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Optical resolution and absolute configuration of the chiral pentamethylcyclopentadienylrhenium carbonyl complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CO)]^+ BF_4^-$

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Abstract

Reaction of racemic ester $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CO_2CH_3)$ and (−)-(*S*)-α-(1-naphthyl)ethylamine gives amide $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CONHCH(CH_3)C_{10}H_7)$ (**3**) as a (*SS*)-/(*RS*)- diastereomer mixture. Crystallization gives the less soluble diastereomer (−)-(*RS*)-**3** (77%, ⩾ 98% diastereomeric excess). Subsequent reaction with CF_3CO_2H and then $NaBF_4$ gives carbonyl complex (−)-(*R*)-$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CO)]^+ BF_4^-$ (91%, ⩾ 99% enantiomeric excess), which is in turn reduced ($Li(C_2H_5)_3BH$/ $BH_3 \cdot THF$) to methyl complex (−)-(*R*)-$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CH_3)$ (97%). These serve as convenient precursors to a variety of other optically active complexes. Preparations of enantiomeric complexes, diastereomer (−)-(*RR*)-**3**, and recycling of the chiral α-(1-naphthyl)ethylamine auxilliary are also described. The structure and absolute configuration of (−)-(*RS*)-**3** is verified crystallographically (orthorhombic, $P2_12_12_1$ (no. 19), *a* 12.348(4), *b* 13.198(5), *c* 22.168(9) Å, $Z = 4$).

Introduction

In 1848, Pasteur reported the first observation of optical activity in an organic compound, sodium ammonium tartrate [1,2]. In 1911, Werner described the first syntheses of optically active inorganic compounds [3,4]. However, following Mond's discovery in 1890 of the first metal carbonyl complex, tetrahedral $Ni(CO)_4$ [5,6], the centennial of which is commemorated by this issue, there elapsed a period of almost 80 years before the first optically active, "chiral-at-metal" carbonyl complex was reported [7,8]. This relatively late development of the field of optically active metal carbonyl complexes is surprising in view of the established value of optically active compounds in mechanistic studies and asymmetric synthesis.

Research involving optically active metal carbonyl complexes was launched by Brunner's landmark 1969 report of the resolution of manganese complex $[(\eta^5\text{-}$

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$C_5H_5)Mn(NO)(PPh_3)(CO)]^+ PF_6^-$ [7,8]. Since that time, additional types of optically active metal carbonyl complexes have been prepared [8–10], including the closely related rhenium complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+ BF_4^-$ in our laboratory [9]. In this paper, we wish to report the optical resolution of the chiral pentamethylcyclopentadienylrhenium carbonyl complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CO)]^+ BF_4^-$ (**1**). This study was undertaken with the anticipation that the bulkier substituted cyclopentadienyl ligand might afford enhanced stereoselectivity in certain types of transformations previously investigated with cyclopentadienyl analogs $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^{n+}$.

