Synthesis, Optical Resolution, and Absolute Configuration of Pseudotetrahedral Organorhenium Complexes $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(X)$

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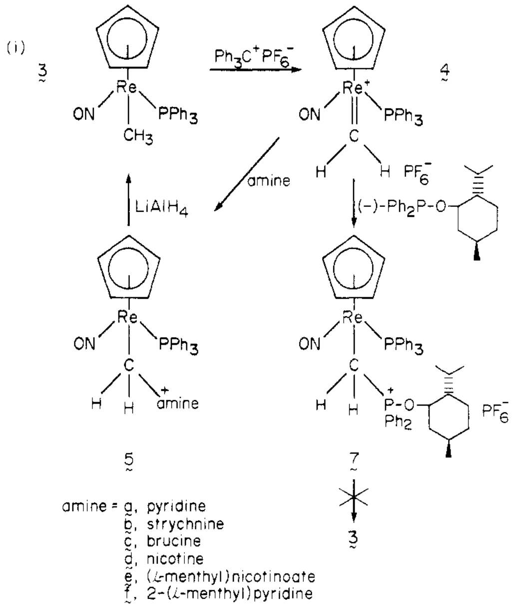
Reaction of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (**1**) with CH_3ONa/CH_3OH affords the "ester" $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COOCH_3)$ (**2**). Reaction of **2** with (−)-(*S*)-α-(1-naphthyl)ethylamine or (+)-(*R*)-α-(1-naphthyl)ethylamine gives "amide" $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CONHCH(CH_3)C_{10}H_7)$ (**8**). The diastereomers of **8** are separated by benzene/hexane recrystallization; (−)-(*RS*)-**8** and (+)-(*SR*)-**8** are least soluble. These are treated with CF_3CO_2H and $NaBF_4$ to give (−)-(*R*)-**1** and (+)-(*S*)-**1**, respectively. Resolved **1** is then used to prepare optically active **2**, $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**3**), $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)]^+PF_6^-$ (**4**), $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ (**9**), $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_3)$ (**10**), and $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ (**11**) via known procedures. An X-ray crystal structure of (−)-(*R*)-**9** (space group $P2_12_12_1$, $a = 12.874$ (5) Å, $b = 11.889$ (3) Å, $c = 16.077$ (7) Å, $Z = 4$, $R = 0.034$) establishes the absolute configurations of resolved **1**–**4** and **8**–**11**. Also described are the following: ORD and CD spectra; several unsuccessful resolution attempts; the synthesis of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2P^+Ph_2(O\text{-}l\text{-menthyl}))]^+PF_6^+$ (**7**) (used as an optical purity assay); comparisons with isostructural chiral organometallic complexes.

Introduction

We recently described the synthesis of pseudotetrahedral electrophilic rhenium alkylidene complexes of the formula $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+PF_6^-$ (R = H, aryl, *n*-alkyl).[2,3] These were found to exist in two photointerconvertible geometrically isomeric forms ($R \neq H$)[3,4] and to undergo stereospecific or stereoselective nucleophilic attack ($Nu = R_3BD^-, R'^-, RO^-, R_3P$) to yield rhenium alkyls $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHRNu)$.[3,5] Homologous vinyl and acetylide complexes, $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CHR)$ and $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CR)$, also undergo stereospecific C–C and C–H bond forming reactions.[6] Since numerous stereospecific metal–carbon bond cleavage reactions have been developed,[7] the availability of optically active $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ compounds would allow these transformations to be utilized in stoichiometric asymmetric organic synthesis. In this paper, we report (a) a convenient optical resolution of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (**1**) via a chiral amine adduct, (b) the synthesis of a series of optically active $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ complexes from **1**, (c) the X-ray crystal structure of (−)-(*R*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$, which allows the assignment of absolute configurations to these compounds, and (d) the ORD and CD spectra of several complexes. These are compared with the spectra of closely related manganese and iron complexes.[8-11]

Scheme I. Some Attempted Resolution Cycles



Results

1. Synthesis of Optically Pure Organorhenium Complexes. The first chiral organometallic complex to be resolved, $[(\eta\text{-}C_5H_5)Mn(NO)(PPh_3)(CO)]^+$, was obtained optically pure via its *l*-menthyl "ester",[12] $(\eta\text{-}C_5H_5)Mn(NO)(PPh_3)(COO\text{-}l\text{-menthyl})$.[8] Only one ester diastereomer was soluble in pentane at −78 °C. Since $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (**1**) is isostructural with $[(\eta\text{-}C_5H_5)Mn(NO)(PPh_3)(CO)]^+$, we attempted an analogous resolution. Cation **1** was first converted to its methyl "ester" (methoxycarbonyl complex),[12,13] $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COOCH_3)$ (**2**), by reaction with $CH_3ONa/$

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[2] (a) Wong, W.-K.; Tam, W.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5440. (b) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *Ibid.* **1982**, *104*, 141.

[3] (a) Kiel, W. A.; Lin, G.-Y.; Gladysz, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3299. (b) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *Ibid.*, **1982**, *104*, 4865. (c) Kiel, W. A.; Lin, G.-Y.; Gladysz, J. A., manuscript in preparation.

[4] McCormick, F. B.; Kiel, W. A.; Gladysz, J. A. *Organometallics* **1982**, *1*, 405.

[5] Constable, A. G.; Gladysz, J. A. *Organomet. Chem.* **1980**, *202*, C21.

[6] Wong, A.; Gladysz, J. A., *J. Am. Chem. Soc.* **1982**, *104*, 4948. Hatton, W., UCLA, unpublished results.

[7] Flood, T. C. *Top. Stereochem.* **1981**, *12*, 37.

[8] (a) Brunner, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 392. (b) Brunner, H.; Schindler, H.-D. *J. Organomet. Chem.* **1970**, *24*, C7.

[9] Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151.

[10] (a) Davison, A.; Krussell, W. C.; Michaelson, R. C. *J. Organomet. Chem.* **1974**, *72*, C7. (b) Davison, A.; Martinez, N. *Ibid.* **1974**, *74*, C17.

[11] (a) Flood, T. C.; DiSanti, F. J.; Miles, D. L. *J. Chem. Soc., Chem. Commun.* **1975**, 336; *Inorg. Chem.* **1976**, *15*, 1910. (b) Chou, C.-K.; Miles, D. L.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7271.

[12] The terms "ester" and "amide" will be used in place of the more familiar[13] "alkoxycarbonyl" and "carbamoyl" ligand nomenclature in this manuscript.

[13] Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335.

Table I. Optical Rotations, Absolute Configurations, and Melting Points of Chiral Organorhenium Complexes Prepared

complex	$[\alpha]^{24.5}_{589}$, deg	*c* (g/L), solvent	abs configuratn	mp, °C	mp of racemate, °C
(−)-1	−184	0.43, CH_2Cl_2	*R*	268-272 dec	277.5-278.5 dec
(−)-2	-165^a	0.28, $CHCl_3$	*R*	172-174 dec	153-155
(−)-3	−178	0.44, $CHCl_3$	*R*	188.5-190	197-200
(−)-4	-43^b	0.22, CH_2Cl_2	*R*		
(−)-7	−239	0.42, $CHCl_3$	R_{Re}	121-124	$159\text{-}161^c$
(+)-7	+191	0.28, $CHCl_3$	S_{Re}	185-186	
(−)-8	−103	0.62, $CHCl_3$	RS^d	208-210 dec	
	-137^e	0.13, $CHCl_3$	RR^d	173-177 dec	
(−)-9	−118	0.37, $CHCl_3$	*R*	234-237 dec	219-221
(−)-10	−116	0.48, $CHCl_3$	*R*	179-180	224-226
(−)-11	−194	0.14, $CHCl_3$	*R*	141-142 dec (darkening ~ 130 °C)	156-157 dec (darkening ~ 135 °C)^f

[a] 98% ee. [b] The rotation was taken immediately after dissolution and is accurate to ±1°; rapid decomposition ensues. [c] Not a true racemate; 7 prepared from racemic 4. [d] Re, C. [e] Contains 0.9 ± 0.1% of the *SR* diasteromer as assayed by ^1H NMR. [f] This value (sealed capillary) is higher than the ca. 91 °C decomposition point previously reported for **11**: Tam, W. Ph.D. Dissertation, UCLA, 1979.[2]

CH_3OH. Subsequent CF_3CO_2H-catalyzed transesterification of **2** with *l*-menthol gave (η-C_5H_5)Re(NO)(PPh_3)(COO-*l*-menthyl) as a labile oil. Unfortunately, pentane extraction of this material gave at best a 60:40 diastereomeric ratio. More practical separation methods could not be found.

