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Generation and reactivity of the chiral rhenium chlorobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$: an improved functional equivalent of the chiral Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+BF_4^-$

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Abstract

Reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**) and $HBF_4 \cdot OEt_2$ in C_6H_5Cl at $-45\,^\circ C$ gives the chlorobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (**5**). The rhenium is bound chiefly to chlorine in **5**, but other species, possibly η^2-arene isomers, are apparent by ^{31}P NMR. The relative amounts change upon warming, and new species appear. Complex **5** reacts with neutral donor ligands L (CH_3CN, $C_6H_5CH_2CH{=}CH_2$, THF) to give the corresponding adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+BF_4^-$, halide ions X^- to give halide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$, and $HSi(OEt)_3$ to give hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (74–91%). When **5** is generated from optically active **1**, analogous reactions with L ((−)-(*S*)-2-phenylbutyronitrile, benzaldehyde) give adducts in high optical yields and with overall retention of configuration at rhenium. For example, carboxylate complex (+)-(*RR*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O(C{=}O)CH(OAc)C_6H_5)$ forms in > 99% d.e. upon treatment of **5** derived from (+)-(*S*)-**1** with (−)-(*R*)-$C_6H_5CH(OAc)COOH$ and then base. Thus, **5** serves as a functional equivalent of the chiral Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$—superior in many aspects to the analogous dichloromethane complex reported earlier.

Introduction

Transition metal complexes of weakly coordinating ligands are currently attracting considerable attention as reagents for the coordination and activation of Lewis bases [1–4]. New classes of complexes have been accessed, and general, high-yield routes to previously known classes of complexes have been developed.

We recently reported that the methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**) and $HBF_4 \cdot OEt_2$ react in CH_2Cl_2 at $-78\,^\circ C$ to give the labile dichloromethane

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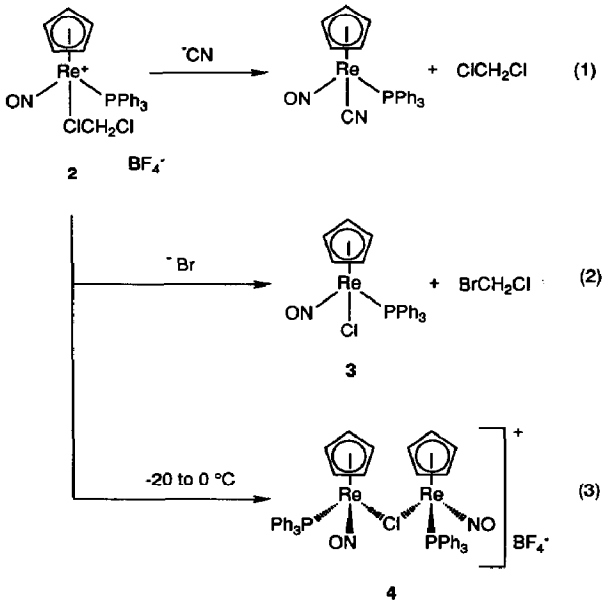


Scheme 1. Representative reactions of dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**2**): (1) substitution at rhenium; (2) substitution at carbon; (3) thermal decomposition.

complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**2**) [4,5]. Complex **2** in turn reacts with a variety of neutral Lewis bases (L) between $-50\,^\circ C$ and $-30\,^\circ C$ to give substitution products $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+BF_4^-$ in high chemical yields. When optically active **1** is utilized, substitution products form with overall retention of configuration at rhenium and in high optical yields [4]. Thus, **2** serves as a functional equivalent of the chiral Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+BF_4^-$ (**I**).

However, several limitations of **2** have become apparent with increasing usage. First, two reactivity modes are observed with anionic Lewis bases, X^-. Some, such as cyanide ion, displace the dichloromethane from rhenium (Scheme 1, eq. 1). Others, such as halide ions, chiefly attack the dichloromethane carbon to give chloride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)$ (**3**) and chloromethanes XCH_2Cl (Scheme 1, eq. 2) [4]. The latter reactivity mode is also found with the analogous alkyl iodide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2R)]^+BF_4^-$, which are easily isolated in pure form [6]. Rate studies show the coordinated alkyl iodides to be $> 10^5$ more reactive than free alkyl iodides at $0\,^\circ C$ [6]. Crabtree has reported similar findings for isolable iridium and ruthenium alkyl iodide complexes [2,7].

