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Coordination of Chiral Amines to Coordinatively Unsaturated Cp*Ir-Amino Acid Complexes Allows Determination of Enantiomeric Purity

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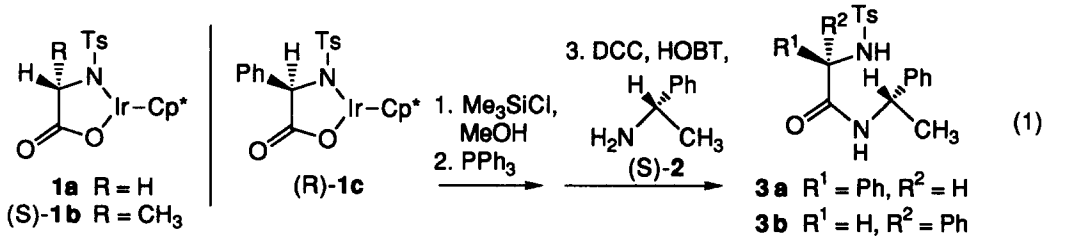
Abstract: Coordinatively unsaturated complexes of the Cp*Ir fragment to the dianion of N-tosylamino acids combine with chiral amines in a highly diastereoselective fashion, such that metallacycle substituents R (amino acid side chain) and Cp* are cis. Observation of adducts between the alanine- and phenylglycine-derived complexes and (S)-α-methylbenzylamine by NMR at low to ambient temperature allows determination of the enantiomeric purity of either component, 1 to 2% impurity being easily detectable. Furthermore, α-methylbenzylamine was analyzed for its enantiomeric purity independent of external chiral reagent, by its conversion to N,N'-bis(1-phenylethyl)urea.

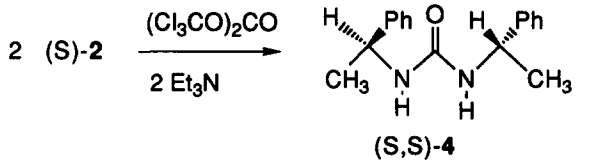
INTRODUCTION

Enantiomerically pure organometallic complexes and ligands play an ever-more important role in the synthesis of scalemic or enantiopure organic compounds.[1] Successful enantioselective synthesis depends critically on the determination of enantiomeric purity, modern methods for which utilize NMR spectroscopy[2] or chromatography.[3] The problems of determining enantiomeric purity of organometallic complexes by optical rotation have been concisely discussed.[4] Recently we reported the synthesis and characterization of rare, coordinatively unsaturated, monomeric amino acid complexes **1**.[5] Because the determination of the enantiomeric purity of **1** using chiral lanthanide shift reagents[6] was unsuccessful due to peak broadening, we resorted to a relatively tedious derivatization: the amino acid-derived ligand was liberated by addition of two moles of HCl, and coupling with (S)-α-methylbenzylamine (S)-**2** mediated by DCC (dicyclohexylcarbodiimide) and HOBT (1-hydroxybenzotriazole) provided diastereomeric amides **3**, eq. 1. In particular, the enantiomeric purity of **1c** (≥ 95%, **3a** to **3b** in a ratio ≥ 20 to 1) was encouraging, in view of the susceptibility of phenylglycine derivatives to epimerization.[7] However, here we report a much more convenient method of evaluating enantiopurity based on



(1)

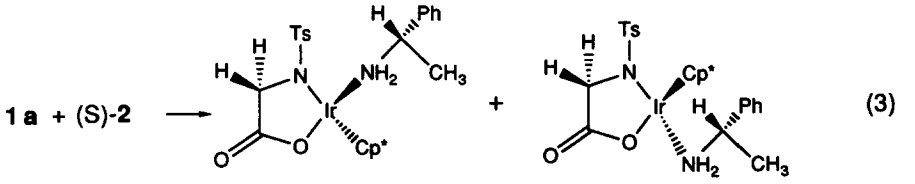
complexation of (S)-**2** to **1**. Conversely, the availability of enantiomerically pure **1** may offer a method of determining the enantiopurity of chiral amines. In addition, we report the independent evaluation of the enantiomeric purity of **2** by conversion to the corresponding symmetrical urea **4**, eq. 2, an application which we have not found in the literature.