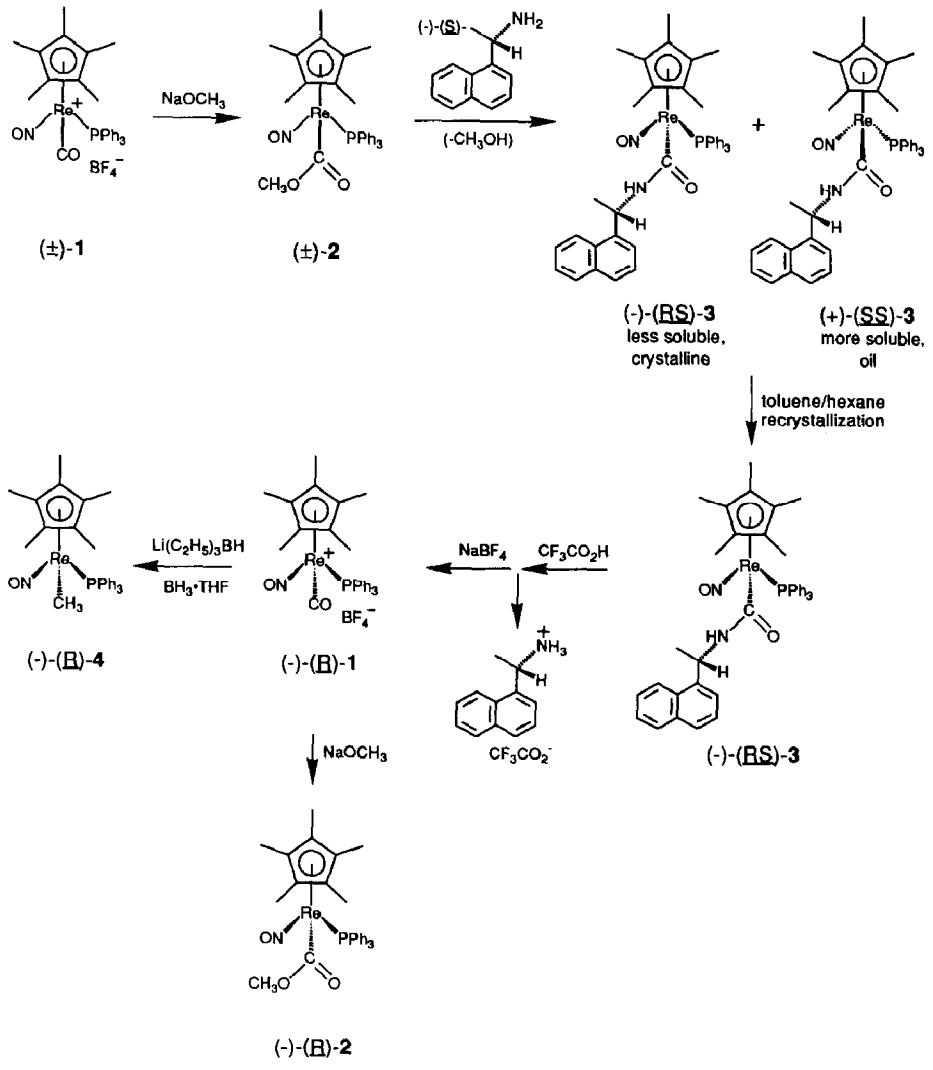
Results

1. Synthesis of optically active rhenium complexes. The chiral, racemic carbonyl complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CO)]^+ BF_4^-$ (**1**) was synthesized from $Re_2(CO)_{10}$ in three steps and 77% overall yield as previously described [11]. Complex **1** was then treated with $NaOCH_3$ to give the methyl ester $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CO_2CH_3)$ (**2**) reported earlier (Scheme 1) [12]. The methoxy substituent in the analogous cyclopentadienyl complex, $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO_2CH_3)$, has been shown to be readily displaced by nucleophiles [9,13]. Hence, **2** and the commercially available chiral, optically active amine (−)-(*S*)-α-(1-naphthyl)ethylamine were treated. A "transesterification"-type process occurred, as assayed by IR (ν(NO), ν(CO)) and NMR monitoring, to give a ca. 50/50 mixture of amides (*RS*)- and (*SS*)-$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CONHCH(CH_3)C_{10}H_7)$ ((*RS*)-**3** and (*SS*)-**3**) [14*,15*]. Carbonyl complex **1** and (−)-(*S*)-α-(1-naphthyl)ethylamine (2 equiv., CH_2Cl_2) did not react, as assayed by IR and ^1H NMR monitoring.

The pentamethylcyclopentadienyl ^1H NMR resonances of diastereomers (*RS*)- and (*SS*)-**3** were distinct (δ 1.72, 1.83), intense (15H) and well-separated from other resonances. Hence, the relative ratios of (*RS*)- and (*SS*)-**3** could be accurately determined. One diastereomer proved to be considerably less soluble and more crystalline than the other. Accordingly, a single toluene/hexane crystallization gave (−)-(*RS*)-3, $[\alpha]_{589}^{27}$ −131°, in 77% yield and ≥ 98% diastereomeric excess (de). This diastereomer assignment was confirmed by a crystal stucture, as described below. A second recrystallization gave (−)-(*RS*)-**3** that ^1H NMR integration indicated to be a 99.7/0.3 mixture of diastereomers (99.4% de). Complex (−)-(*RS*)-**3** was characterized by microanalysis, and IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy, as described in the experimental section.

Attention was next turned to detaching the amine auxilliary from (−)-(*RS*)-**3**. First, (−)-(*RS*)-**3** was treated with excess CF_3CO_2H (Scheme 1). This cleaved the amide linkage to give the trifluoroacetate salts of carbonyl complex **1** and protonated (−)-(*S*)-α-(1-naphthyl)ethylamine. Workup with $NaBF_4$ gave yellow prisms of optically active carbonyl complex (−)-(*R*)-**1**, $[\alpha]_{589}^{27}$ −260°, in 91% yield. The absolute configuration was assigned on the assumption that the rhenium stereochemistry should not be affected by this ligand-based reaction. This was supported by the conversion of (−)-(*R*)-**1** back to amide (−)-(*RS*)-**3** as described below.

* Reference numbers with asterisks indicate notes in the list of references.



Scheme 1. Optical resolution of carbonyl complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CO)]^+ BF_4^-$ (**1**).

Following the above crystallization of amide (−)-(*RS*)-**3**, the supernatant was enriched in the more soluble diastereomer, (+)-(*SS*)-**3**. This material was similarly converted to carbonyl complex (+)-(*S*)-**1** of 64% ee (calculated from the optical rotation), and was subjected to a second resolution cycle utilizing (+)-(*R*)-α-(1-naphthyl)ethylamine. This ensured that the less soluble diastereomer (+)-(*SR*)-**3**, enantiomeric with the (−)-(*RS*)-**3** crystallized above, would predominate. An analogous workup gave (+)-(*SR*)-**3** in > 98% de and 45% overall yield for four steps from racemic ester **2**. It was similarly converted to optically active carbonyl complex (+)-(*S*)-**1**.

We sought to recover the optically active auxilliaries (−)-(*S*)- and (+)-(*R*)-α-(1-naphthyl)ethylamine from the preceding amide cleavage reactions. Accordingly, the amine trifluoroacetate salts initially produced were neutralized with K_2CO_3. The resulting amines were extracted into dichloromethane and purified by vacuum

distillation. The (−)-(*S*)-α-(1-naphthyl)ethylamine recovered from amide (−)-(*RS*)-**3** (76%) gave $[\alpha]_{589}^{25}$ −60°, compared to −59° for the starting material. This sample was treated with (−)-menthylchloroformate to give the previously reported urethane *N*-(−)-menthyloxycarbonyl-(−)-(*S*)-α-(1-naphthyl)ethylamine [16]. Capillary GC analysis [16] indicated a de of 99.5%.

We next sought to bound the optical purity of carbonyl complex (−)-(*R*)-**1**. Accordingly, (−)-(*R*)-**1** was treated with $NaOCH_3$ (5.0 equiv.) at −24°C to give optically active ester (−)-(*R*)-**2**, $[\alpha]_{589}^{25}$ −185°, in 96% yield. This ligand-based transformation was presumed to proceed with retention of configuration at rhenium, and when conducted at room temperature gave (−)-(*R*)-**2** of comparable rotation. However, partial racemization was noted in the corresponding reaction of optically active cyclopentadienyl analog $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+ BF_4^-$ [9]. Subsequent reaction of (−)-(*R*)-**2** and (−)-(*S*)-α-(1-naphthyl)ethylamine gave the less soluble amide diastereomer (−)-(*RS*)-**3** in 85% yield after crystallization. Integration of the pentamethylcyclopentadienyl ^1H NMR resonances in the reaction mixture indicated the crude product to be of 99.8% de. Hence, the optical purities (ee) of (−)-(*R*)-**1** and (−)-(*R*)-**2** must be comparable.