Another limitation is that **2** decomposes above $-20\,^\circ C$ to the bridging chloride complex $(SS,RR)\text{-}[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2Cl^+BF_4^-$ (**4**; Scheme 1, eq. 3) [4]. Hence, weaker donor ligands such as alkynes and disubstituted alkenes do not give high yields of substitution products. Interestingly, only the *d,l* diastereomer of **4** forms. Further, when optically active **2** is utilized, **4** is obtained with retention of configuration at rhenium and in high optical yield. Thus, the rate of decomposition of **2** is much faster than the rate of racemization.

We sought to develop a functional equivalent of the Lewis acid **I** that would not be subject to the preceding limitations. In particular, chlorobenzene would be expected to be less susceptible than dichloromethane to the types of carbon–chlo-

rine bond cleavages shown in eqs. 2 and 3 of Scheme 1. We therefore set out to generate the chlorobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (**5**), and evaluate its stability and reactivity. Importantly, the corresponding iodobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(IC_6H_5)]^+BF_4^-$ (**6**) had previously been isolated and characterized [6].

Results

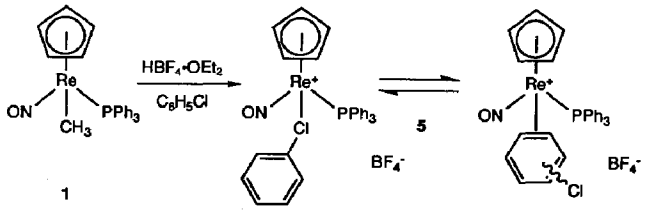
1. Spectroscopically monitored reactions

The methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**) [8] was dissolved in chlorobenzene (melting point $-45.6\,^\circ C$) in a NMR tube. The sample was cooled to $-45\,^\circ C$ (CH_3CN/liquid N_2 slurry) and $HBF_4 \cdot OEt_2$ (1.0 equiv.) was added (Scheme 2). Gas evolution commenced and continued for several minutes. A ^{31}P NMR spectrum was then recorded at $-44\,^\circ C$ (Fig. 1A). Although numerous products were evident, the spectrum was dominated by a resonance at 12.5 ppm (35–40% of integral trace; 20.1 ppm, 10–15%). Ethyl halide complexes, $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(XCH_2CH_3)]^+BF_4^-$, have previously been shown to exhibit a monotonic trend in ^{31}P NMR chemical shifts (ppm, CH_2Cl_2): X = I, 11.8; Br, 12.9; Cl, 13.6 [6]. Iodobenzene complex **6** gives a ^{31}P NMR resonance at 10.2 ppm in CH_2Cl_2 [6] and 11.4 ppm in chlorobenzene. Thus, 12.5 ppm is a plausible chemical shift for the chlorine-ligated form of target complex **5**.

The sample was kept for 2.5 h at $-44\,^\circ C$. Only minor qualitative changes occurred in the spectrum in Fig. 1A. The sample was then warmed in the NMR probe. The 12.5 ppm ^{31}P resonance diminished as resonances at 5.5, 11.0, 15.6, 16.1, and 19.3 ppm appeared and/or intensified (Fig. 1B). These resonances persisted at room temperature (Fig. 1C). Multiple runs were conducted, and the spectra in Fig. 1 were, with minor variations, routinely reproduced.

An analogous experiment was conducted in C_6D_5Cl. A ^1H NMR spectrum ($-45\,^\circ C$) showed a number of cyclopentadienyl resonances between δ 5.0 and 6.0 (δ 5.20, major). No rhenium hydride resonances were observed. The sample was slowly warmed in the NMR probe, and kept at room temperature for 1.5 h. A ^1H NMR spectrum showed many cyclopentadienyl resonances between δ 5.4 and 6.2 (δ 6.22, 5.35, 5.32, major). A $^{13}C\{^1H\}$ NMR spectrum showed principal cyclopentadienyl resonances at 97.2, 92.5, and 91.6 ppm.

An IR spectrum of a $-45\,^\circ C$ sample was taken at room temperature. Two ν(NO) were observed (1695 cm^{-1} vs, 1761 cm^{-1} m). A second spectrum was recorded after 1 h, and was qualitatively similar (1693 cm^{-1} vs, 1765 cm^{-1} m). In other samples, a third ν(NO) was observed (1741 cm^{-1} w). Iodobenzene complex **6** exhibits a ν(CO) at 1688 cm^{-1} (vs) [6].