(S,S)-**4** (2)

RESULTS AND DISCUSSION

At the outset of this investigation, we knew[5] that complexes **1** are red, air-stable compounds which bind within seconds to CO and phosphines to produce yellow, coordinatively saturated derivatives. Titration of a red solution of achiral **1a** in $CDCl_3$ in an NMR tube with 1.0 equiv of (S)-**2** gave a yellow solution exhibiting one set of resonances in its ^1H and ^{13}C NMR spectra (Table 1). Based on earlier work, the changes occurring upon amine addition in both the solution color (red to yellow) and in the position of the strong IR absorption for the carboxylato C=O function (from 1684 to 1642 cm^{-1} in CH_2Cl_2) were indicative of achieving coordinative saturation of the metal, presumably by amine coordination through nitrogen as in **5a**, eq. 3.[8] Furthermore, in the ^1H NMR spectrum of the mixture, a set of two mutually coupled doublets at δ 3.68 and 3.75 ppm (J = 16.5 Hz)



(3)

($S_{Ir}S_{amine}$)-**5a** = (S,S)-**5a** ($R_{Ir}S_{amine}$)-**5a** = (R,S)-**5a**

indicated that the methylene protons of the glycine unit were diastereotopic, consistent with the creation of a chiral center at Ir upon amine complexation. However, in principle, both diastereomeric complexes (S,S)- and (R,S)-**5a** could have been present, and it was difficult to imagine how complexation of (S)-**2** to **1a** would proceed with *complete* diastereoselectivity. Our working hypothesis was that amine exchange at ambient probe temperatures was sufficiently rapid so as to lead to an averaged spectrum. Indeed, observation of spectra at temperatures below -25 °C showed two sets of resonances in a ratio of 1.2 to 1, revealing a slight diastereoselection, although it is not known which isomer predominates. For an representative illustration of the effects of temperature on ^1H NMR spectra of amine adducts **5**, see Fig. 1.

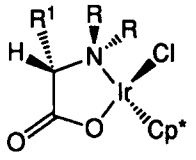
Our next task was to determine if complexation of chiral **1** to amines was a diastereoselective reaction. Previous experiments[5] indicated that the reaction of chiral complexes **1b** and **1c** with CO and sterically undemanding phosphines (PMe_3, PMe_2Ph) proceeds with diastereoselectivity of at least 25 or 50 to 1. nOe experiments on the adducts established a cis arrangement of side chain R and Cp*, a result rationalized by preferred approach of the ligand to **1** from the side of the metallacycle opposite R.[5] This was shown for PMe_3 to be a result of *both* kinetic control (in additions at room temperature) and thermodynamic control (in equilibration at 80 °C, half-life = 14 h).[5b] The solution resulting from addition of achiral primary amine $PhCH_2NH_2$ to **1b**

Table 1. ^{1}H NMR Data[a] (δ, ppm) for Adducts of Complexes **1** and Amine (S)-**2** in $CDCl_3$.