We sought to isolate the more soluble amide diastereomer (−)-(*RR*)-**3**. Accordingly, (−)-(*R*)-**2** and (+)-(*R*)-α-(1-naphthyl)ethylamine were reacted to give (−)-(*RR*)-**3**. Integration of the pentamethylcyclopentadienyl ^1H NMR resonances in the crude reaction mixture indicated a 99.1% de. Complex (−)-(*RR*)-**3** resisted all crystallization attempts, and could only be isolated as a foam (86%) of ca. 95% spectroscopic purity. It was characterized by IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy, as described in the experimental section.

Next, in a procedure analogous to that previously reported for the racemate [11], carbonyl complex (−)-(*R*)-**1** was reduced with $Li(C_2H_5)_3BH/BH_3 \cdot THF$ to optically active methyl complex (−)-(*R*)-$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CH_3)$ ((−)-(*R*)-**4**), $[\alpha]_{589}^{26}$ −245°, in 97% yield (Scheme 1). This ligand-based transformation was also

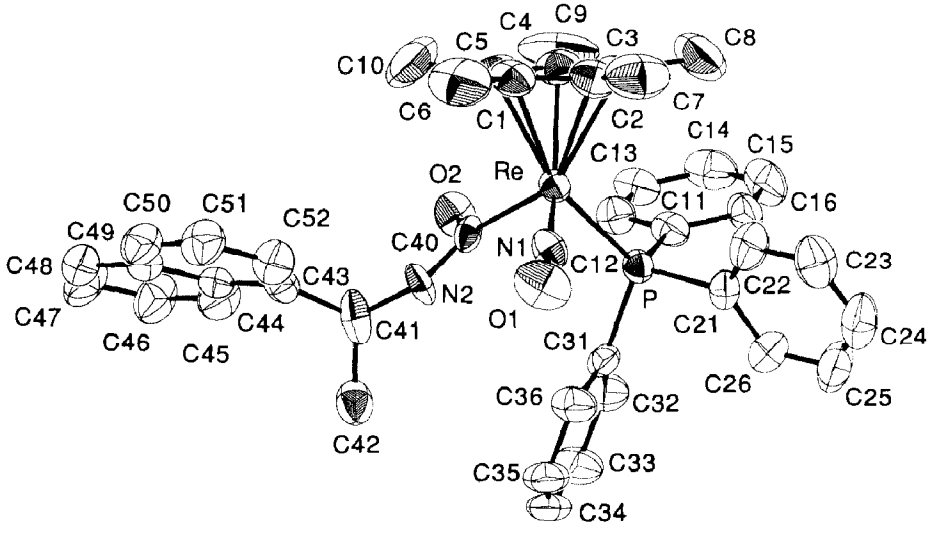


Fig. 1. Molecular structure of the amide (−)-(*RS*)-$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CONHCH(CH_3)C_{10}H_7)$ ((−)-(*RS*)-**3**).

presumed to proceed with retention at rhenium. Complex (−)-(*R*)-**4** provides an optically active precursor to the previously reported methylidene complex [11] $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(=CH_2)]^+ X^-$ and dichloromethane complex [17] $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+ X^-$, cyclopentadienyl analogs which have been elaborated into a variety of other complexes [18,19].

Finally, a reaction sequence beginning with racemic ester **2** and (+)-(*R*)-α-(1-naphthyl)ethylamine was utilized to prepare the enantiomeric complexes (+)-(*SR*)-**3**, (+)-(*S*)-**1**, and (+)-(*S*)-**4**. These were characterized by optical rotations and microanalyses (experimental section), and spectroscopic properties matched those of their enantiomers.

2. Crystal structure of (−)-(RS)-(η^5-C_5Me_5)Re(NO)(PPh$_3$)(CONHCH(CH$_3$)C$_{10}$H$_7$) ((−)-(RS)-3). X-ray data were acquired on amide (−)-(*RS*)-**3** as summarized in Table 1. Refinement, described in the experimental section, yielded the structure shown in Fig. 1. Bond lengths, bond angles, and atomic coordinates are summarized in Tables 2–4. These data, and tables of anisotropic thermal parameters and

Table 1

Summary of crystallogaphic data for the amide (−)-(*RS*)-(η^5-C_5Me_5)Re(NO)(PPh$_3$)(CONHCH(CH$_3$)C$_{10}$H$_7$) ((−)-(*RS*)-**3**)

Molecular formula	$C_{41}H_{42}N_2O_2PRe$
Molecular weight	811.978
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (No. 19)
Temperature of collection	16(1)° C
Cell dimensions	
a, Å	12.348(4)
b, Å	13.198(5)
c, Å	22.168(9)
V, Å^3	3612.73
Z	4
d_{obsvd}, g/cm^3	1.470
d_{calcd}, g/cm^3	1.493
Crystal dimensions, mm	0.35 × 0.23 × 0.19
Radiation, Å	λ (Mo-K_α) 0.71073
Data collection method	$\theta/2\theta$
Scan speed, deg/min	Variable, 3–8
Range/indices (h, k, l)	0 14, 0 15, 0 25
Scan range	$K_{\alpha 1}$ −1.0 to $K_{\alpha 2}$ +1.0
Total bkgd. time/scan time	0.5
No. of reflections between std.	98
Total unique data	3218
Observed data, $I > 3\sigma(I)$	2648
Abs. coeff. (μ), cm^{-1}	34.872
Min. transmission factor	0.89
Max. transmission factor	0.99
No. of variables	424
$R = \Sigma(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\Sigma\lvert F_o\rvert$	0.0298
$R_w = \Sigma(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)w^{1/2}/\Sigma\lvert F_o\rvert w^{1/2}$	0.0336
Goodness of fit	2.86
$\Delta\rho$(max), e/Å^3	0.558