Scheme 2. Generation of chlorobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (**5**).

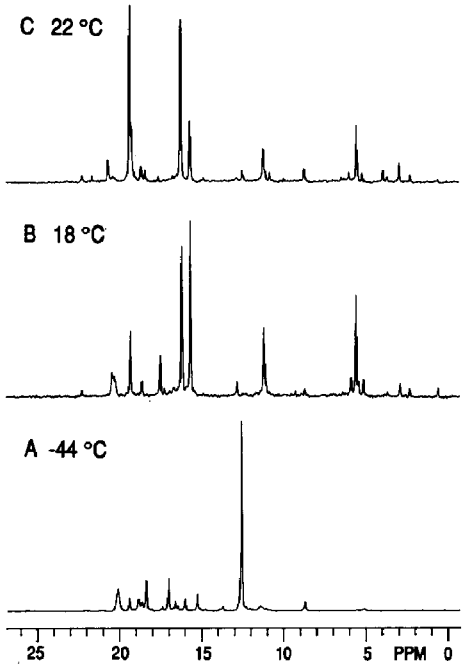


Fig. 1. ^{31}P NMR spectra of the reaction of methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**) and $HBF_4\cdot OEt_2$ in chlorobenzene. A: after mixing at −44 °C. B: after 0.5 h at 18 °C. C: after 3.5 h at 22 °C.

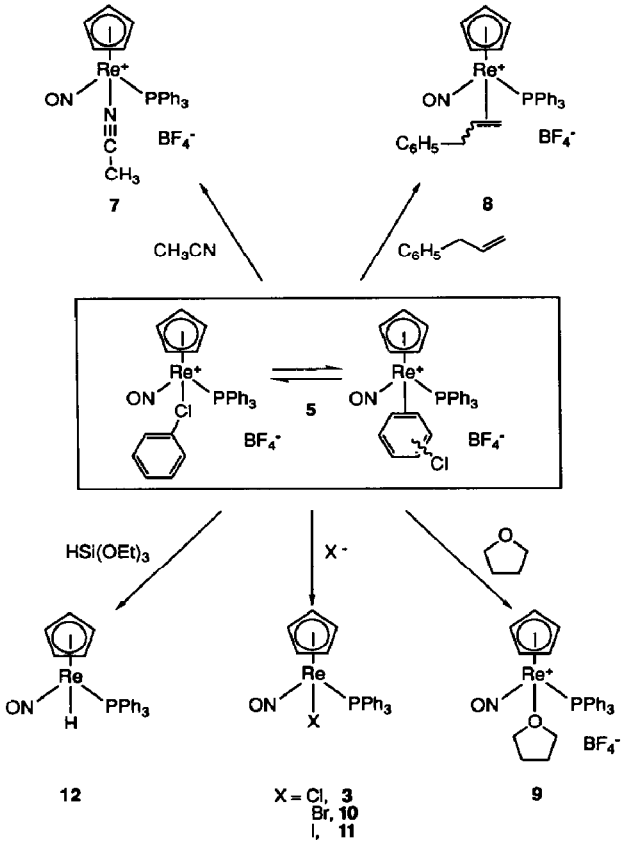
Next, **5** was generated in a NMR tube as above, and acetonitrile (10 equiv.) was added at −44 °C (Scheme 3). The 12.5 and 20.1 ppm ^{31}P NMR resonances were immediately replaced by a 16.1 ppm resonance. This was assigned to the previously characterized acetonitrile complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+BF_4^-$ (**7**) [4]. The other resonances in Fig. 1A also converted to the 16.1 ppm resonance (**7**), but rates were appreciable only when the sample was warmed to 0 °C. Further, the 5.5, 11.0, 15.6, 16.1, and 19.3 ppm resonances noted above (Fig. 1B,C) never intensified beyond their original concentrations in Fig. 1A. A comparable preparative reaction gave **7** in 91% yield after workup.