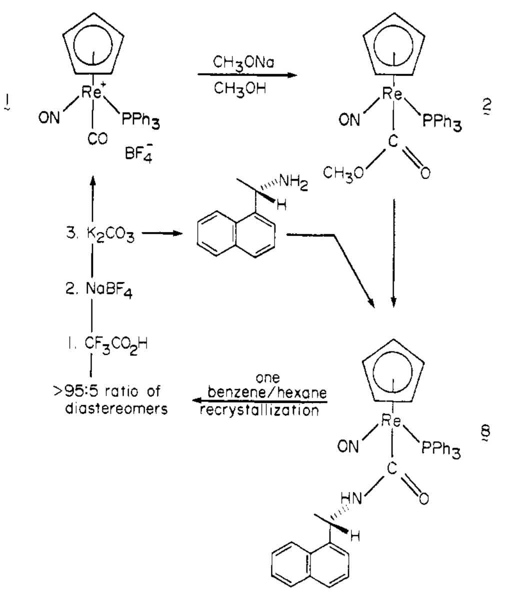
Attempts were then made to resolve the methyl complex (η-C_5H_5)Re(NO)(PPh_3)(CH_3) (**3**), which is the $NaBH_4$ reduction product of **1**.[2b] As previously described,[2] **3** and $Ph_3C^+PF_6^-$ react to give the methylidene **4** (Scheme I). Amine, alkoxide, phosphorus,[2] and sulfur[14] nucleophiles readily attack **4**. We had previously shown that the pyridine adduct of **4**, **5a**, could be reduced with $LiAlH_4$ to **3**. This closes a stereochemical cycle, as shown in Scheme I.[15] Hence we studied the reactions of methylidene **4** with approximately 20 chiral amines.

Representative amines **b–f** (Scheme I) afforded methylidene adducts **5b–f** in excellent spectroscopic yields. Pairs of diastereomers could in most cases be distinguished by a 1–4 Hz separation of their η-C_5H_5 ^1H NMR resonances at 200 MHz. However, numerous attempts to separate the diastereomers of **5b–f** by recrystallization or HPLC (reverse phase C18) were unsuccessful.

A similar resolution scheme was attempted with sodium *l*-menthoxide. Its reaction with **4** gave the alkyl (η-C_5H_5)Re(NO)(PPh_3)(CH_2O-*l*-menthyl) (**6**). Although diastereomers of the isostructural iron carbonyl complex have been separated by recrystallization,[10,11] **6** was a labile oil at room temperature and low-temperature extraction did not afford any diastereomer enrichment.

Reaction of **4** with Ph_2P(O-*l*-menthyl) yielded the phosphonium salt **7** (Scheme I). Purification of **7** to a >95:5 ratio of diastereomers was achieved by a single acetone/ether recrystallization. Unfortunately, we were unable to reduce **7** to **3** or otherwise cleave the $ReCH_2$–P bond without totally destroying the complex. However, adduct **7** proved valuable as an optical purity assay (vide infra), since the η-C_5H_5 ^1H NMR resonances of its two diastereomers were widely separated (13.4 Hz at 200 MHz).

Scheme II. Resolution of
[(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+$BF$^-$ (1)



We abandoned the resolution strategy in Scheme I and returned to derivatives of **1**. Reactions of the methyl ester **2** with primary amines were found to give "amides"[12,13] (η-C_5H_5)Re(NO)(PPh_3)(CONHR) (Scheme II). The diastereomeric amides obtained from **2** and *l*-α-phenethylamine or nopinylamine did not separate under the crystallization conditions investigated. However, the diastereomeric amides prepared from **2** and α-(1-naphthyl)ethylamine, **8** (Scheme II), were readily separable by benzene/hexane recrystallization. Their η-C_5H_5 ^1H NMR resonances differed by 16.5 Hz at 200 MHz and were used to determine diastereomeric purity.

The less soluble diastereomer of **8** was recrystallized to constant rotation. The amide linkage was cleaved with CF_3CO_2H, and the optically active [(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+CF_3CO_2^-$ thus formed was metathesized to the more crystalline BF_4^- salt, **1**. Both enantiomers of α-(1-naphthyl)ethylamine are commercially available. When (−)-(*S*)-α-(1-naphthyl)ethylamine was used in Scheme I, (−)-**1** was obtained (Table I).[15] When (+)-(*R*)-α-(1-naphthyl)ethylamine was used, (+)-**1** was obtained. The α-(1-naphthyl)ethylamine was recovered without loss of optical activity following K_2CO_3 neutralization of its CF_3CO_2H salt. In all cases, the more soluble

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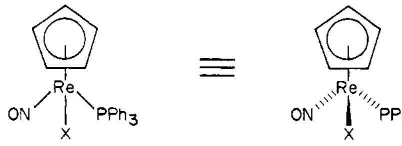
[14] McCormick, F. B.; Gladysz, J. A. *J. Organomet. Chem.* **1981**, *218*, C57.

[15] We employ the following convention for converting planar representations of (η-C_5H_5)Re(NO)(PPh_3)(X) compounds into three-dimensional structures.



Unless otherwise specified, (+)- and (−)- refer to rotations at 589 nm.

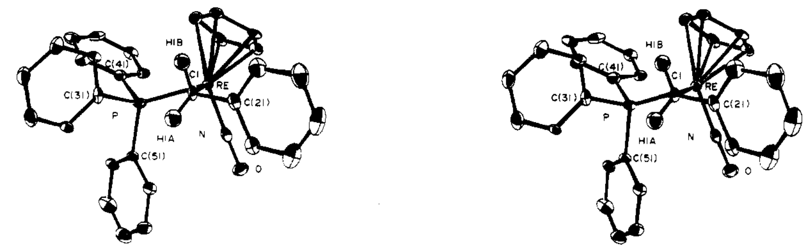


Figure 1. Stereoview of the molecular structure of (–)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) ((–)-(*R*)-**9**).

diastereomer of **8** was isolated from the benzene/hexane supernate (Scheme II) and similarly converted to **1** (ca. 70% ee). This optically enriched **1** was converted to **2** and reacted with the enantiomer of the α-(1-naphthyl)ethylamine originally employed. This gave principally the less soluble diastereomer of **8** but now with the *mirror-image* configuration at rhenium.

The optical purity of (–)-**1** and (+)-**1**[15] was assayed by reduction to **3** and subsequent conversion in CD_2Cl_2 to phosphonium salt **7** (Scheme I). Only one of the two η-C_5H_5 ^1H NMR resonances present in **7** prepared from racemic **1** was detected. A $CDCl_3$ solution of (+)-**7** (from (+)-**1**) was doped with 1% of the *diastereomer* (–)-**7**. The minor isomer was clearly visible in the ^1H NMR spectrum, and the two η-C_5H_5 resonances integrated within the range (99.0 ± 0.2): (1.0 ± 0.2). It was estimated that 0.5–0.3% of one diastereomer could be detected in the presence of the other. Thus compounds we claim to be "optically pure" are at least 99% ee.

Optically pure **1** was treated with CH_3ONa/CH_3OH at room temperature. Product **2** was significantly racemized (ca. 72% ee), as assayed by conversion to **8** and integration of the η-C_5H_5 ^1H NMR resonances of the two diastereomers. The same reaction was run to partial conversion by using a deficiency of CH_3ONa. Starting **1** was recovered in ≥98% ee. Reaction of **1** with CH_3ONa/CH_3OH at –24 °C (Scheme II) gave **2** in 98% ee. Isolated **2** mutorotated (vide infra) slightly over the course of a few minutes when dissolved. Prior to attaining the equilibrium value in Table I, $[\alpha]^{24.5}_{589}$ for (–)-**2** was ca. –186°. Ester **2** was otherwise configurationally stable at room temperature in CH_2Cl_2, $CHCl_3$, and CH_3OH.

Optically pure **1** was converted to the previously reported[3] rhenium alkyls (η-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) (**9**) and (η-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3) (**10**) as outlined in Scheme III. The formyl (η-C_5H_5)Re(NO)(PPh_3)(CHO) (**11**) was prepared by $NaBH_4$ (THF/H_2O) reduction of **1**.[2b] The ee of **11** was shown to be >99% by BH_3·THF reduction to **3**.[2] Other reactions[3] placed similar limits on the optical purities of **9** and **10**. These compounds were configurationally stable at room temperature and gave the rotations summarized in Table I.