Complex	Temp (°C), Freq (MHz)	$C_5(CH_3)_5$	amino acid C*H*R and R	Ts	amine aryl H, C*H* and CH_3	amine N*H*
1a	25, 500	1.62 (s, 15H)	3.77 and 3.70 (two d, each J = 16.5 Hz, 1H)	7.47 (d, J = 8, 2H) 7.14 (d, J = 8, 2H) 2.35 (s, 3H)	7.34-7.40 (m, 3H) 7.27-7.34 (m, 2H) 4.03-4.14 (m, 1H) 1.49 (d, J = 7, 3H)	[b]
	-50, 500	1.58 (s, 15H, maj)[c] 1.68 (s, 15H, min)	[b]	7.17 (d, J = 8, 2H, maj) 7.12 (d, J = 8, 2H, min) 2.35 (s, 3H, maj + min)	7.3-7.45 (m), 7.22-7.27(m) 1.51 (d, J = 7, 3H, maj) 1.47 (d, J = 7, 3H, min)	4.17-4.30[d] (m) 4.04-4.14 (m) 3.59-3.88 (m)
(S)-**1b**	25, 400	1.70 (s, 15H)	3.73 (q, J = 7, 1H) 1.16 (d, J = 7, 3H)	7.44 (d, J = 8, 2H) 7.10 (d, J = 8, 2H) 2.352 (s, 3H)	7.33-7.40 (m, 2H) 7.25-7.32 (m, 3H) 3.93 (br q, J ≈ 6, 1H) 1.49 (d, J = 6, 3H)	[b]
	-50, 400	1.71 (s, 15H)	3.67 (q, J = 7, 1H) 1.20 (d, J = 7, 3H)	7.39-7.44 (m, 2H) 7.11(d, J = 8, 2H) 2.353 (s, 3H)	7.35-7.38[d] (m, 3H) 7.25 (dd, J = 7, 1, 2H) 1.47 (sl br d, J = 5.5, 3H)	4.53 (sl br d, J = 10, 1H) 3.63-3.8[b] (m, 2H)
(RS)-**1b**[e]	25, 400	1.69 (s, 15H)	3.74 (q, J = 7, 1H) 1.15 (d, J = 7, 3H)	7.42 (d, J = 8, 2H) 7.09 (d, J = 8, 2H) 2.358[e](s, 3H)	7.26-7.46[f] (m, 10H) 1.49 (d, J = 6, 6H) [d]	4.05[f] (br s, $w_{1/2}$ ≈ 60 Hz)
		1.57 (s, 15H)	3.85 (q, J = 7, 1H) 1.07 (d, J = 7, 3H)	7.54 (d, J = 8, 2H) 7.16 (d, J = 8, 2H) 2.341[e](s, 3H)	[f]	
	-50, 400	1.71 (s, 15H)	3.67 (q, J = 7, 1H) 1.20 (d, J = 7, 1H)	7.10[g] (d, J = 8, 2H) 2.357[e] (s, 3H)	7.25[g] (d, J = 7, 2H) 1.46[e] (sl br d, J = 5.2, 3H)	4.53[e,f] (sl br d, J = 9, 1H) 4.28 (sl br dd, J = 12, 4, 1H) 3.89 (sl br t, J = 9, 1H)
		1.57 (s, 15H)	3.78 (q, J = 7, 1H) 1.11 (d, J = 7, 1H)	7.16 (d, J = 8, 2H) 2.350[e,g] (s, 3H)	1.48 [e,g] (d, J = 6.4, 3H)	4.06-4.16 (m, 1H) 3.6-3.8 (m, 2H)
(R)-**1c**	25, 500	1.49 (s, 15H)	4.98[h] (s, 1H)	2.26[h] (s, 3H)	4.21[h] (q, J = 6, 1H) 1.55 (d, J = 6, 3H)	
	-50, 500	1.41 (s, 15H)	4.99[i] (s, 1H)	2.25[i] (s, 3H)	4.16-4.24[i] (m, 1H) 1.58 (d, J = 5.5, 3H)	4.97-5.04 (m, 1H) 4.16-4.24 (m, 1H)
(RS)-**1c**[e]	25, 500	1.47 (s, 15H)	4.99[j] (s, 1H)	2.25[j] (s, 3H)	4.06-4.22[f,j] (m, 2H) 1.57 (d, J = 6, 6H)	[b]
		1.65 (s, 15H)	4.96[j] (s, 1H)	2.22[j] (s, 3H)		
	-50, 500	1.41 (s, 15H)	5.00[k] (s, 1H)	2.25[k] (s, 3H)	4.16-4.24[d] (m, 2H)	5.16[d] (sl br d, J = 11, 1H) ~5.0 (1H), 3.9-4.0 (m, 2H)
		1.64 (s, 15H)	4.99[k] (s, 1H)	2.20[k] (s, 3H)		