Table 2

Bond lengths (Å) in (−)-(*RS*)-**3**

Re–P	2.368(2)	C13–C14	1.37(1)
Re–N1	1.750(6)	C14–C15	1.38(1)
Re–C1	2.304(7)	C15–C16	1.41(1)
Re–C2	2.312(7)	C21–C22	1.34(1)
Re–C3	2.309(8)	C21–C26	1.39(1)
Re–C4	2.313(8)	C22–C23	1.39(1)
Re–C5	2.311(7)	C23–C24	1.37(1)
Re–C40	2.101(6)	C24–C25	1.36(1)
P–C11	1.819(6)	C25–C26	1.38(1)
P–C21	1.839(7)	C31–C32	1.392(9)
P–C31	1.816(6)	C31–C36	1.39(1)
N1–O1	1.192(7)	C32–C33	1.40(1)
O2–C40	1.246(8)	C33–C34	1.36(1)
N2–C40	1.362(8)	C34–C35	1.34(1)
N2–C41	1.436(9)	C35–C36	1.40(1)
C1–C2	1.43(1)	C41–C42	1.52(1)
C1–C5	1.41(1)	C41–C43	1.53(1)
C1–C6	1.51(1)	C43–C44	1.448(9)
C2–C3	1.41(1)	C43–C52	1.36(1)
C2–C7	1.47(1)	C44–C45	1.41(1)
C3–C4	1.42(1)	C44–C49	1.430(9)
C3–C8	1.51(1)	C45–C46	1.36(1)
C4–C5	1.41(1)	C46–C47	1.41(1)
C4–C9	1.49(1)	C47–C48	1.36(1)
C5–C10	1.53(1)	C48–C49	1.39(1)
C11–C12	1.41(1)	C49–C50	1.41(1)
C11–C16	1.38(1)	C50–C51	1.35(1)
C12–C13	1.39(1)	C51–C52	1.41(1)

calculated and observed structure factors, have been deposited with the Cambridge Crystallographic Data Center. The N1–Re–C40–O2 torsion angle was found to be 170.6(8)°.

Discussion

The optical resolution outlined in Scheme 1 is easy to execute on a large scale, and parallels that previously developed for the corresponding cyclopentadienyl complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+ BF_4^-$. Thus, optically active α-(1-naphthyl)ethylamine may have considerable generality as a chiral auxilliary for the resolution of metal carbonyl cations. In each series of compounds, the (−)-(*RS*)- or (+)-(*SR*)- amide diastereomers are the least soluble in toluene/hexanes. Thus, by utilizing the correct enantiomer of α-(1-naphtyl)ethylamine in Scheme 1, either enantiomer of carbonyl complex **1** can be prepared in > 98% ee.

It has been previously noted that sufficiently electrophilic cationic carbonyl complexes $[L_nMCO]^+ X^-$ condense directly with amines RNH_2 to give amides $L_nMCONHR$ [20]. However, carbonyl complex **1** and α-(1-naphthyl)ethylamine do not react. Further, such condensations require two equivalents of amine, one to neutralize the HX by-product. In the preparation of amides **3** from methyl ester **2**, the methoxy group serves as the base for the α-(1-naphthyl)ethylamine proton that

Table 3

Bond angles (°) in (−)-(*RS*)-**3**

P–Re–C40	87.0(2)	C2–C3–C8	127(1)
P–Re–N1	92.2(2)	C4–C3–C8	123(1)
N1–Re–C40	97.6(3)	C3–C4–C9	128.5(9)
Re–N1–O1	172.0(6)	C5–C4–C9	124(1)
Re–C40–O2	123.4(5)	C1–C5–C10	124.7(9)
Re–C40–N2	118.4(4)	C4–C5–C10	127(1)
O2–C40–N2	118.0(6)	Re–P–C11	115.2(2)
C40–N2–C41	124.1(6)	Re–P–C21	114.9(2)
N2–C41–C42	112.2(6)	Re–P–C31	116.5(2)
N2–C41–C43	112.4(7)	C11–P–C21	103.8(4)
C42–C41–C43	109.4(6)	C11–P–C31	104.2(3)
C41–C43–C44	120.0(6)	C21–P–C31	100.3(3)
C41–C43–C52	121.3(7)	P–C11–C12	117.0(5)
C44–C43–C52	118.5(7)	P–C11–C16	123.3(6)
C43–C44–C45	123.3(6)	C12–C11–C16	119.6(7)
C43–C44–C49	118.7(7)	C11–C12–C13	120.2(7)
C45–C44–C49	117.9(7)	C12–C13–C14	118.7(8)
C44–C45–C46	121.2(7)	C13–C14–C15	122.5(8)
C45–C46–C47	119.7(8)	C14–C15–C16	118.8(8)
C46–C47–C48	120.7(8)	C11–C16–C15	120.1(8)
C47–C48–C49	120.6(8)	P–C21–C22	120.5(6)
C44–C49–C48	119.8(8)	P–C21–C26	121.0(6)
C48–C49–C50	121.6(8)	C22–C21–C26	118.5(7)
C44–C49–C50	118.6(7)	C21–C22–C23	121.9(8)
C49–C50–C51	122.5(8)	C22–C23–C24	119.7(9)
C50–C51–C52	119.0(8)	C23–C24–C25	118.9(8)
C43–C52–C51	122.4(8)	C24–C25–C26	121.1(8)
C1–C2–C3	106.6(8)	C21–C26–C25	119.9(8)
C2–C3–C4	109.2(8)	P–C31–C32	124.0(5)
C3–C4–C5	107.3(8)	P–C31–C36	118.2(6)
C4–C5–C1	108.3(7)	C32–C31–C36	117.9(6)
C5–C1–C2	108.6(8)	C31–C32–C33	119.5(7)
C2–C1–C6	125.0(9)	C32–C33–C34	121.6(8)
C5–C1–C6	126.4(9)	C33–C34–C35	119.0(8)
C1–C2–C7	125.7(9)	C34–C35–C36	121.7(8)
C3–C2–C7	127.2(9)	C31–C36–C35	120.3(8)

is lost. In view of the low IR ν(C=O) in **2** (1583 cm^{-1}) [12], this reaction most likely proceeds via an elimination/addition mechanism.