Addition of acetonitrile to dichloromethane complex **2** also gives **7**. The rate of this reaction has been measured under pseudo-first order conditions at −38.5 °C [4]. The k_{obs} depend upon the acetonitrile concentration. However, under conditions comparable to those employed in Scheme 3, the rate of disappearance of **2** ($t_{1/2}$ 7–20 min) is much slower than that of the 12.5 ppm resonance. Conversely, the rate of disappearance of **2** is much faster than those of the other resonances in Fig. 1A.

Next, a sample of **5** that had been "annealed" at room temperature (Fig. 1C) was cooled to −45 °C and treated with acetonitrile (5 equiv.). The sample was slowly warmed and monitored by ^{31}P NMR. No significant reaction occurred at 0 °C, or soon after warming to 18 °C. The sample was kept at room temperature for 2 h, after which time conversion to **7** was ca. 80% complete.

2. Syntheses of racemic complexes

Preparative reactions of **5** and less reactive neutral donor ligands were attempted next. First, **5** was treated with allylbenzene (4 equiv., −45 °C). The previously



Scheme 3. Substitution reactions of racemic chlorobenzene complex **5**.

characterized allylbenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2\text{-}C_6H_5)]^+BF_4^-$ (**8**, Scheme 3) [9] formed as a $(70 \pm 2):(30 \pm 2)$ mixture of (*RS,SR*)/(*RS,SS*) diastereomers, and was isolated in 82% yield. The diastereomers differ in the alkene enantioface bound to the chiral metal fragment [9].

Complex **5** was similarly treated with excess tetrahydrofuran. Workup gave the tetrahydrofuran complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(THF)]^+BF_4^-$ (**9**, Scheme 3) [10], in 89% yield. In an attempt to clarify the origin of some of the ^{31}P NMR resonances in Fig. 1C, a similar experiment was conducted with ether (5 equiv.). Note that ether (1 equiv.) is also introduced with the acid $HBF_4 \cdot OEt_2$. The room temperature ^{31}P NMR spectrum showed a small amount of a new resonance (17.6 ppm), which closely matched that reported earlier for ether complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)\text{-}(OEt_2)]^+PF_6^-$ [10]. However, varying amounts of the 5.5, 15.6, 16.1, 19.3, and 20.2 ppm resonances of Fig. 1B persisted.

Reactions of **5** and anionic donor ligands were examined next. Accordingly **5** was treated with the halide ion sources PPN^+Cl^- [11*], $Ph_3PEt^+Br^-$, and $Ph_3PMe^+I^-$ (2.0–2.5 equiv.). Subsequently isolated in 82–87% yields were halide complexes [12] $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)$ (**3**), $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Br)$ (**10**), and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**11**) (Scheme 3). In a related series of experiments, methyl

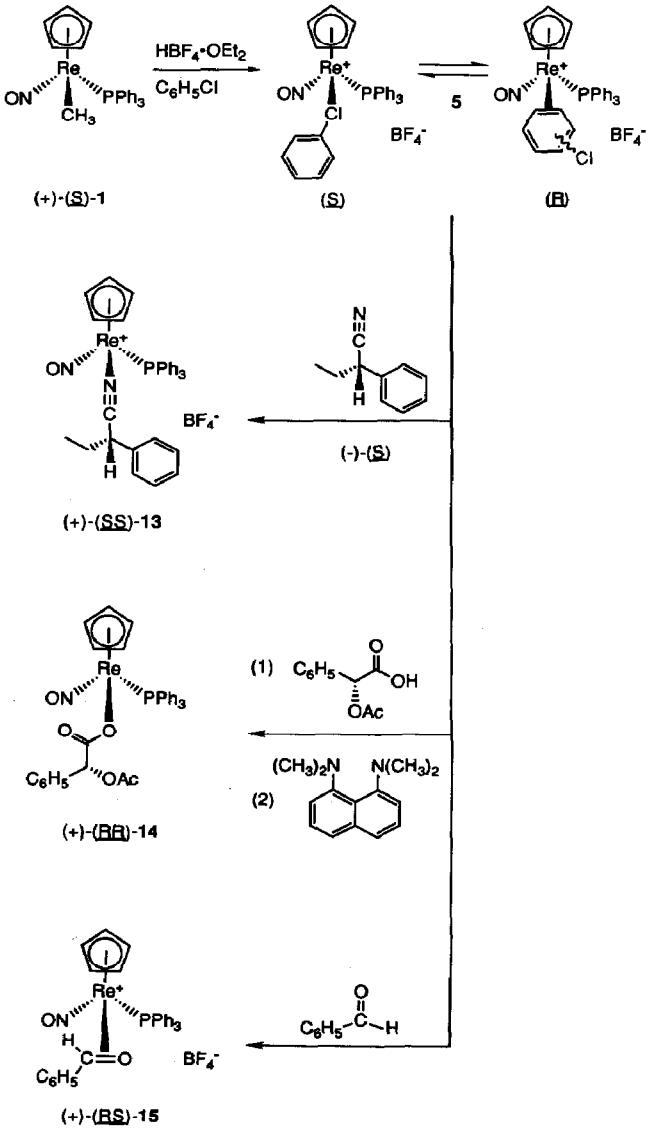
* Reference number with asterisk indicates a note in the list of references.