[a]Coupling constants in Hz [b]Resonances not listed are obscured, broadened or otherwise unassignable. [c]maj and min refer to assignments made where possible to major and minor species, present in a ratio of 1.2 to 1. [d]Resonances for amine N*H* and C*H* unassignable or uncertain. [e]Two species present in equal amounts; indicated assignments uncertain. [f]Overlapping peaks for both species present. [g]Unlisted peaks presumed to be included in multiplet, 7.32-7.48. [h]7.35-7.44 (m, 6H), 7.30 (t, J = 7, 1H), 6.9-7.05 (m, 7H). [i] 7.38-7.45 (m, 4H), 7.30-7.36 (m, 4H), 6.96-7.04 (m, 3H), 6.93 (d, J = 8, 2H), 6.89 (d, J = 8, 2H). [j] 7.27-7.42 (m, ~7H); 6.85-7.04 (m, ~7H). [k] 7.3-7.45 (m, ~12H); 7.23 (d, J = 7, 2H), 6.91-7.04 (m, ~9H), 6.89 (d, J = 8, 2H), 6.84 (d, J = 8, 2H).

exhibited NMR resonances for a single adduct at all temperatures examined.[5b] Exchange of the amine ligand was shown to be rapid at room temperature. Complexation of the heterocyclic amine DMAP to **1b** gave a mixture of adducts in a ratio of 6 to 1. nOe and NOESY data for the major component of the mixture at -60 °C allowed the conclusion that ligand exchange was slow enough to observe enhancements between DMAP and Cp* protons, and that irradiation of the alanine CH_3 doublet led to enhancement of the $C_5(CH_3)_5$ singlet, consistent with cis orientation of alanine CH_3 and Cp* substituents on the metallacycle.[5b] Thus, like phosphines or CO, amines bind so as to place the larger metallacycle substituents R and Cp* (at stereogenic centers C and Ir) cis to each other. Presumably the octahedral environment about iridium makes transannular interaction of the pseudoaxial substituent L and the substituents at stereogenic carbon the determining factor in stability. We[9] and others[10] have observed similar results in formation and reactions of Cp*IrCl complexes **6**.



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Having established that the stereogenic center of the amino acid ligand determines the stereochemistry at Ir, we considered using a chiral, enantiopure amine to evaluate the enantiomeric purity of chiral **1**. Initially, we thought that rapid amine exchange meant that complexation of **2** or other amines to chiral **1** would not permit determination of enantiomeric purity, because of averaged spectra. Happily, this is *not* the case, even at ambient

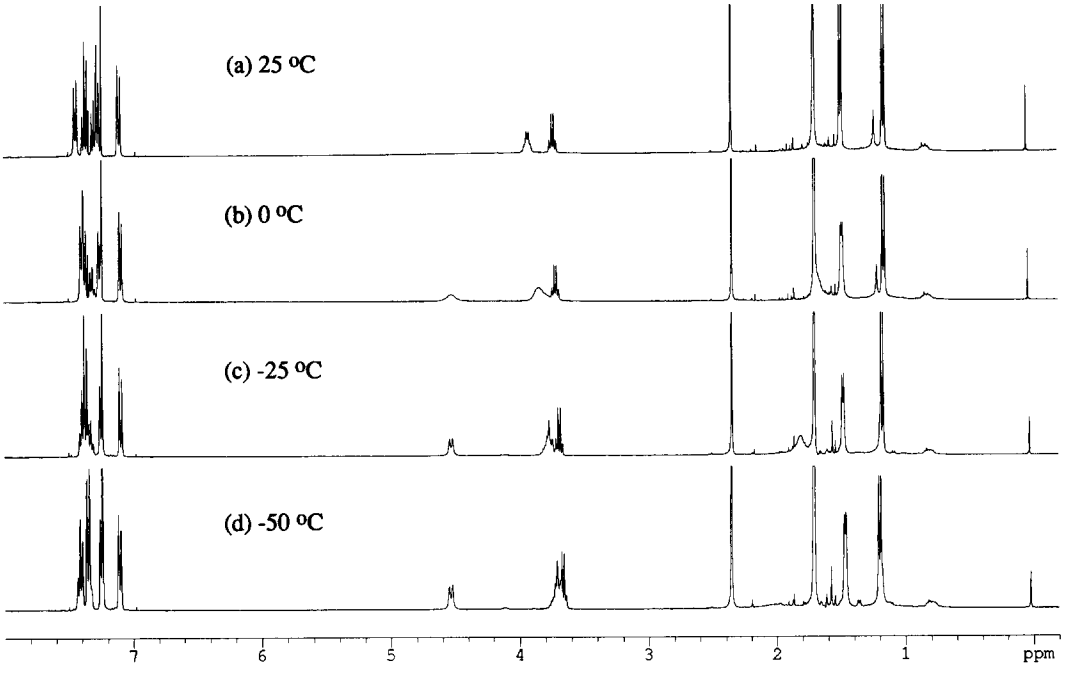
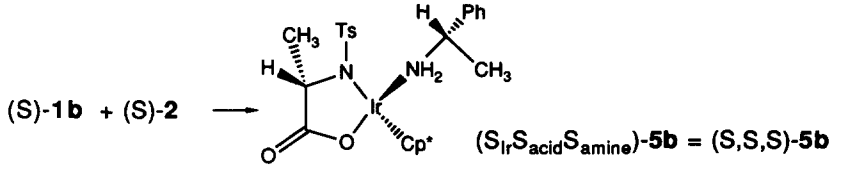