2. X-ray Crystal Structure of (–)-(η-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) ((–)-9). In order to establish the absolute configurations of the chiral compounds in Table I, the X-ray crystal structure of the benzyl complex (–)-**9**[15] was executed. Suitable crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of (–)-**9** at room temperature. X-ray data were collected at –158 °C by using monochromated Mo Kα (0.710 69 Å) radiation on a Syntex P$\bar{1}$ automatic diffractometer. Three standard reflections were taken every 100 reflections; these varied by less than 3%. The unit cell was orthorhombic with lattice parameters a = 12.874 (5) Å, b = 11.889 (3) Å, and c = 16.077 (7) Å. Systematic absences were consistent with the space group $P2_12_12_1$. Of 4964 reflections collected with $2\theta < 50°$, 4581 reflections with $I \geq 3\sigma$ were used in the final refinement.

Scheme III. Syntheses of Other Chiral Organorhenium Complexes

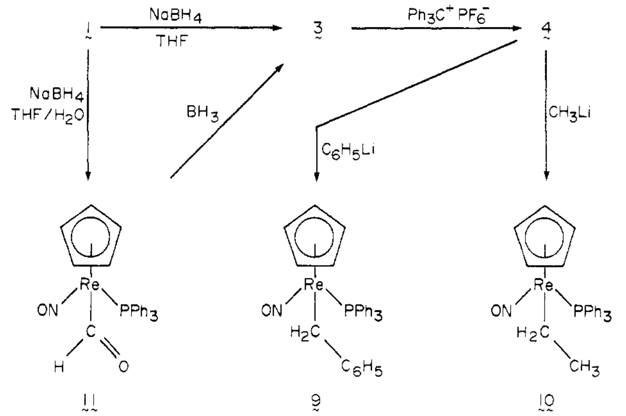


Table II. Selected Bond Lengths and Bond Angles in (–)-(*R*)-9

atoms	dist, Å	atoms	angle, deg
Re-C1	2.203 (8)	C21-C1-Re	110.3 (6)
Re-P	2.365 (3)	C1-Re-N	93.8 (3)
Re-N	1.740 (7)	C1-Re-P	87.4 (3)
Re-C_5H_5[a]	2.300	N-Re-P	93.9 (3)
N-O	1.230 (9)	Re-N-O	177.9 (7)
C1-C21	1.501 (11)	H1A-C1-Re[b]	119
C1-H1A[b]	1.02	H1B-C1-Re[b]	113
C1-H1B[b]	1.12	H1A-C1-H1B[b]	111

[a] Average distance from Re to C_5H_5 carbons; exact values vary from 2.360 to 2.217 Å. The tilt of the C_5H_5 least-squares plane with respect to the vector between Re and the C_5H_5 centroid is 85.7°. [b] H1A and H1B were not refined.

The position of the rhenium was obtained from a three-dimensional Patterson map. Fourier synthesis combined with least-squares refinement yielded all non-hydrogen atoms. Absorption corrections were applied, and all non-hydrogen atoms were refined with anisotropic temperature factors.[16] All hydrogens were located from a difference Fourier map and were not refined. The final R index was 0.034 with R_w = 0.040.[17]

The preceding structure analysis of (–)-**9** was conducted with the rhenium in the R[18] configuration (opposite to the formulas in this paper).[15] The configuration was inverted through a mirror plane by changing the sign of the y coordinates. An identical series of refinements of the resulting S molecule gave an R factor (0.051; R_w = 0.060)

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(16) In-house programs were used for data refinement. One of these incorporated modifications of the programs CARESS by R. W. Broach (University of Wisconsin) and PROFILE by P. Coppens, P. Becker, and R. H. Blessing (SUNY, Buffalo).

(17) All least-squares refinements computed the agreement factors R and R_w according to $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2}$, where F_o and F_c are the observed and calculated structure factors, respectively, and $w_i^{1/2} = 1/\sigma(F_o)$. The function minimized in all least-squares refinements was $\sum w_i||F_o| - |F_c||^2$.

(18) (a) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. (b) Sloan, T. *Top. Stereochem.* **1981**, *12*, 1.

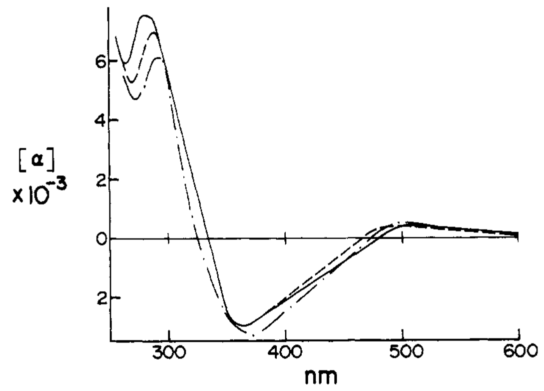

Figure 2. ORD spectra of (*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ ((*S*)-**3**) (—), (S)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ ((*S*)-**9**) (-·-) and (*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_3)$ ((*S*)-**10** (---).

significantly greater than that of the *R* molecule. This difference, according to Hamilton's *R* factor significance test,[19] indicates that the probability of (-)-**9** having an *R* configuration is >99.5%.

The molecular structure of (-)-(*R*)-**9** thus obtained is shown in Figure 1. An exhaustive list of bond distances and angles, and two crystal packing diagrams are provided in the supplementary material. Important bond distances and angles are summarized in Table II. There are two important structural features in (-)-(*R*)-**9**. First, the molecule adopts the conformation approximated by Newman projection I. Logically, the phenyl resides between

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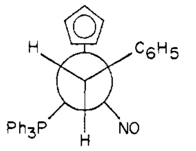

the two smallest ligands, $\eta\text{-}C_5H_5$ and NO. Second, the Re–C1–C21 plane is nearly perpendicular (∠ = 84.5 ± 0.5°) to the least-squares plane of the phenyl ring. This may be a consequence of steric interactions and/or Re–C1 bond/phenyl ring hyperconjugation.

According to accepted mechanisms, all of the transformations shown in Schemes I–III should proceed with retention of configuration at rhenium. The absolute configurations summarized in Table I are assigned accordingly.

3. Optical and Chiroptical Properties. The UV-visible spectra of **1** (yellow), **2** (yellow), **3** (orange-red), **7** (gold), **8** (yellow), **9** (orange-red), **10** (orange-red), and **11** (honey yellow) were measured in $CHCl_3$. Each was qualitatively similar to the published spectrum[4] of propylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHCH_2CH_3)]^+PF_6^-$, which featured an extended tail into the visible region with weak peaks and/or shoulders. Data were as follows: **1**, 259 (pk, ε 7100), 312 nm (sh, 900); **2**, 261 (pk, ε 6900), 290 nm (sh, 3600); **3**, 262 (pk, ε 6050), 312 nm (sh, 2800); (+)-(S_{Re})-**7**, 262 (sh, ε 6700), 304 nm (pk, 2700); (-)-(*RS*)-**8**, 274 and 283 nm (2 pk, ε 10 800); **9**, 270 (pk, ε 11 700), 307 nm (sh, 5300); **10**, 261 (pk, ε 6100), 310 nm (sh, 2400); **11**, 261 (pk, ε 7300), 305 nm (sh, 3200). The ORD and CD spectra of **1–3** and **7–11** (Figures 2–7) were somewhat more complex. These data will be interpreted in the Discussion.

Discussion

To our knowledge, Scheme II constitutes the first resolution of a metal carbonyl compound via an "amide"[12] derivative. It is interesting that resolution strategies which

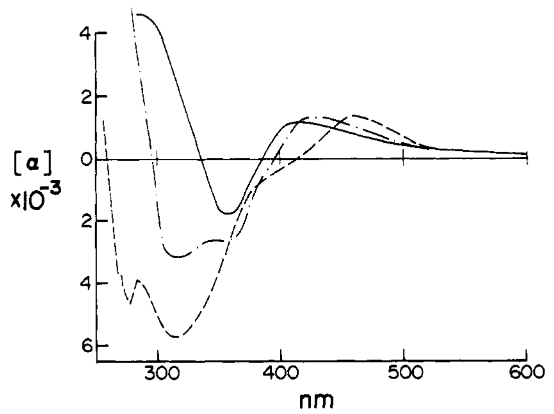

Figure 3. ORD spectra of (*S*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ ((*S*)-**1** (---), (*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COOCH_3)$ ((*S*)-**2** (-·-) and (*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ ((*S*)-**11** (—).