Several chiroptical features of the pentamethylcyclopentadienyl complexes are similar to those of the cyclopentadienyl analogs. First, the optical rotations at 589 nm closely correspond in each series of compounds. Second, the diastereomeric amides (−)-(*RS*)-**3** and (−)-(*RR*)-**3** are both levorotatory. Hence, the sign of the optical rotation at 589 nm is determined by the configuration at rhenium. Analogous phenomena have been observed with other diastereomeric organometallic complexes [8]. Third, the signs of the optical rotations of (−)-(*R*)-**1**, (−)-(*R*)-**2**, and (−)-(*R*)-**4** at 589 nm also correlate to the configuration at rhenium. Finally, note that the configuration at rhenium in the crystallographically characterized amide, (−)-(*RS*)-**3**, is opposite to that conventionally shown in our papers. Hence, the optically active compounds in Scheme 1 are enantiomeric to those usually depicted.

Table 4

Atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms in (−)-(*RS*)-**3** [a]

Atom	*x*	*y*	*z*	B(Å^2)
Re	0.15692(3)	−0.02913(3)	−0.11319(2)	2.792(6)
P	0.1755(2)	0.0190(2)	−0.0108(1)	2.91(5)
O1	0.1786(8)	−0.2474(6)	−0.0908(4)	6.3(2)
O2	0.3557(6)	0.0955(5)	−0.1288(3)	4.2(2)
N1	0.1732(7)	−0.1576(6)	−0.0959(4)	3.6(2)
N2	0.3941(6)	−0.0701(6)	−0.1289(4)	3.7(2)
C1	0.0766(9)	−0.0489(9)	−0.2063(5)	4.3(3)
C2	−0.0078(9)	−0.041(1)	−0.1622(5)	5.0(3)
C3	−0.0004(9)	0.057(1)	−0.1371(5)	5.0(3)
C4	0.087(1)	0.109(1)	−0.1644(5)	4.7(3)
C5	0.134(1)	0.043(1)	−0.2073(4)	5.1(3)
C6	0.097(1)	−0.140(1)	−0.2460(7)	8.6(4)
C7	−0.094(1)	−0.117(1)	−0.1521(8)	7.7(4)
C8	−0.081(1)	0.108(1)	−0.0959(7)	8.6(4)
C9	0.118(1)	0.217(1)	−0.1582(8)	8.5(4)
C10	0.225(1)	0.068(2)	−0.2517(6)	9.3(6)
C11	0.160(1)	0.1538(7)	0.0040(4)	3.4(2)
C12	0.236(1)	0.2194(8)	−0.0234(5)	3.8(2)
C13	0.229(1)	0.3237(9)	−0.0143(6)	4.6(3)
C14	0.145(1)	0.3610(9)	0.0199(6)	5.4(3)
C15	0.070(1)	0.299(1)	0.0473(6)	5.6(3)
C16	0.078(1)	0.194(1)	0.0392(5)	4.5(3)
C21	0.0782(8)	−0.0407(9)	0.0410(4)	3.7(2)
C22	−0.015(1)	−0.080(1)	0.0201(5)	5.0(3)
C23	−0.091(1)	−0.122(1)	0.0582(7)	5.6(3)
C24	−0.074(1)	−0.122(1)	0.1192(6)	5.8(3)
C25	0.020(1)	−0.083(1)	0.1410(6)	6.1(3)
C26	0.097(1)	−0.042(1)	0.1028(5)	5.3(3)
C31	0.3020(8)	−0.0144(8)	0.0258(4)	2.9(2)
C32	0.3663(9)	0.0541(8)	0.0574(5)	4.4(3)
C33	0.463(1)	0.021(1)	0.0841(5)	5.3(3)
C34	0.496(1)	−0.078(1)	0.0801(5)	5.1(3)
C35	0.434(1)	−0.144(1)	0.0493(5)	4.9(3)
C36	0.337(1)	−0.1145(8)	0.0223(5)	4.4(2)
C40	0.3216(7)	0.0071(7)	−0.1234(4)	2.9(2)
C41	0.5078(9)	−0.0561(8)	−0.1397(5)	4.4(3)
C42	0.5771(9)	−0.115(1)	−0.0953(5)	4.8(3)
C43	0.5403(9)	−0.0844(8)	−0.2040(5)	3.5(2)
C44	0.6325(8)	−0.0357(9)	−0.2321(4)	3.7(2)
C45	0.6854(9)	0.0492(9)	−0.2073(5)	4.4(3)
C46	0.774(1)	0.090(1)	−0.2343(6)	5.5(3)
C47	0.814(1)	0.047(1)	−0.2883(5)	6.1(3)
C48	0.763(1)	−0.032(1)	−0.3145(5)	6.1(3)
C49	0.672(1)	−0.0752(9)	−0.2879(5)	4.2(2)
C50	0.617(1)	−0.156(1)	−0.3150(5)	5.4(3)
C51	0.528(1)	−0.198(1)	−0.2901(6)	5.1(3)
C52	0.489(1)	−0.1605(9)	−0.2344(5)	4.5(3)

[a] Atoms refined anisotropically are given in the form of the isotropic equivalent displacement parameter, defined as: $(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