complex **1** was dissolved in chlorobenzene and treated with aqueous acids HX. Halide complexes **3**, **10**, and **11** were subsequently isolated in 83–85% yields.

A number of attempts have been made to reduce dichloromethane complex **2**, as well as halide complexes **3**, **10**, and **11**, to the hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**12**) [13]. All efforts to date have been unsuccessful. However, reaction of **5** and the hydride donor [14] $HSi(OEt)_3$ (4 equiv.) gave **12** in 74% yield after workup (Scheme 3).

3. Syntheses of optically active complexes

We next sought to generate **5** in optically active form. When the dichloromethane complex **2** is prepared from optically active methyl complex (+)-(*S*)-**1** [15*],



Scheme 4. Generation and substitution reactions of optically active chlorobenzene complex **5**.

subsequent addition of optically active (−)-(*S*)-2-phenylbutyronitrile ((−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$) gives the crystallographically characterized nitrile complex (+)-(*SS*)-[(η^5-C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]$^+BF_4^-$ ((+)-(*SS*)-**13**) [4,16]. This transformation is both diastereospecific and enantiospecific, and occurs with overall retention of configuration at rhenium. When either precursor is not optically pure, a corresponding decrease in the diastereomeric purity of (+)-(*SS*)-**13** is observed.

Accordingly, optically active (+)-(*S*)-**1** [15*] was treated with $HBF_4 \cdot OEt_2$ in chlorobenzene at −45°C. Then (−)-(*S*)-2-phenylbutyronitrile (86% e.e., or 93:7 (*S*)/(*R*)) was added (Scheme 4). Complex (+)-(*SS*)-**13** formed in quantitative yield as a (94 ± 2):(6 ± 2) mixture of (*SS*)/(*SR*) diastereomers (88% d.e., > 99% of theory), as assayed by ^1H and ^{31}P NMR. Workup of a preparative reaction gave (+)-(*SS*)-**13** in 93% yield and 86% d.e. Hence, **5** can serve as the functional equivalent of a chiral, optically active, transition metal Lewis acid.

Additional preparative experiments were conducted with optically active compounds. First, optically active **5** was generated as above and sequentially treated with (−)-(*R*)-*O*-acetylmandelic acid ((−)-(*R*)-$C_6H_5CH(OAc)COOH$, ≥ 99.5% e.e.) and 1,8-bis(dimethylamino)naphthalene. The previously synthesized [17] *O*-acetylmandelate complex (+)-(*RR*)-(η^5-C_5H_5)Re(NO)(PPh_3)(O(C=O)CH(OAc)C_6H_5) ((+)-(*RR*)-**14**) formed in quantitative spectroscopic yield and > 99% d.e., as assayed by ^1H and ^{31}P NMR spectra of the crude product. Workup gave (+)-(*RR*)-**14** in 86% yield and > 99% e.e. The opposite diastereomer has been independently prepared and characterized [17], and is formed in equal amounts when racemic **5** is similarly reacted with racemic or optically active *O*-acetylmandelic acid.

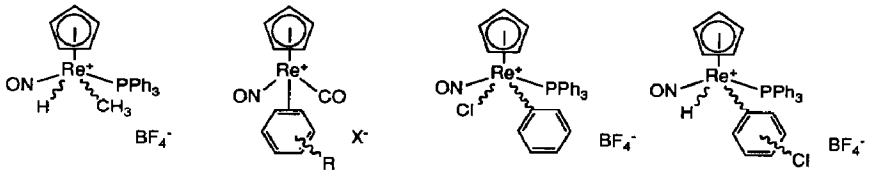
Optically active **5** was next treated with the achiral Lewis base benzaldehyde (5 equiv.). Workup gave the previously reported [17] optically active π-benzaldehyde complex (+)-(*RS*)-[(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-O=CHC_6H_5)]$^+BF_4^-$ ((+)-(*RS*)-**15**$^+BF_4^-$) in 93% yield and > 99% e.e.