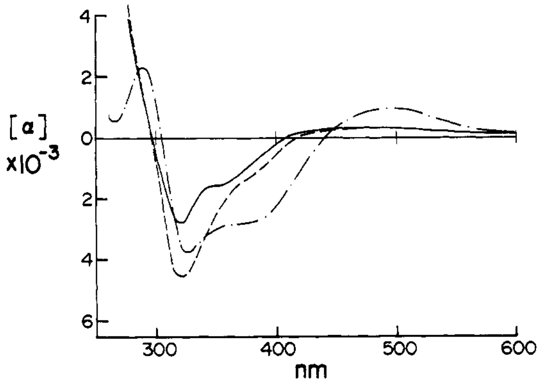

Figure 4. ORD spectra of ((S_{Re})-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2P^+Ph_2(O\text{-}l\text{-menthyl}))]^+PF_6^-$ ((S_{Re})-**7**) (-·-), (*SR*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CONHCH(CH_3)C_{10}H_7)$ ((*SR*)-**8**) (---), and (*SS*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CONHCH(CH_3)C_{10}H_7)$ ((*SS*)-**8**) (—).

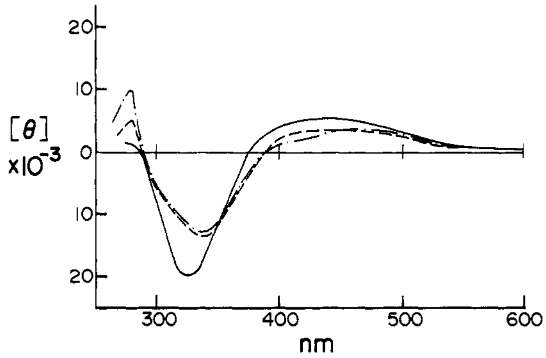

Figure 5. CD spectra of (*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3))$ (CH_3) ((*S*)-**3**) (-·-), (*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ ((*S*)-**9**) (---), and (*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_3)$ ((*S*)-**10**) (—).

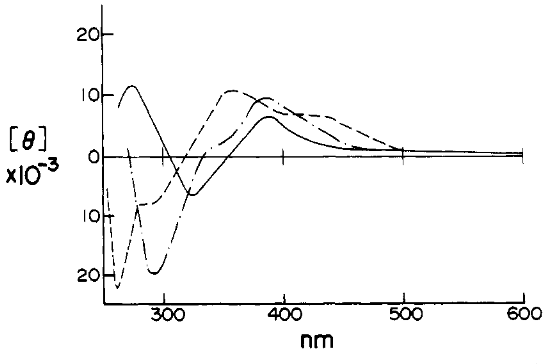

Figure 6. CD spectra of (*S*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ ((*S*)-**1**) (---), (*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COOCH_3)$ ((*S*)-**2**) (-·-), and (*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ ((*S*)-**11**) (—).

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[19] Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

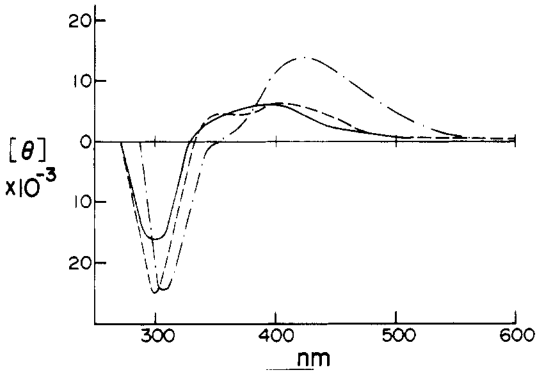

Figure 7. CD spectra of ((S_{Re})-[(η-C_5H_5)Re(NO)(PPh_3)($CH_2P^+Ph_2$(O-*l*-menthyl))]$^+$ PF_6^- ((S_{Re})-**7**) (-·-), (*SR*)-(η-C_5H_5)Re(NO)(PPh_3)(CONHCH(CH_3)$C_{10}H_7$) (*SR*)-**8**) (---), and (*SS*)-(η-C_5H_5)Re(NO)(PPh_3)(CONHCH(CH_3)$C_{10}H_7$) ((*SS*)-**8**) (—).

were successful with isostructural manganese and iron complexes failed so dramatically when extended to rhenium. Difficulty with the HPLC separation of diastereomeric organometallic complexes has also been encountered by other groups.[20]

Absolute configurations at rhenium are assigned according to the Baird/Sloan modification of the Cahn–Ingold–Prelog priority rules.[17] The C_5H_5 ligand is considered to be a pseudoatom of atomic number 30. Hence by our convention,[15] all structures in this paper (except I and Figure 1) have an *S*-rhenium configuration.

The crystal structure of (-)-(*R*)-**9** (Figure 1) can be compared with those of several homologous rhenium complexes. The Re–C1 bond length, 2.203 (8) Å, is essentially the same as that found in the substituted benzyl complex (*SS,RR*)-(η-C_5H_5)Re(NO)(PPh_3)(CH($CH_2C_6H_5$)C_6H_5) (2.215 (4) Å).[3b] However, it is considerably longer than the Re–C bond lengths in formyl (η-C_5H_5)Re(NO)(PPh_3)(CHO) (2.055 (10) Å)[21] and benzylidene *ac*-[(η-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+PF_6^-$ (1.949 (6) Å).[3b] Contractions are expected on the basis of the superior π-accepting (multiple bonding) capabilities of these ligands.

The substituted benzyl (*SS,RR*)-(η-C_5H_5)Re(NO)(PPh_3)(CH($CH_2C_6H_5$)C_6H_5) adopts, like I, a solid-state conformation with the α-carbon phenyl ring gauche to the η-C_5H_5 and NO ligands.[3b] As was noted with (-)-(*R*)-**9**, this phenyl ring is also perpendicular to the Re–C_α–C_{ipso} plane. The X-ray crystal structure of another cyclopentadienylbenzylrhenium complex, (η-C_5H_5)Re(CO)$_2$(H)($CH_2C_6H_5$), has been reported by Fischer and Frank.[22] Its Re–CH_2-C_6H_5 bond, 2.29 (1) Å, is longer than that of (-)-(*R*)-**9**. This may be due to an increased coordination number and/or a "semibridging" hydride. Schrock, Guggenberger, and Stucky have described crystal structures of two tantalum–benzyl complexes: (η-C_5H_5)$_2$Ta(=CHC_6H_5)($CH_2C_6H_5$) (Ta–$CH_2C_6H_5$ = 2.30 (1) Å)[23] and (η-C_5Me_5)Ta(=CHC_6H_5)($CH_2C_6H_5$)$_2$ (Ta–$CH_2C_6H_5$ = 2.188 (15) and 2.233 (14) Å).[24]

Other interesting solid state data include the melting points listed in Table I. There is no regular trend: enantiomerically pure complexes melt both higher and lower than the corresponding racemates. In one case, a mixture of diastereomers, (-)-(R_{Re})-**7** and (+)-(S_{Re})-**7**, melted at a temperature *between* the melting points of the pure components.

While the ORD and CD spectra of **1**–**3** and **7**–**11** (Figures 2–7) are somewhat complex, there are some easily interpretable features. First, the gross morphologies are similar. Nearly all of the spectra cross the *x* axis twice. The CD spectra of the homologous methyl ((+)-(*S*)-**3**), ethyl ((+)-(*S*)-**10**), and benzyl ((+)-(*S*)-**9**) complexes are qualitatively identical. For the limited range of compounds examined, the sign of the ORD or CD spectrum at >500 nm (or the sign of the region between the two *x*-axis crossings) correlates to the rhenium absolute configuration.

The spectra of the diastereomers (+)-(*SR*)-**8** and (+)-(*SS*)-**8** (Figures 4 and 7) are quite similar. This has been previously noted for diastereomeric manganese and iron complexes which possess the same metal configuration.[9,11b] Thus the ligand chirality contributes only slightly to the ORD and CD spectra.

No simple relationship exists between the UV and CD maxima. In all cases, at least three Cotton effects are observed. Carbonyl cation (+)-(*S*)-**1**, phosphonium salt (+)-(S_{Re})-**7**, and possibly (+)-(*S*)-**2**, (+)-(*SR*)-**8**, and (+)-(*SS*)-**8** exhibit more.

Flood has elegantly discussed the problems involved in relating the absolute configurations of (η-C_5H_5)Fe(CO)(PPh_3)(X) complexes to their ORD and CD spectra.[11b] The present level of theoretical sophistication allows only somewhat tenuous empirical correlations to be made. Alkyls (*S*)-(η-C_5H_5)Fe(CO)(PPh_3)(CH_3) and (*S*)-(η-C_5H_5)Fe(CO)(PPh_3)(CH_3CH_3) are both dextrorotatory at 579–589 nm. Interestingly, we find that the isostructrual rhenium complexes (*S*)-**3** and (*S*)-**10** are also dextrorotatory.