Fig.1. Effect of temperature on the ^1H NMR spectrum ($CDCl_3$,400 MHz) of (S,S,S)-**5b** derived from (S)-**1b** and (S)-**2**.

temperatures, as evidenced by the following experiments. A yellow solution formed from (S)-**1b** and (S)-**2** in $CDCl_3$ exhibited a single set of resonances, attributed to (S,S,S)-**5b** (eq. 4), because the amino acid stereocenter determines stereochemistry at the metal. As expected, a similar solution from *racemic* complex (RS)-**1b** and (S)-**2** showed two sets of resonances of equal intensity, attributed to (S,S,S)- and (R,R,S)-**5b**, eq. 5. In the latter spectrum, readily identifiable peaks which showed the greatest separation were the 15-proton singlet ascribable to the Cp* group, and the doublet for the methyl protons on the alanine side chain. The only unresolved resonances were those expected for the amine NH_2 protons, which were broadened over about 1 ppm as revealed by integration. Cooling the sample to -50 °C sharpened these signals to the point that mutual geminal



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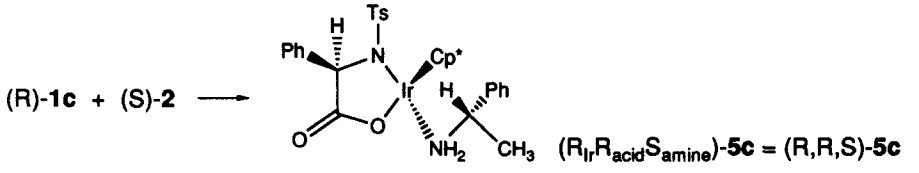

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coupling between the two NH_2 protons of 9 Hz could be seen. Otherwise, lowering sample temperature did not appreciably change the appearance or chemical shift of resonances other than those in the region δ 7.2-7.5 ppm; see Fig. 1 for these observations on the solution derived from (S)-**1b** and (S)-**2**. The experience with (S)-**2** and (R)-**1c** and the corresponding racemate (RS)-**1c** was similar, the phenyl resonances in particular changing as the sample was cooled. Changes in π-stacking of aryl residues may be responsible for these effects.[11]