Complex (−)-(*RS*)-**3** exhibits several interesting structural features. First, the N1–Re–C40–O2 torsion angle (171°) is very close to those found in cyclopentadienyl-acyl and -formyl complexes (η^5-C_5H_5)Re(NO)(PPh_3)(COR) (176–180°) [21]. As analyzed in detail elsewhere [21], these Re–C_α conformations maximize overlap of the rhenium *d* orbital HOMO with the C_α= $\Sigma\pi^\star$ acceptor orbital. Accordingly, the Re=C_α bond length in (−)-(*RS*)-**3** (2.101(6) Å) is close to those of acyl and formyl complexes (η^5-C_5H_5)Re(NO)(PPh_3)(COR) (2.081(7), 2.055(10) Å), and intermediate between the Re–C_α bond lengths in alkyl complexes (η^5-C_5H_5)Re(NO)(PPh_3)(R) (2.203–2.215 Å) [9,22] and the Re=C_α bond length in benzylidene complex [(η^5-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+$ PF_6^- (1.949(6) Å) [22]. The amide N=C_α bond in (−)-(*RS*)-**3** (1.362(8) Å) is shorter than the N–CH_3 bond (1.436(9) Å), and the same length as the N=C bond in formamide (1.368(3) Å) [23]. Hence, there is also considerable delocalization of the amide nitrogen lone pair into the C=O $\pi^\star$ acceptor orbital.

In summary, carbonyl complex **1**, ester **2**, and methyl complex **4** can now easily be prepared in optically active form and of known absolute configuration. These complexes are versatile precursors to a variety of other classes of rhenium compounds [11–13,18,19,22,24]. Accordingly, the preparation of new types of optically active pentamethylcyclopentadienyl complexes will be reported in future publications from this laboratory.

Experimental

General. Reactions were conducted under a dry N_2 atmosphere unless noted. IR spectra were recorded on Perkin–Elmer Model 521 and Mattson Polaris FT-IR spectrometers. NMR spectra were recorded on a Varian XL-300 spectrometer, and were referenced to internal $(CH_3)_4Si$ (^1H, ^{13}C) or external H_3PO_4 (^{31}P). Optical rotations were measured on a Perkin–Elmer 241 MC polarimeter in a thermostatted cell. Elemental analyses were conducted by Schwarzkopf and Atlantic Microlab laboratories.

Solvents were purified by distillation: toluene and hexanes, from Na; CH_2Cl_2, from P_2O_5; THF, from Na/benzophenone; CH_3OH, from CaH_2. Reagents were obtained as follows: $NaOCH_3$ (25 weight% in CH_3OH), $Li(C_2H_5)_3BH$, $BH_3 \cdot THF$ (Aldrich), used as received; CF_3CO_2H (EM Science) and $NaBF_4$ (Matheson, Coleman and Bell), used as received; (−)-(*S*)- and (+)-(*R*)-α-(1-naphthyl)ethylamine (Norse Laboratories), used as received ($[\alpha]_{589}^{20}$ (CH_3OH) −59° and 59°). The amines were treated with (−)-menthylchloroformate to give previously reported urethanes *N*-(−)-menthyloxycarbonyl-(−)- and -(+)-α-(1-napthyl)ethylamine [16], which capillary GC (Hewlett Packard 5890 gas chromatograph, HP-5 column (crosslinked 5% phenyl methyl silicone, 25 m × 0.2 mm × 0.33 μm film), 0.6 ml/min helium flow) [16] showed to be 98.6% and 98.8% de, respectively.

Preparation of (−)-(RS)-(η^5-C_5Me_5)Re(NO)(PPh_3)($CONHCH(CH_3)C_{10}H_7$) ((−)-(RS)-3). A Schlenk flask was charged with (η^5-C_5Me_5)Re(NO)(PPh_3)(CO_2-CH_3) (**2**; 1.00 g, 1.49 mmol) [12], freshly distilled CH_2Cl_2 (ca. 5 ml), and a stir bar. The flask was capped with a septum and freeze-pump-thaw degassed twice. Then (−)-(*S*)-α-(1-naphthyl)ethylamine (0.290 ml, 1.80 mmol) was added by syringe and the solution was stirred for 6 h. The solvent was removed by rotary evaporation to give a red-orange oil. A ^1H NMR spectrum of the crude product showed the η^5-C_5Me_5 resonance of **2** ($CDCl_3$, δ 1.75) to be absent. The oil was dissolved in

toluene (1–2 ml) and layered with hexane (ca. 80 ml). Orange red cubes of (−)-(*RS*)-**3** formed, which were collected by filtration (0.461 g, 0.57 mmol, 77%, ≥ 98% de). These were recrystallized by an identical procedure to give (−)-(*RS*)-**3** (0.308 g, 0.38 mmol, 51%, 99.4% de), m.p. 212–214°C dec. Characterization: $[\alpha]_{589}^{27}$ −131° (*c* 1.05 mg/ml, $CHCl_3$); IR (cm^{-1}, thin film) ν(NO) 1630 s, ν(CO) 1535 m; ^1H NMR (δ, $CDCl_3$) naphthyl at 8.18–8.11 (m, 1H), 7.84–7.77 (m, 1H), 7.73-7.65 (m, 1H), naphthyl and phenyl at 7.59–7.35 (m, 19H), 5.64 (pseudoquintet, *J*(HH) ≃ 7 Hz, NCH), 5.26 (d, *J*(HH) 7.1 Hz, NH), 1.72 (s, C_5Me_5), 0.82 (d, *J*(HH) 6.9 Hz, CH_3); $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$) 199.3 (d, *J*(CP) 11.9 Hz, C=O), aryl carbons at 141.6 (s), 135.4 (d, *J*(CP) 54.0 Hz, *ipso* PPh_3), 134.1 (d, *J*(CP) 10.4 Hz), 133.9 (s), 131.2 (s), 129.8 (s), 128.4 (s), 128.1 (d, *J*(CP) 10.5 Hz), 127.0 (s), 125.5 (s), 125.24 (s), 125.21 (s), 124.5 (s), 122.4 (s); 102.0 (s, C_5Me_5), 44.6 (s, CH), 20.7 (s, $CHCH_3$), 9.9 (s, C_5Me_5); $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$) 21.4 (s). Anal. Found: C, 60.55; H, 5.16; N, 3.29; P, 4.11. $C_{41}H_{42}N_2O_2PRe$ calcd.: C, 60.65; H, 5.21; N, 3.45; P, 3.81%.