Brunner has reported the following rotations for (+)-[(η-C_5H_5)Mn(NO)(PPh_3)(CO)]$^+PF_6^-$:[8b] $[\alpha]^{20}_{579}$ 375°; $[\alpha]^{20}_{549}$ 595°; $[\alpha]^{20}_{436}$ -1490. To our knowledge, the absolute configuration of this complex has not been established. Its CD most closely resembles that of rhenium carbonyl cation enantiomer (+)-(*S*)-**1** (Table I and Figure 3) but with a somewhat greater specific rotation in the 575–590-nm range.

Brunner has reported that the manganese carbonyl cation [(η-C_5H_5)Mn(NO)(PPh_3)(CO)]$^+PF_6^-$ is configurationally stable at 25 °C.[8b] However, diastereomerically pure (η-C_5H_5)Mn(NO)(PPh_3)(COO-*l*-menthyl) epimerizes in solution at room temperature.[8a,25] Similarly, optically pure (η-C_5H_5)Mn(NO)(PPh_3)($COOCH_3$)[25] and (η-C_5H_5)-Mn(NO)(L)(COR)[26] complexes racemize slowly in solution at 25 °C. Brunner has shown that epimerization and/or racemization are initiated by phosphine dissociation.[26-28] We attribute the configurational stability of our rhenium complexes to the reluctance of PPh_3 to dissociate. For instance, the formyl **11** does not undergo phosphine exchange with P(C_2H_5)$_3$ at temperatures up to 80 °C.[2b] However, (+)-(η-C_5H_5)Mn(NO)(PPh_3)($COOCH_3$) exchanges readily (with retention) with P(*p*-$C_6H_4OCH_3$)$_3$ at 20 °C.[27] Speculatively, we suggest that the small amount of racemization we encountered in the synthesis of optically active **2** may be due to an electron-transfer side reaction. Manganese and rhenium complexes with 17 or 19

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(20) Goldman, M.; Kustanovich, Z.; Weinstein, S.; Tishbee, A.; Gil-Av, E. *J. Am. Chem. Soc.* **1982**, *104*, 1093.

(21) Wong, W.-K.; Tam, W.; Strouse, C. E.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1979**, 530.

(22) Fischer, E. O.; Frank, A. *Chem. Ber.* **1978**, *111*, 3740.

(23) Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3793.

(24) Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. *J. Am. Chem. Soc.* **1980**, *102*, 6744.

(25) Brunner, H.; Schindler, H.-D. *Chem. Ber.* **1971**, *104*, 2467.

(26) (a) Brunner, H.; Langer, M. *J. Organomet. Chem.* **1975**, *87*, 223. (b) Brunner, H.; Aclasis, J. A. *Ibid.* **1976**, *104*, 347.

(27) Brunner, H.; Aclasis, J.; Langer, M.; Steger, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 810.

(28) The configurational instability of Brunner's complexes appears to correlate with the "cis-labilizing" effect of certain ligands (COR, CO_2R) noted by Brown: Brown, T. L.; Bellus, P. A. *Inorg. Chem.* **1978**, *17*, 3726.

valence electrons are known to be substitutionally and configurationally labile.[29,30]

The low IR $\nu_{C=O}$ of 2, 1580 cm^{-1}, suggests the importance of a zwitterionic $Re^+{=}C(OCH_3)O^-$ resonance contributor. Since we have observed that $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHR)]^+$ alkylidenes can exist in two geometric isomeric forms,[3,4] the apparent mutorotation of optically active **2** noted above may be due to easily interconverted Re$\overset{\cdots}{-}$C geometric isomers. This phenomenon can be anticipated whenever the precipitation or crystallization method employed yields a nonequilibrium isomer distribution. An interesting related example involving the endo/exo isomerization of chiral π-allyl molybdenum complexes has been recently reported by Faller and Shvo.[31]

Conclusion

The optical resolution of **1** outlined in Scheme II is convenient and easily executed on a multigram scale. The X-ray structure of (–)-(*R*)-**9** establishes the absolute configuration of resolved **1** and many other chiral organorhenium complexes. Previously, numerous reactions of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ complexes (X = carbon-bound ligand) have been found in which a new, ligand-based chiral center is generated stereospecifically or with high stereoselectivity.[3,5,6] Since methods exist for the stereospecific cleavage of metal–carbon bonds,[7] this study provides a firm groundwork for the rational application of these reactions in asymmetric organic synthesis.

Finally, the utility of chiral organometallic complexes in the elucidation of reaction mechanisms has received frequent emphasis.[9–11,32] Mechanistic aspects of the homogeneous chemistry of methylidene and formyl complexes are currently of intense interest,[2,33,34] and this investigation has provided the first examples of such species (**4**, **11**) in optically pure form.[35] Resolved **4** and **11** will both play pivotal roles in future studies from our laboratory.

Experimental Section

General Data. All reactions were carried out under an atmosphere of dry N_2. Benzene, toluene, THF, and ether were purified by distillation from benzophenone ketyl (Na or K). Hexane was distilled from potassium metal, and CH_2Cl_2 was distilled from P_2O_5. Chloroform, acetonitrile, and methanol were reagent grade and degassed prior to use. CD_2Cl_2 was distilled from P_2O_5 and degassed.

IR spectra were recorded on a Perkin-Elmer Model 521 spectrometer. ^1H and ^{13}C NMR spectra were (unless otherwise noted) recorded at ambient probe temperature on a Brüker WP-200 spectrometer at 200 and 50 MHz, respectively, and referenced to $(CH_3)_4Si$. Optical rotations were measured on a Perkin-Elmer 241MC polarimeter. UV/vis and ORD spectra were recorded on Cary 219 and 60 spectrometers, respectively. CD spectra were obtained on a Jasco Model J-10 spectropolarimeter. Mass spectra were obtained on an AEI-M59 instrument. Melting points were recorded on a Büchi Schmeltzpunktbestimmungsapparat and were not corrected. Microanalyses were conducted by Galbraith.

Starting Materials. Carbonyl $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ was prepared as described previously.[2b] $Ph_3C^+PF_6^-$ was purchased from Aldrich and Columbia Organic Chemicals and was purified by recrystallization from CH_2Cl_2/hexane under N_2.[36] Alkyls C_6H_5Li (2.0 *M* in C_6H_6/ether) and $CH_3Li{\cdot}LiBr$ (1.4 *M* in THF) were purchased from Aldrich and used without standardization. Other achiral reagents were available from common commercial sources and used without purification.

Samples of (–)- and (+)-α-(1-naphthyl)ethylamine ($[\alpha]^{25}{}_{589}$ –76° (neat) and +76° (neat)) originated (long ago) from Aldrich Chemical Co. and Pfaltz and Bauer, respectively, and were purified by vacuum distillation. Fairfield Chemical Co. is a contemporary supplier of these amines. Nopinylamine ($[\alpha]^{22}{}_{589}$ –19° (*c* 1.3, CH_3OH)) and *l*-(–)-α-phenethylamine ($[\alpha]^{20}{}_{589}$ –39° (neat)) were purchased from Aldrich and purified by distillation. Styrchnine, brucine, and nicotine were obtained from Aldrich and used without further purification. (–)-*l*-Menthol was used as obtained from Matheson, Collman and Bell. (–)-Ph_2P(O-*l*-menthyl) ($[\alpha]^{25}{}_{579}$ –62° (*c* 0.96, C_6H_6)),[37] (*l*-menthyl)nicitinoate,[38] and (–)-2-(*l*-menthyl)pyridine ($[\alpha]^{25}{}_{579}$ –43.8° (*c* 1.96, 95% C_2H_5OH))[39] were prepared via literature procedures.

Preparation of (±)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COOCH_3)$ ((±)-2). To 75 mL of CH_3OH was added 3.00 g (4.56 mmol) of (±)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (**1**). To this slurry was added Na (0.4 g, 17 mmol). The reaction was stirred for 1 h, and the solvent was then removed under vacuum. The resulting yellow residue was dissolved in CH_2Cl_2 and filtered through celite. The solvent was removed under vacuum to yield a light yellow foam-up solid, which was washed with cold hexanes and vacuum dried to give 2.63 g (4.37 mmol, 96%) of **2**: IR (cm^{-1}, $CHCl_3$) 1670 ($\nu_{N\equiv O}$, s), 1580 ($\nu_{C=O}$, m); ^1H NMR (δ, $CDCl_3$) 7.97–7.37 (m, 15 H), 5.25 (s, 5 H), 3.11 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 196.5 (d, $J_{^{13}C-^{31}P}$ = 4.8 Hz), 135.2 (d, *J* = 55 Hz), 133.2 (d, *J* = 11.0 Hz), 130.0, 128.0 (d, *J* = 10.6 Hz), 91.6 49.0; mass spectrum (70 eV), *m/e* 603 (M^+, ^{187}Re, 16%), 572 ($M^+ - OCH_3$, 100), 544 ($M^+ - CO_2CH_3$, 52).