The ability to detect small amounts of enantiomeric impurity in **5** was probed by spiking a solution of (S,S,S)-**5b** from (S)-**1b** with a solution of the 1 to 1 mixture of (S,S,S)- and (R,R,S)-**5b** from racemic **1b**. Even at ambient temperature, at the level of 4% added racemate, new peaks for the 2% of (R,R,S)-diastereomer present could be readily seen (Fig. 2), although quantitation by integration was made difficult in some cases by tailing of the baseline in the vicinity of the resonances from the major component. A convenient internal reference is provided by coupling of natural abundance ^{13}C to the protons of the Cp* ligand, which gives rise to two satellite resonances, each 0.5% the size of the parent at 1.70 ppm. The results of the spiking experiment confirmed that in the unspiked mixture of (S,S,S)-**5b** [Fig. 2(a)], approximately 0.5% of impurity was present, which would be either (R,R,S)-**5b** [from (R)-**1b** impurity] or a combination of (R,R,S)- *and* (S,S,R)-**5b** [the latter from (R)-**2** impurity in the derivatizing agent]. Regardless, the e.e. of (S)-**1b** was at least 99%. A similar set of experiments in (R)-**1c**, (RS)-**1c**, and (S)-**2** indicated that (R)-**1c** had been obtained earlier[5] with an e.e. of at least 96% (2% impurity detected).

Because the enantiomeric purity of (S)-**2** was of concern, we sought independent verification of this property. Amine **2** has figured prominently in the development of asymmetric catalysis and analytical methods for chiral compounds.[12] Coupling of amines to chiral acids or isocyanates, or salt formation with chiral acids has been used on numerous occasions for determination of enantiomeric purity.[13] However, we desired a method which did not depend on the enantiomeric purity of a derivatizing reagent, recently shown for the example of Mosher's acid not to be something taken for granted.[14] The original proposal of Horeau[15] to create diastereomeric mixtures by coupling two parts of scalemic chiral material inspired preparation of the symmetrical

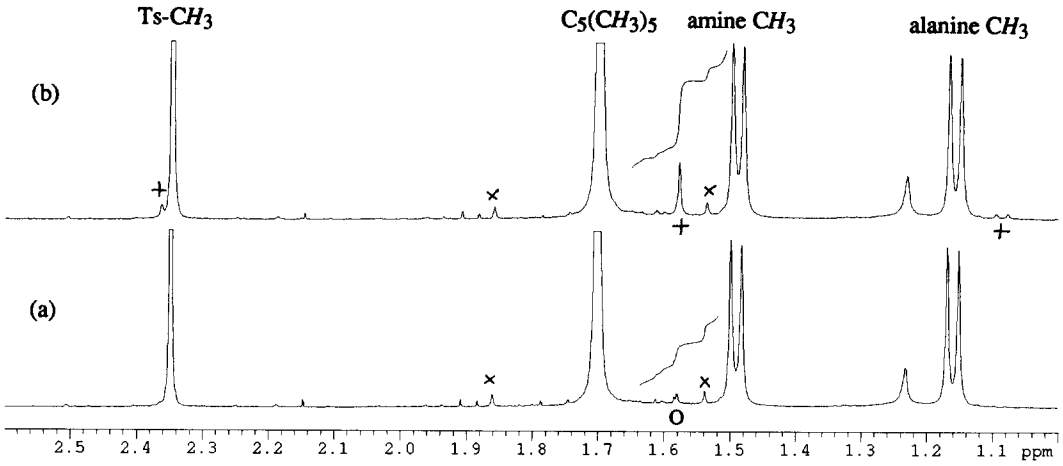

Fig.2. A portion of the ^1H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of (S,S,S)-**5b** derived from (S)-**1b** and (S)-**2**. Peaks marked with x are satellites of the resonance at 1.70 ppm, due to coupling to natural abundance ^{13}C, $^1J_{CH}$ = 129 Hz. (a) pure (S)-**1b** and (S)-**2**. One of the peaks marked with a circle is assigned to the singlet for $C_5(CH_3)_5$ of either (R,R,S)-**5b** alone or of (R,R,S)- and (S,S,R)-**5b**. See text. (b) The mixture in (a), to which was added 0.04 equiv of a similar mixture of racemic complex (RS)-**1b** and (S)-**2**. The peaks marked with a + are ascribed primarily to the added (R,R,S)-**5b** (0.02 equiv).