Preparation of (+)-(SR)-(η^5-C_5Me_5)Re(NO)(PPh_3)(CONHCH(CH_3)$C_{10}H_7$) ((+)-(SR)-3). This compound was prepared from **2** (1.10 g, 1.63 mmol), CH_2Cl_2 (ca. 5 ml), and (+)-(*R*)-α-(1-naphthyl)ethylamine (0.31 ml, 1.91 mmol) in a manner identical to (−)-(*RS*)-**3**. Workup gave (+)-(*SR*)-**3** as orange-red crystals (0.487 g, 0.60 mmol, 74%, > 98% de), m.p. 212–214°C dec; a second crystallization gave (+)-(*SR*)-**3** of 99.5% de. Characterization: $[\alpha]_{589}^{25}$ 132° (*c* 1.14 mg/ml, $CHCl_3$); IR and NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) spectra were identical with those of (−)-(*RS*)-**3**. Anal. Found: C, 60.61; H, 5.24; N, 3.47. $C_{41}H_{42}N_2O_2PRe$ calcd.: C, 60.65; H, 5.21; N, 3.45%.

Preparation of (−)-(R)-[(η^5-C_5Me_5)Re(NO)(PPh_3)(CO)]$^+$ BF_4^- ((−)-(R)-1). A round-bottom flask was charged with (−)-(*RS*)-**3** (0.50 g, 0.62 mmol), CH_2Cl_2 (ca. 10 ml), and a magnetic stir bar. No precaution was taken to exclude air. Then CF_3CO_2H (0.110 ml, 1.43 mmol) was added and the reaction was stirred for 20 min. Solvent was removed by rotary evaporation, and the resulting oil was dissolved in methanol (ca. 20 ml). Then H_2O (ca. 50 ml) and solid $NaBF_4$ (0.15 g, 1.37 mmol) were added, and the resulting yellow precipitate was collected by filtration and dried under oil pump vacuum. The precipitate was recrystallized from CH_2Cl_2/hexanes to give (−)-(*R*)-**1** as yellow prisms, which were collected by filtration, washed with ether, and dried under oil pump vacuum (0.41 g, 0.56 mmol, 91%), m.p. 226–227°C dec. Characterization: $[\alpha]_{589}^{27}$ −260° (*c* 1.07 mg/ml, CH_2Cl_2). Anal. Found: C, 47.88; H, 4.18; N, 1.92. $C_{29}H_{30}NBF_4O_2PRe$ calcd.: C, 47.81; H, 4.15; N, 1.92%.

The aqueous solution from which (−)-(*R*)-1 precipitated was neutralized with K_2CO_3 and the resulting milky white suspension was extracted with CH_2Cl_2. The extract was washed with brine and dried over Na_2CO_3. The CH_2Cl_2 was removed by rotary evaporation to give (−)-(*S*)-α-(1-naphthyl)ethylamine as a slightly yellow oil (0.080 g, 0.47 mmol, 76%), $[\alpha]_{589}^{25}$ −60° (*c* 6.51 mg/ml, CH_3OH).

Preparation of (+)-(S)-[(η^5-C_5Me_5)Re(NO)(PPh_3)(CO)]$^+$ BF_4^- ((+)-(S)-1). A. This compound was prepared from (+)-(*SR*)-**3** (1.00 g, 1.23 mmol), CH_2Cl_2 (ca. 20 ml), CF_3CO_2H (0.22 ml, 2.86 mmol) and $NaBF_4$ (0.30 g, 2.73 mmol) in a manner identical to (−)-(*R*)-**1**. Workup gave (+)-(*S*)-**1** as a yellow powder (0.83 g, 1.14 mmol, 93%), m.p. 220–222°C dec. Characterization: $[\alpha]_{589}^{25}$ 261° (*c* 1.03 mg/ml, CH_2Cl_2). Anal. Found: C, 47.82; H, 4.17; N, 1.94. $C_{29}H_{30}NBF_4O_2PRe$ calcd.: C, 47.81; H, 4.15; N, 1.92%.

B. The amide remaining in the supernate from the above preparation of (−)-(*RS*)-**3** (principally (+)-(*SS*)-**3**) was converted to (+)-(*S*)-**1** (ca. 64% ee) as described for (−)-(*R*)-**1** above. This (+)-(*S*)-**1** was converted to crystalline (+)-(*SR*)-**3** (0.264 g, 0.32 mmol, 45% from racemic **2**), ≥ 98% de, as described for (−)-(*RS*)-**3** above.

Preparation of (−)-(R)-(η^5-C_5Me_5)Re(NO)(PPh_3)(CH_3) ((−)-(R)-4). This compound was synthetized by a procedure analogous to that published for the racemate [11], utilizing (−)-(*R*)-**1** (1.07 g, 1.47 mmol), freshly distilled THF (ca. 30 ml), 1.0 *M* $Li(C_2H_5)_3BH$ in THF (2.94 ml) and 1.0 *M* $BH_3 \cdot THF$ (7.35 ml). Workup gave (−)-(*R*)-**4** as a red-orange powder (0.890 g, 1.42 mmol, 97%), m.p. 195–196 °C dec. Characterization: $[\alpha]_{589}^{26}$ −245° (*c* 0.62 mg/ml, C_6H_6). Anal. Found: C, 55.49; H, 5.34. $C_{29}H_{33}NOPRe$ calcd.: C, 55.40; H, 5.29%.