Preparation of (–)-(*RS*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CONHCH(CH_3)C_{10}H_7)$ ((–)-(*RS*)-8). Ester **2** (3.00 g, 4.98 mmol) was dissolved in 100 mL of toluene, and (–)-(*S*)-α-(1-naphthyl)ethylamine (1.70 g, 9.94 mmol) was added. The reaction was stirred for 2 h, and the toluene was then removed under vacuum to give a dark yellow-brown oil/solid mixture. This was dissolved in 50 mL of benzene, upon which 150 mL of hexane was layered. The layers were allowed to diffuse, and the resulting yellow-orange precipitate was collected and washed twice with hexane to give (–)-(*RS*)-**8** of ≥95% diastereomeric purity (1.48 g, 1.29 mmol, 80%). The (–)-(*RS*)-**8** was recrystallized two to three additional times until a constant rotation (Table I) was reached: IR (cm^{-1}, $CHCl_3$) 1644 ($\nu_{N\equiv O}$, s), 1532 ($\nu_{C=O}$, m); ^1H NMR (δ, $CDCl_3$) naphthyl H at 8.18 (d, $J_{^1H-^1H'}$ = 7.8 Hz, 1 H), 7.83 (d of d, *J* = 7.9, 2.2 Hz, 1 H), 7.72 (d of d, *J* = 7.9, 2.2 Hz, 1 H), naphthyl and phenyl H at 7.56–7.40 (m, 19 H), 5.74 (pseudoquintet, *J* = 7 Hz, $CH_3CH(Np)NH$), 5.58 (d, *J* = 7.8 Hz, NH), 5.21 (s, C_5H_5), 0.99 (d, *J* = 6.6 Hz, CH_3), decoupling of the 0.99 resonance converted the 5.74 resonance to a doublet (*J* = 7.7 Hz); ^{13}C NMR (ppm, $CDCl_3$) 189.7 (d, $J_{^{13}C-^{31}P}$ = 12.0 Hz, ReCONHR), aryl carbons at 141.2 (Np), 136.2 (d, *J* = 55.4 Hz, ipso PPh_3), 133.8 (d, *J* = 11.5 Hz), 131.4, 130.2, 128.5 (d, *J* = 11.2 Hz), 128.2, 127.2, 126.9, 125.6, 125.4, 125.3, 124.5, 122.2, 92.2 (C_5H_5), 44.2 (CH_3C), 20.9 (CH_3); mass spectrum (70 eV), *m/e* 742 (M^+, ^{187}Re, 14%); 572 ($M^+ - C_{10}H_7CH(CH_3)NH$, 71), 544 ($M^+ - C_{10}H_7CH(CH_3)NHCO$, 24), 262 ($PPh_3$, 100). Anal. Calcd for $C_{36}H_{32}N_2O_2PRe$: C, 58.29; H, 4.35; N, 3.78; P, 4.18. Found: C, 58.05; H, 4.40; N, 3.76; P, 4.07.

Preparation of (–)-(*R*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+PF_6^-$ ((–)-(*R*)-1). To CH_2Cl_2 (40 mL) was added 2.00 g (2.70 mmol) of (–)-(*RS*)-**8**. CF_3CO_2H (0.70 g, 6.0 mmol) was then added, and

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(29) (a) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527. (b) Kidd, D. R.; Brown, T. L. *Ibid.* **1978**, *100*, 4095.

(30) Rox, A.; Malito, J.; Poe, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1052.

(31) Faller, J. W.; Shvo, Y.; Chao, K.; Murray, H. H. *J. Organomet. Chem.* **1982**, *226*, 251.

(32) (a) Miles, S. L.; Miles, D. L.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7278. (b) Faller, J. W.; Shvo, Y. *Ibid.* **1980**, *102*, 5396. (c) Quinn, S.; Shaver, A.; Day, V. W. *Ibid.* **1982**, *104*, 1096. (d) Attig, T. G.; Teller, R. G.; Wu, S.-M.; Bau, R.; Wojciki, A. *Ibid.* **1979**, *101*, 619.

(33) (a) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1. (b) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsy, S. G. *J. Mol. Catal.* **1981**, *13*, 43.

(34) (a) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389. (b) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *Ibid.* **1980**, *102*, 1203.

(35) The reaction of chiral trialkylborohydrides with appropriate metal carbonyl precursors may give formyl complexes of very low ee: Gladysz, J. A.; Merrifield, J. H. *Inorg. Chim. Acta* **1978**, *30*, L317.

(36) Patton, A. T.; Strouse, C. E.; Gladysz, J. A., manuscript in preparation.

(37) Brunner, H.; Doppelberger, J. *Chem. Ber.* **1978**, *111*, 673.

(38) Chardnnat, R.; Harispe, M.; Harispe, J. V.; Chevillard, L. *Bull. Soc. Chim. Fr.* **1948**, *15* (series 5), 1014.

(39) Hengtes, S. G. Ph.D. Dissertation, Stanford University, 1980.

the reaction was stirred for 10 min. The solvent was removed by rotary evaporation to give a dark yellow oil which was extracted with H_2O until the H_2O extracts were colorless (ca. 400 mL). The extracts were added to a solution of $NaBF_4$ (0.50 g, 5.4 mmol) in 25 mL of H_2O. The resulting yellow precipitate was collected by filtration and recrystallized from CH_2Cl_2/hexanes to give 1.74 g (2.64 mmol, 98%) of (–)-(*R*)-1. The aqueous supernate was neutralized with K_2CO_3, and the resulting milky white suspension was extracted with CH_2Cl_2 to give (after brine washing, drying, and CH_2Cl_2 removal) (–)-(*S*)-α-(1-naphthyl)ethylamine as a slightly yellow oil, $[\alpha]^{25}{}_{589}$ –76°.

Preparation of (+)-(*S*)-[(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+$$PF_6$ ((+)-(*S*)-1). The amide remaining in the supernate (principally (+)-(*SS*)-8) from the above preparation of (–)-(*RS*)-8 was converted to (+)-(*S*)-1 (ca. 70% ee) as described for (–)-(*R*)-1 above. This (+)-(*S*)-1 was subjected to a second resolution cycle using (+)-(*R*)-α-(1-naphthyl)ethylamine, so that the less soluble (+)-(*SR*)-8 precipitated. The (+)-(*SR*)-8 was converted to (+)-(*S*)-1 by the same procedure as employed above for its enantiomer.

Preparation of (–)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)($COOCH_3$) ((–)-(*R*)-2). To 50 mL of CH_3OH was added 0.150 g (6.5 mmol) of sodium. After the sodium dissolved, the solution was cooled to –24 °C (CCl_4/CO_2 bath). Then (–)-(*R*)-1 (1.00 g, 1.52 mmol) was added. The (–)-(*R*)-1 dissolved over several minutes, and then a new yellow solid precipitated. The reaction mixture was stirred for an additional 20 min and then worked up as above for (±)-**2** to give 0.95 g (1.58 mmol, 96%) of (–)-(*R*)-**2**.

Preparation of (–)-(*RR*)-(η-C_5H_5)Re(NO)(PPh_3)-($CONHCH(CH_3)C_{10}H_7$) ((–)-(*RR*)-8). Ester (–)-(*R*)-**2** (0.212 g, 0.352 mmol) was dissolved in 30 mL of toluene, and (+)-(*R*)-α-(1-naphthyl)ethylamine (0.061 g, 0.356 mmol) was then added. The reaction was stirred for 2 h and worked up as described above for (–)-(*RS*)-8. A benzene/hexane recrystallization gave 0.248 g (0.334 mmol, 95%) of (–)-(*RR*)-8 which by examination of the η-C_5H_5 region in the ^1H NMR spectrum was judged to be contaminated with 0.9 ± 0.1% of (+)-(*SR*)-8: IR (cm^{-1}, $CHCl_3$) 1643 ($\nu_{N\equiv O}$, s), 1539, ($\nu_{C=O}$, m); ^1H NMR (δ, $CDCl_3$) naphthyl H at 8.00 (d, $J_{^1H-^1H'}$ = 8.6 Hz, 1 H), 7.82 (d of d, *J* = 7.7, 1.1 Hz, 1 H), 7.76 (d, *J* = 8.2 Hz, 1 H), naphthyl and phenyl H at 7.44–6.99 (m, 19 H), 5.66–5.74 (br m, 2 H, CH_3CH(Np)NH), 5.29 (s, C_5H_5), 1.49 (br d, *J* = 6.0 Hz, CH_3); ^{13}C NMR (ppm, $CDCl_3$) 191.2 (d, $J_{^{13}C-^{31}P}$ = 4.4 Hz, ReCONHR), aryl carbons at 141.2 (Np), 135.6 (d, *J* = 55.1 Hz, ipso PPh_3), 133.9, 133.5 (d, *J* = 10.9 Hz), 129.9, 127.9 (d, *J* = 10.2 Hz), 127.2, 126.8, 125.6, 125.5, 125.4, 125.2, 124.1, 122.8, 92.7 (C_5H_5), 44.2 (CH_3C), 24.2 (CH_3).