urea **4**[16] from **2**. To the best of our knowledge, this is the first time that a potentially scalemic amine has been scrutinized in this way, although alcohols have been converted to pentavalent phosphorus derivatives in a similar strategy.[2] Thus, triphosgene[17] was combined with racemic amine (RS)-**2** and Et_3N to give a mixture of diastereomeric ureas. By integration of the two doublets near δ 1.35 ppm in the ^1H NMR spectrum, the ratio of the two components was 1.04 ± 0.05 to 1, indicating that asymmetric induction from the first amine component in coupling to the second was negligible. Identical treatment of (S)-**2** gave (S,S)-**4**. Closer scrutiny of the ^1H NMR spectrum of the crude enantiomerically pure urea showed that the doublet attributed to the methyl protons was accompanied by smaller peaks which could be due to the corresponding doublet for the meso diastereomer. Integration established the areas of the two sets of resonances were in a ratio of 175 to <3, corresponding to a minimum value of the ratio between (S)- and (R)-**2** of 116 to 1. Considering Fig.2, this would be consistent with impurity in (S)-**2**, not (S)-**1b**, but additional analytical methodology will be needed to verify the purity of the amino acid complex beyond the level of 99% e.e. suggested by Figure 2.

In summary, the complexation of a chiral primary amine to chiral, coordinatively unsaturated amino acid complexes **1** in $CDCl_3$ allows the enantiomeric purity of milligram amounts of either component to be determined. Further, transformation of two moles of a chiral amine to the corresponding symmetrical urea with triphosgene permits determination of enantiomeric purity without reliance on an external derivatizing agent.

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EXPERIMENTAL SECTION

General. Unless otherwise specified, all reactions were conducted under nitrogen atmosphere. NMR solvent $CDCl_3$ (Cambridge Isotope Labs) was passed through basic Al_2O_3 before dissolving organometallic complexes. Resealable NMR tubes featuring a teflon threaded cap were manufactured by J. Young, Ltd.

Infrared spectra were acquired on samples prepared in KBr pellets or dissolved in the specified solution and held in a NaCl cell in either a Mattson 2020 Galaxy or a Nicolet FT-IR. NMR spectra were acquired at ambient probe temperatures (ca. 25 °C) unless otherwise stated using a Varian Gemini 300, Unity Plus 400, Bruker 400, or Varian 500 MHz instrument. ^1H NMR spectra are referenced to residual solvent peak $CHCl_3$ = δ 7.24 ppm. A resonance described by "~d" resembles a doublet. ^{13}C NMR spectra are referenced to $CDCl_3$ solvent resonance at δ 77.00 ppm. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA.

(RS)-1c. Following the published procedure for enantiomerically pure material, THF (14 mL) was added to a flask containing racemic N-tosylphenylglycine (44.5 mg, 0.146 mmol), $[Cp^*IrCl(\mu\text{-}Cl)]_2$ (57.7 mg, 0.0725 mmol), K_2CO_3 (43.0 mg, 0.311 mmol), and a stir bar. The flask was capped with a septum and nitrogen was bubbled through the mixture for 5 min. The mixture was stirred 2.7 d. The residue remaining after rotary evaporation was diluted with CH_2Cl_2 and filtered through a pad of Celite, additional CH_2Cl_2 being used in portions to rinse reaction flask and Celite pad until virtually colorless. The combined red filtrates were concentrated, the foamy product was triturated with a little Et_2O, pentane was added, and the supernatant was removed using a pipet. After storage over P_4O_{10} under vacuum, **1c** (80.3 mg, 0.127 mmol, 88%) was obtained. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.40 (~d, J ≈ 8, 2 H), 6.97-7.08 (m, 8H), 4.59 (s, 1H), 2.30 (s, 3H), 1.84 ppm (s, 15H).