Preparation of (+)-(S)-(η^5-C_5Me_5)Re(NO)(PPh_3)(CH_3) ((+)-(S)-4). This compound was prepared from (+)-(*S*)-**1** (2.03 g, 2.79 mmol), THF (ca. 60 ml), 1.0 *M* $Li(C_2H_5)_3BH$ in THF (5.59 ml) and 1.0 *M* $BH_3 \cdot THF$ (14.0 ml) in a manner identical to (−)-(*R*)-**4**. Workup gave (+)-(*S*)-**4** as a red-orange powder (1.66 g, 2.64 mmol, 95%), m.p. 190–192 °C dec. Characterization: $[\alpha]_{589}^{25}$ 247° (*c* 0.49 mg/ml, C_6H_6). Anal. Found: C, 55.36; H, 5.33. $C_{29}H_{33}NOPRe$ calcd.: C, 55.40; H, 5.29%.

Preparation of (−)-(R)-(η^5-C_5Me_5)Re(NO)(PPh_3)(CO_2CH_3) ((−)-(R)-2). A Schlenk tube was charged with (−)-(*R*)-**1** (0.330 g, 0.45 mmol), freshly distilled CH_2Cl_2 (5 ml), and a stir bar. The tube was capped with a septum, freeze-pump-thaw degassed twice, and cooled to −24 °C (CCl_4/CO_2). A solution of $NaOCH_3$ in CH_3OH (0.517 ml, 25 weight%, 4.37 *M*) was then added. The reaction was stirred at −24 °C for 20 min, and the solvent was removed by rotary evaporation without heating. The resulting yellow powder was dissolved in CH_2Cl_2 and dried over Na_2SO_4. The solvent was removed by rotary evaporation, and the resulting light yellow foam was dried under oil pump vacuum to give (−)-(*R*)-**2** (0.293 g, 0.43 mmol, 96%), m.p. 198–200 °C dec. Characterization: $[\alpha]_{589}^{26}$ −185° (*c* 1.15 mg/ml, CH_2Cl_2). Anal. Found: C, 53.65; H, 4.95; N, 2.08. $C_{30}H_{33}NO_3PRe$ calcd.: C, 53.56; H, 4.94; N, 2.08%.

Preparation of (−)-(RR)-(η^5-C_5Me_5)Re(NO)(PPh_3)(CONHCH(CH_3)$C_{10}H_7$) ((−)-(RR)-3). A Schlenk flask was charged with (−)-(*R*)-**2** (0.167 g, 0.25 mmol), freshly distilled CH_2Cl_2 (ca. 1 ml) and a stir bar. The flask was capped with a septum and freeze-pump-thaw degassed twice. Then (+)-(*R*)-α-(1-naphthyl)ethylamine (0.041 ml, 0.25 mmol) was added by syringe and the orange solution was stirred for 12 h. The solvent was removed by rotary evaporation and the residue was dissolved in a minimum of CH_2Cl_2 (0.2 ml). The orange solution was deposited on a 2 × 2 cm plug of celite. The celite was washed with pentane, and solvent was removed from the washings under oil pump vacuum. This gave (−)-(*RR*)-**3** as an orange foam (0.173 g, 0.21 mmol, 86%; ca. 95% purity by ^1H NMR), which was contaminated with some amine and (−)-(*R*)-**2**. Characterization: $[\alpha]_{589}^{25}$ −158° (*c* 0.95 mg/ml, $CHCl_3$); IR (cm^{-1}, thin film) ν(NO) 1629 s, ν(CO) 1540 m; ^1H NMR (δ, $CDCl_3$) naphthyl at 8.00 (d, *J*(HH) 8.5 Hz, 1H), 7.80 (d, *J*(HH) 7.8 Hz, 1H), 7.69 (d, *J*(HH) 8.0 Hz, 1H), naphthyl and phenyl at 7.55–7.16 (m, 19H), 5.72 (pseudoquintet, *J*(HH) ≈ 7 Hz, NCH), 5.52 (d, *J*(HH) 7.6 Hz, NH), 1.83 (s, C_5Me_5), 1.47 (d, *J*(HH) 6.6 Hz, CH_3); $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$) 199.0 (d, *J*(CP) 11.5 Hz, CO), aryl carbons at 141.4 (s), 134.7 (d, *J*(CP) 54.2 Hz, *ipso*-PPh_3), 133.6 (d, *J*(CP) 12.4 Hz), 130.8 (s), 129.3 (s), 128.1 (s), 127.5 (d, *J*(CP) 10.1 Hz),

126.5 (s), 125.4 (s), 125.3 (s), 125.1 (s), 124.1 (s), 122.0 (s); 101.8 (s, C_5Me_5), 43.5 (s, CH), 25.2 (s, $CHCH_3$), 10.0 (s, C_5Me_5); $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$) 20.8 (s).

Crystal structure of (−)-(RS)-3. An orange crystal was mounted on a glass fiber for preliminary data collection on a Syntex P1 diffractometer. Cell constants (Table 1) were obtained from least squares refinement, using the setting angles of 15 reflections in the range $20° < 2\theta < 30°$. The space group was determined from systematic absences ($h00$ $h = 2n$, $0k0$ $k = 2n$, $00l$ $l = 2n$) and subsequent least squares refinement.

Lorentz and polarization corrections, and an empirical absorption correction based upon a series of ψ scans, were applied to the data. The intensities of standard reflections remained constant within experimental error. The structure was solved by the Patterson heavy-atom method. The structure was refined in full-matrix least-squares, where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with a weight of 1.0 for all observed reflections. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and not refined. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature [25]. Anomalous dispersion effects were included in F_c [26]. All calculations were performed on a VAX 8300 computer with the SDP/VAX package [27].

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