Preparations of (–)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(CH_3) ((–)-(*R*)-3) and (+)-(*S*)-(η-C_5H_5)Re(NO)(PPh_3)(CH_3) ((+)-(*S*)-3). The conversions of (–)-(*R*)-1 to (–)-(*R*)-**3** and (+)-(*S*)-1 to (+)-(*S*)-**3** were effected with $NaBH_4$ analogous to the published procedure for racemic material.[2b]

Preparations of (–)-(*R*)-[(η-C_5H_5)Re(NO)(PPh_3)(=CH_2)]$^+$$PF_6^-$ ((–)-(*R*)-4) and (+)-(*S*)-([(η-C_5H_5)Re(NO)-(PPh_3)(=CH_2)]$^+$$PF_6^-$ ((+)-(*S*)-4). These were synthesized from (–)-(*R*)-**3** and (+)-(*S*)-**3**, respectively, using $Ph_3{}^+PF_6^-$ as previously described for the racemate.[2b]

Preparations of (+)-(*S*$_{Re}$)- and (–)-(*R*$_{Re}$)-[(η-C_5H_5)Re-(NO)(PPh_3)($CH_2P^+Ph_2$(O-*l*-menthyl))]PF_6^- ((+)-(*S*$_{Re}$)-7 and (–)-(**R**$_{Re}$)-7). Methyl complex (+)-(*S*)-**3** (0.130 g, 0.233 mmol) was dissolved in 20 mL of CH_2Cl_2. The solution was cooled to –78 °C, and $Ph_3C^+PF_6^-$ (0.091 g, 0.234 mmol) was added. After 0.5 h, (–)-Ph_2P(O-*l*-menthyl) (0.090 g, 0.264 mmol) was added. The resultant yellow solution was stirred for 15 min at –78 °C and then allowed to warm to room temperature. The solvent was removed under vacuum and the remaining yellow residue triturated with hexanes. Crystallization from CH_2Cl_2/hexanes gave 0.231 g (0.222 mmol, 96%) of (+)-(*S*$_{Re}$)-**7**. The less crystalline (–)-(*R*$_{Re}$)-**7** diastereomer was prepared in a similar fashion from (–)-(*R*)-**3** and purified by trituration. To assay for the ee of **3**, the above reaction was conducted in CD_2Cl_2 in a 5-mm NMR tube.[2b] Typical reaction quantities: 0.027 mmol of **3**; 0.030 mmol of $Ph_3C^+PF_6^-$; 0.35 mmol of (–)-$(C_6H_5)_2P$(O-*l*-menthyl). The relative integrals of the η-C_5H_5 ^1H NMR resonances of (+)-(*S*$_{Re}$)-**7** and (–)-(*R*$_{Re}$)-**7** were determined in situ.

Data on (+)-(*S*$_{Re}$)-**7**: IR (cm^{-1}, $CHCl_3$) 1661 ($\nu_{N\equiv O}$, s); ^1H NMR (δ, $CDCl_3$) 7.73–7.30 (m, 25 H), 4.79 (s, 5 H), 3.76 (m, POCHRR′), 2.74 (pseudo d), 2.66 (m, $ReCH_2P$), menthyl resonances at 1.93 (quintet, *J* = 7.1 Hz, 1 H), 1.50 (m, 5 H), 1.03 (m), 0.87 (d, *J* = 7.1 Hz), 0.75 (d, *J* = 6.1 Hz), 0.28 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) aryl carbons at 134.4, 134.2, 134.1, 133.8, 133.6, 133.4, 133.3, 133.2, 133.1, 130.8, 129.4, 129.1, 129.0, 128.9, 128.3, 126.3 (some resonances part of ^{31}P-coupled doublets), 90.3 (C_5H_5), 82.8 (d, $J_{^{13}C-^{31}P}$ = 10.6 Hz, POC), 48.8 (d, *J* = 6.0 Hz, $ReCH_2P$), other menthyl resonances at 56.9, 42.8, 33.5, 31.4, 25.5, 22.5, 21.9, 21.0, 15.3.

Data on (–)-(*R*$_{Re}$)-**7**: IR (cm^{-1}, $CHCl_3$) 1660 ($\nu_{N\equiv O}$, s); ^1H NMR (δ, $CDCl_3$) 7.74–7.10 (m, 25 H), 4.79 (s, 5 H), 3.78 (m, POCHRR′), 2.85 and 2.68 (two d of d, $ReCH_2P$, which each collapse to d, $J_{^1H-^1H}$ = 13.2 Hz with ^{31}P decoupling), menthyl resonances at 1.74–0.94 (m), 0.88 (d, *J* = 7.6 Hz), 0.80 (d, *J* = 4.9 Hz), 0.17 (d, *J* = 6.9 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) aryl carbons at 135.5, 134.1, 133.8, 133.3, 133.2, 133.0, 130.9, 129.6, 129.5, 128.9, 128.3, 126.3 (some resonances part of ^{31}P-coupled doublets), 90.4 (C_5H_5), 82.4 (d, $J_{^{13}C-^{31}P}$ = 8.1 Hz, POC), 48.6 (br s, $ReCH_2P$), other menthyl resonances at 56.9, 43.1, 33.5, 31.7, 25.4, 22.6, 22.5, 21.8, 21.0, 15.2.

Anal. Calcd for $C_{46}H_{49}F_6NO_2P_3Re$ (mixture of (+)-(*S*$_{Re}$)-**7** and (–)-(*R*$_{Re}$)-**7**): C, 53.08; H, 4.74; N, 1.35; P, 8.93. Found: C, 53.07; H, 4.92; N, 1.35; P, 8.75.

Preparations of 5b–f, 6, and Other (η-C_5H_5)Re(NO)-(PPh_3)(COOR) and (η-C_5H_5)Re(NO)(PPh_3)(CONHR) Adducts. Because of our understandably provisional interest in these adducts, they were not characterized to the same extent as the other new rhenium complexes. The synthesis of **5b–f** closely followed the published synthesis of **5a**[2b] and (+)-(*S*$_{Re}$)-**7** above: ^1H NMR (η $CDCl_3$, η-C_5H_5 resonances of diastereomers) **5b**, 5.310 and 5.291, **5c**, 5.270 and 5.263, **5d**, 5.109 and 5.098, **5e**, 5.137 and 5.114, **5f**, 4.989 and 4.948. Oily alkyl **6** was prepared from **4** in a fashion analogous to the published synthesis of (η-C_5H_5)Re-(NO)(PPh_3)(CH_2OCH_3):[2b] ^1H NMR (δ $CDCl_3$, η-C_5H_5) 5.383 and 5.363. The reactions of *l*-α-phenethylamine and nopinylamine with **2** were conducted in a fashion identical with that of (–)-(*S*)-α-(1-naphthyl)ethylamine above. Amide adducts analogous to **8** formed with η-C_5H_5 ^1H NMR resonances at (δ, $CDCl_3$) 5.234, 5.218 and 5.238, 5.216, respectively. Ester (η-C_5H_5)Re(NO)-(PPh_3)(COO-*l*-menthyl) was prepared by the reaction of **2** (2.00 g, 3.32 mmol) with *l*-menthol (0.622 g, 3.99 mmo) in toluene (150 mL) containing two drops of CF_3CO_2H. The toluene was removed under vacuum, and the resulting yellow oil was extracted with pentane until the extracts were colorless. The pentane extracts were cooled to –78 °C for 2 h, and the resulting yellow solid product was isolated by Schlenk filtration. Upon warming to room temperature, the ester (0.740 g, 1.02 mmol, 31%) oiled. The C_5H_5 ^1H NMR resonances (δ, $CDCl_3$) indicated some diastereomer enrichment: 5.234, 5.218; ca. 60:40 ratio.