Typical procedure for complexation of (S)-2 to 1. To a red solution of (RS)-**1c** (14.2 mg, 0.0225 mmol) in $CDCl_3$ (0.8 mL) in a resealable NMR tube was added (S)-**2** (3.0 μL, 0.023 mmol), whereupon the solution became yellow. After observing the NMR data reported in Table 1, the solution was concentrated and the cream-yellow solid was stored over P_4O_{10} under oil pump vacuum, leaving **5c** (16.6 mg, 0.0220 mmol, 98%). For NMR data, see Table 1. Anal. Calcd for $C_{33}H_{39}IrNO_4S$ (751.97): C, 52.71; H, 5.23; N, 3.72. Found: C, 52.50; H, 5.30; N, 3.69. IR for (R)-**1c** and (S)-**2** ($CDCl_3$, NaCl) $\nu_{C=O}$ 1639 cm^{-1}.

Spiking experiment portrayed in Fig.2. By the typical procedure described above, (S)-**1b** (4.0 mg, 0.0070 mmol) in $CDCl_3$ (0.7 mL) and (S)-**2** (0.9 μL) were combined to provide **5b**. The spiking experiment illustrated in Fig. 2 was performed by adding to this solution 11.2 μL of a solution from racemic (RS)-**1b** (11.1 mg, 0.0195 mmol) and (S)-**2** (2.5 μL, 0.0193 mmol) in $CDCl_3$ (0.8 mL). Concentration of the solution left pale yellow solid. IR (KBr) $\nu_{C=O}$ 1628 cm^{-1}. Anal. Calcd for $C_{28}H_{37}IrN_2O_4S$ (677.90): C, 47.84; H, 5.50; N, 4.13. Found: C, 48.62; H, 5.64; N, 3.96.

Urea (S,S)-4. To a stirred solution of (S)-**2** (63.6 mg, 0.525 mmol) and Et_3N (56.0 mg, 0.553 mmol, 1.05 equiv) in CH_2Cl_2 in an ice-cooled flask was added $(Cl_3CO)_2CO$ (27.6 mg, 0.093 mmol, 1.06 equiv). After seven min, the ice bath was removed and the mixture was stirred for a further 21 h before Et_2O (10 mL) and aq HCl (10 mL, 1N) were added. In a separatory funnel, the Et_2O layer and some white solid were removed and the aq phase was extracted with Et_2O (2 x 10 mL). Combined organic phases were washed with water (10 mL), brine (10 mL). The organic phase was diluted with CH_2Cl_2 (ca 25 mL) to dissolve all solids and the resulting solution was dried, filtered, and concentrated, leaving crude (S,S)-**4** (57.1 mg, 0.213 mmol, 81%) as a white solid, m.p. 204.5-206 °C (lit.[16c] 210 °C). ^1H NMR ($CDCl_3$, 300 MHz) δ 7.15-7.3 (m, 6H), 7.11 (~d, J ≈ 8 Hz, 4H), 4.73 (q, J = 7.1 Hz, 2H), 1.34 ppm (d, J = 7.1 Hz, 6H) (integration suggested that a very broad signal, which might be ascribed to the two NH protons, appeared between ca. 4 and 5 ppm) ; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 157.14, 144.29, 128.85, 127.37, 125.91, 50.15, 23.15 ppm.

By a similar procedure, (RS)-**2** (200.7 mg, 1.66 mmol), Et_3N (253 μL, 1.82 mmol, 1.09 equiv), and $(Cl_3CO)_2CO$ (83.3 mg, 0.281 mmol, 1.02 equiv) afforded crude urea (179.9 mg, 0.670 mmol, 81%) as a white solid, m.p. 120-150 °C. ^1H NMR spectral data of the mixture were consistent with the presence of two isomers in a ratio of 1.04 ± 0.05 to 1. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.15-7.3 (m, 16H), 7.11 (~d, $J \approx 8$ Hz, 4H), 4.8-4.94 (m, 2H, NH), 4.75 (q, J = 7.1 Hz, 2H), 4.72 (q, J = 7.1 Hz, 2H), 1.32 (d, J = 7.1 Hz, 6H), 1.29 ppm (d, J = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 157.38, 157.24, 144.51, 144.42, 128.79, 128.77, 127.34, 127.24, 126.04, 125.92, 49.94 (slightly broad), 23.12, 22.91 ppm.

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