Butyl methyl sulfoxide can be recovered from 1A and 1B by decomplexation with iodide, as shown in eq 2. After the ruthenium was recovered as the CpRu(CO)-

(13) Variable-temperature ^{1}H NMR experiments were carried out on the *t*-BuMeS complex to study the conformational equilibrium with respect to the coordination of the metal to the enantiotopic lone pairs on sulfur. A large difference in the diastereomeric populations of the *t*-BuMeSO complex may have been anticipated on the basis of the high chiral recognition shown by [CpRu(CO)(PPh_3)(*t*-BuMeS)]SbF_6. The presence of one predominant diastereomer in its sulfide counterpart was observed in low-temperature NMR studies. A parallel could be drawn between these two systems by assuming that replacement of a lone pair by an oxygen atom would only have a modest effect on the conformational preference. The similarity in conformational preference in sulfides and sulfoxides in binding to [CpRe(NO)(PPh_3)]$^+$ has been pointed out by Gladysz (Quirós Méndes, N.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1991**, *10*, 2199.)

(14) The analogous *p*-tolyl methyl sulfoxide complex was formed with a $\sim$50:50 diastereomeric ratio. No significant variation in this ratio was observed at room temperature over a period of 10 days. Low-temperature ^{1}H NMR spectra showed that the equilibrium ratio of the two diastereomeric conformations of [CpRu(CO)(PPh_3)(*p*-tolyl methyl sulfide)]$^+$ was 40:60. This indicated that there was only a modest chiral recognition for the sulfide and presumably also for the sulfoxide. The epimerization rate appears to be slower in this system.

(15) Attempts to convert enantiomerically enriched 1A to other nonracemic [CpRu(CO)(PPh_3)(L)]$^+$ complexes has met with limited success. In order to prepare an enantiomerically pure metal center from the one coordinated to the sulfoxide, the substitution by other ligands must proceed faster than racemization of the 16-electron [CpRu(CO)(PPh_3)]$^+$ fragment if the pathway is dissociative.

$(PPh_3)I$ complex, it was converted to $[CpRu(CO)(PPh_3)(t\text{-BuMeSO})]^+ + I^- \rightarrow CpRu(CO)(PPh_3)I + t\text{-BuMeSO}$ (2)

$(PPh_3)(acetone)]SbF_6$ for reuse. The optical purity of the sulfoxide could be determined by the ^1H NMR spectrum of the neomenthylcyclopentadienyl analogue of 1 (Figure 2), which was generated by the reaction between $[NMCpRu(CO)(PPh_3)]SbF_6$ and the sulfoxide. The differentiation of the resonances in (R_{Ru},R_S) and (S_{Ru},S_S) centers arises because they are diastereomeric in the presence of the neomenthyl group. The 490-MHz ^1H spectra in Figure 2 illustrate the improvement possible in a single precipitation. The spectrum in Figure 2a shows the initial ratio of enantiomers, and Figure 2b shows the ratio after the sulfoxide is released from the product remaining in solution after precipitation of the racemates. Minor variations in chemical shift are observed with concentration changes.

Chiroptical Properties. Negative rotations are observed at the Na_D line for both (S_{Ru},S_S)-**1A** and (R_{Ru},S_S)-**1B** owing to an intense negative CD band at 277 nm in both of them. Two much weaker negative CD bands are observed in (–)-(S_{Ru},S_S)-**1A** at 317 and 379 nm.

Conclusion

The efficacy of $[CpRu(CO)(PPh_3)]SbF_6$ as a reagent for the resolution of sulfoxides has been demonstrated. As the racemate of either **1A** or **1B** is less soluble than the pure enantiomer, enhancement of the enantiomeric purities of the soluble enantiomers is readily effected via precipitation of the racemate. The thermodynamic stability of **1A** relative to **1B** effectively provides a route to transform a racemic $CpRu(CO)(PPh_3)X$ complex into a complex with a nearly pure stereogenic Ru center.

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Supplementary Material Available: Tables of bond distances and angles and U values (3 pages). Ordering information is given on any current masthead page.

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Synthesis and Crystal Structure of $[\{Li(2,4,6\text{-}^tBu_3C_6H_2)\}\{LiP(H)(2,4,6\text{-}^tBu_3C_6H_2)\}]_2$: A Compound with an Unusual $(LiPLiC)_2$ Eight-Membered Ring

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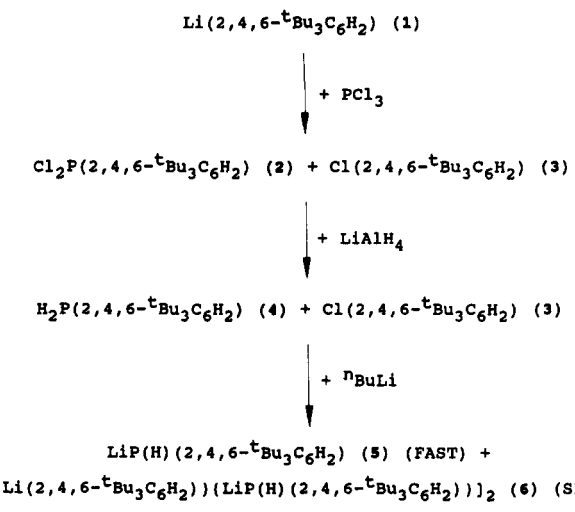
Summary: $[\{Li(2,4,6\text{-}^tBu_3C_6H_2)\}\{LiP(H)(2,4,6\text{-}^tBu_3C_6H_2)\}]_2$ is formed during the synthesis of $LiP(H)(2,4,6\text{-}^tBu_3C_6H_2)$. The X-ray structural analysis shows the presence of four two-coordinate Li atoms, of which two exhibit a short Li–C(aryl) σ-bond. The other two Li atoms exhibit nearly six identical Li–C(aryl) distances (Li–C 2.31 Å) and a short lithium to ring center distance (1.83 Å). The latter suggests an η^6 coordination of the aromatic system to the lithium atom.

In addition to being indispensible reagents for preparative organometallic and organic chemistry, lithium compounds often exhibit fascinating structures in the solid state.[1] In the compounds studied up to now, the Li atom exhibits a pronounced tendency to interact with electron-rich ligands or donor molecules. In many cases, the structures cannot be explained in terms of classical bonding theory. Thus the formation of covalent multicenter bonds and σ-bonds as well as interactions with π-systems is observed. We now report the structure of compound **6** in which the two lithium reagents $Li(2,4,6\text{-}^tBu_3C_6H_2)$ (**1**) and $LiP(H)(2,4,6\text{-}^tBu_3C_6H_2)$ (**5**) associate with formation of a central eight-membered $(LiPLiC)_2$ ring.

The reaction of $Li(2,4,6\text{-}^tBu_3C_6H_2)$ (**1**) with PCl_3, followed by reduction with $LiAlH_4$, is reported to give $H_2P(2,4,6\text{-}^tBu_3C_6H_2)$ (**4**) in almost quantitative yield.[2] However, when we reacted **4**, prepared by the literature method, with ^{n}BuLi in hexane, we obtained $LiP(H)(2,4,6\text{-}^tBu_3C_6H_2)$ (**5**) in only 62% yield. After 3 days, large colorless crystals of $[\{Li(2,4,6\text{-}^tBu_3C_6H_2)\}\{LiP(H)(2,4,6\text{-}^tBu_3C_6H_2)\}]_2$ (**6**) were isolated from the filtrate. We subsequently found, by means of Cl analysis, that the reaction of **1** with PCl_3 followed by $LiAlH_4$ reduction gives a mix-

Scheme I



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