Preparations of (–)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) ((–)-(*R*)-9) and (+)-(*S*)-(η-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) ((+)-(*S*)-9). These were synthesized by the sequential treatment of (–)-(*R*)-**3** and (+)-(*S*)-**3**, respectively, with $Ph_3C^+PF_6^-$ and C_6H_5Li, as described previously for the racemate.[3b]

Preparations of (–)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3) ((–)-(*R*)-10) and (+)-(*S*)-(η-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3) ((+)-(*S*)-10). These were synthesized by the sequential treatment of (–)-(*R*)-3 and (+)-(*S*)-3, respectively, with $Ph_3C^+PF_6^-$ and CH_3Li as described previously for the racemate.[3c]

Preparations of (–)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(CHO) ((–)-(*R*)-11) and (+)-(*S*)-(η-C_5H_5)Re(NO)(PPh_3)(CHO) ((+)-(*S*)-11). These synthesized by $NaBH_4$ reduction of (–)-(*R*)-1 and (+)-(*S*)-1, respectively, in THF/H_2O as previously described for the racemate.[2b]

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Registry No. 1, 82293-78-5; (–)-(*R*)-1, 82236-19-4; (+)-(*S*)-1, 82336-21-8; (±)-**2**, 82293-79-6; (–)-(*R*)-**2**, 82336-22-9; (–)-(*R*)-**3**, 82336-23-0; (+)-(*S*)-**3**, 82336-24-1; (–)-(*R*)-**4**, 82336-26-3; (+)-(*S*)-**4**,

82336-28-5; **5b**, 82293-81-0; **5c**, 82293-83-2; **5d**, 82322-76-7; **5e**, 82293-85-4; **5f**, 82293-87-6; **6**, 82293-88-7; (+)-(S_{Re})-**7**, 82293-90-1; (–)-(R_{Re})-**7**, 82336-30-9; (–)-(*RR*)-**8**, 82293-91-2; (+)-(*SR*)-**8**, 82372-77-8; (*SS*)-^{8}, 82336-31-0; (–)-(*R*)-**9**, 82336-32-1; (+)-(*S*)-**9**, 82336-33-2; (–)-(*R*)-^{1}0, 82336-34-3; (+)-(*S*)-**10**, 82336-35-4; (–)-(*R*)-**11**, 82336-36-5; (+)-(*S*)-**11**, 82336-37-6; (–)-(*S*)-*α*-(1-naphthyl)ethylamine, 10420-89-0; (+)-(*R*)-*α*-(1-naphthyl)ethylamine, 3886-70-2; $Ph_3C^+PF_6^-$, 437-17-2; (–)-Ph_2P(O-*l*-menthyl), 67392-57-8.

Supplementary Material Available: Figure 8, numbering of atoms in (–)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) ((–)-(*R*)-**9**), Figure 9, crystal packing diagram of (–)-(*R*)-**9** as viewed down axis *a*, Figure 10, crystal packing diagram of (–)-(*R*)-**9** as viewed down axis *b*, Table III, summary of crystallographic data for (–)-(*R*)-**9**, Table IV, bond lengths and short interatomic nonbonded contacts in (–)-(*R*)-**9**, Table V, bond angles in (–)-(*R*)-**9**, Table VI, calculated atomic coordinates and thermal factors of (–)-(*R*)-**9**, Table VII, atomic coordinates of (–)-(*R*)-**9** (atoms refined anisotropically), and Table VIII, calculated and observed structure factors for (–)-(*R*)-9 (29 pages) Ordering information is given on any current masthead page.

Oxidative Addition of Halogens to Thiolato-Bridged Dinuclear Iridium(I) Complexes. Preparation of Several Iridium(II) and Iridium(III) Species. X-ray Structure of $Ir_2(\mu\text{-}t\text{-BuS})_2(CO)_2(PMe_2Ph)_2I_2$[1]

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Several oxidative reactions of different halogens to dinuclear complexes $Ir_2(\mu\text{-}t\text{-BuS})_2(CO)_2L_2$ (L = CO, $P(OMe)_3$, PMe_2Ph, PMe_3) have been carried out in nondonor solvents such as toluene or dichloromethane. Different behavior has been observed depending upon the nature of the halogen. Addition of 1 molar equiv of iodine leads to quantitative formation of Ir(II) complexes of general formula $Ir_2(\mu\text{-}t\text{-BuS})_2(CO)_2L_2I_2$. Further addition of a second molar equivalent of iodine gives rise to dinuclear iridium(III) compounds $Ir_2(\mu\text{-}t\text{-BuS})_2(CO)_2L_2I_4$. Isomorphous complexes have been formed by addition of bromine. However, Ir(II) species could never be prepared quantitatively since Ir(III) complexes are always formed preferentially. Oxidative addition of chlorine has also been observed. However, substitution of both thiolato groups by chlorine atoms to give Ir(III) dinuclear complexes, $Ir_2(\mu\text{-Cl})_2(CO)_2L_2Cl_4$, is a competitive process. An X-ray diffraction study of $Ir_2(\mu\text{-}t\text{-BuS})_2(CO)_2(PMe_2Ph)_2I_2$ has been performed. This compound crystallizes with four formula units in the monoclinic space group C_{2h}^5—$P2_1/c$ in a cell of dimensions a = 16.997 (2) Å, b = 14.911 (3) Å, c = 13.411 (3) Å, and β = 91.17 (1)°. On the basis of 3390 unique reflections the structure was refined by full-matrix least-squares techniques to conventional indices $R(F)$ = 0.046 and $R_w(F)$ = 0.055. The molecular architecture of this dinuclear complex can be described in terms of two square-planar pyramids around each iridium atom sharing an edge formed by the two sulfur atoms. The flap angle between the two basal planes is 83.8°. The two iodine atoms occupy the two axial positions, and the two phosphine ligands are mutually cis; the Ir–Ir separation is of 2.702 (1) Å. Other bond distances of interest are the following: Ir (1)–I(1) = 2.742 (2) Å, Ir(2)–I(2) = 2.712 (2) Å, Ir(1)–P(1) = 2.318 (5) Å, Ir(2)–P(2) = 2.311 (5) Å, Ir (1)–S(1) = 2.383 (5) Å, Ir(1)–S(2) = 2.373 (5) Å, Ir(2)–S(1) = 2.372 (5) Å, Ir(2)–S(2) = 2.391 (5) Å.

Introduction

During our investigations of the reactivity of dinuclear iridium(I) complexes toward alkyl halides we observed the very fast reaction of 1 molar equiv of CH_3I to give appreciable amounts of complexes $Ir_2(\mu\text{-}t\text{-BuS})_2(CO)_2(PR_3)_2I_2$. Such compounds, formulated as iridium(II) species, were of interest to us, and a systematic study of their preparation by direct oxidative addition of iodine was undertaken. An extension of such reactions to the other halogens has been carried out. Such complexes are, in principle, starting materials for the preparation of other such complexes by substitution of the iodide ligands. Moreover, there are very few known dinuclear iridium(II) complexes,[3–10] and since some of them were proposed as intermediates during the oxidative addition of alkyl halides to mononuclear iridium(I) complexes, the relevance to the mechanism of the addition prompted us to study the addition of iodine in more detail.

Experimental Section

Synthetic Work and Spectroscopic Data. The complexes $Ir_2(\mu\text{-}t\text{-BuS})_2(CO)_4$ (**1**) and $Ir_2(\mu\text{-}t\text{-BuS})_2(CO)_2L_2$ where L = P-

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(1) Preliminary communication: Bonnet, J.-J.; Kalck, Ph.; Poilblanc, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 551.

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(3) Moers, F. G.; de Jong, J. A. N.; Beaumont, P. M. H. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1915.

(4) Angoletta, M.; Bellon, P. L.; Manassero, M.; Sansoni, M. *J. Organomet. Chem.* **1974**, *81*, C40.

(5) Mason, R.; Thomas, K. M.; Empsall, H. D.; Fletcher, S. R.; Heys, P. N.; Hyde, E. M.; Jones, C. E.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1974**, 612.

(6) Aranes, A.; Morazzoni, F.; Napoletano, T. *J. Chem. Soc.*, Dalton *Trans.* **1975**, 2039.

(7) Pilloni, G.; Schiavon, G.; Zotti, G.; Zecchin, S. *J. Organomet. Chem.* **1977**, *134*, 305.

(8) Angoletta, M.; Malatesta, L.; Caglio, G. *J. Chem. Soc.*, Dalton *Trans.* **1977**, 2131.

(9) Bonnet, J.-J.; Thorez, A.; Maisonnat, A.; Galy, J.; Poilblanc, R. *J. Am. Chem. Soc.* **1979**, *101*, 5940.

(10) Kalck, Ph.; Bonnet, J.-J.; Poilblanc, R. *J. Am. Chem. Soc.* **1982**, *104*, 3069.

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