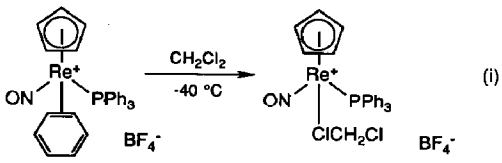
Finally, optically active methyl complex (+)-(*S*)-**1** was dissolved in chlorobenzene and treated with aqueous HI. Workup gave optically active iodide complex (+)-(*R*)-(η^5-C_5H_5)Re(NO)(PPh_3)(I) ((+)-(*R*)-**11**) [12] in 75% yield and > 99% e.e. A parallel experiment was conducted in which (+)-(*S*)-**1** was first converted to optically active **5**, and then treated with iodide salt $Ph_3PMe^+I^-$. Workup gave racemic **11**. Although **11** normally exhibits excellent configurational stability, racemization in the presence of certain reagents has previously been noted [17].

Discussion

The preceding data show that the reaction of methyl complex **1** and $HBF_4 \cdot OEt_2$ in chlorobenzene at −45°C leads to a compositionally inhomogeneous material (**5**) that serves as the functional equivalent of the chiral Lewis acid [(η^5-C_5H_5)Re(NO)-(PPh_3)]$^+$ (**I**). Many of the preparative difficulties associated with the dichloromethane complex **2** are avoided with **5**. Also, **5** duplicates the reactivity profile of **2** —e.g., identical ratios of diastereomeric allylbenzene complexes **8** are obtained in both cases.

Complex **5** is presumed to form via the protonated methyl complex [(η^5-C_5H_5)Re(NO)(PPh_3)(H)(CH_3)]$^+BF_4^-$ (**16**). Complex **16** can be observed in dichloromethane below −85°C [4], but rapidly eliminates methane at higher temperatures





to give dichloromethane complex **2**. Gas evolution occurs rapidly under the conditions of Scheme 2, but the detection of **16** is precluded by the higher freezing point of chlorobenzene (−45.6 °C).

Although the 12.5 ppm ^{31}P NMR resonance in Fig. 1A,B can be confidently attributed to the chlorine-ligated isomer of chlorobenzene complex **5**, it is considerably more difficult to assign the other resonances. Consider first the possibility of the η^2-arene isomers depicted in Schemes 2–4. Binding of **I** to any of the six chlorobenzene C=C bonds affords a distinct diastereomer. This stereochemical situation has previously been analyzed in detail by Graham, who prepared several closely related rhenium monosubstituted η^2-arene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)(\eta^2\text{-}C_6H_5R)]^+X^-$ (**17**) [18].

However, we recently reported the generation of the η^2-benzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}C_6H_6)]^+BF_4^-$ (**18**) in CH_2Cl_2 at −80 °C [19]. Complex **18** exhibits a ^{31}P NMR PPh_3 resonance at 8.1 ppm—considerably upfield from the major unassigned resonances in Fig. 1A, but close to the 5.5 ppm resonance in Fig. 1B. Also, the η^2-benzene ligand exhibits a single ^1H and ^{13}C NMR resonance, evidencing rapid fluxional behavior. Thus, it is not probable that more than one of the ^{31}P NMR resonances in Fig. 1A,B can be attributed to an η^2-arene isomer. Also, the η^2-benzene ligand in **18** is displaced by dichloromethane solvent at −40 °C (eq. i).

Experiments described above show that none of the ^{31}P NMR resonances in Fig. 1A–C can be attributed to the known ether complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OEt_2)]^+BF_4^-$ [10]. Another species that might form would be the μ-tetrafluoroborate complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(FBF_3)$. Independent syntheses of this compound are under investigation. However, present data suggest a ^{31}P NMR chemical shift of 8.1 ppm, and a very rapid displacement of the tetrafluoroborate ligand by dichloromethane solvent at −78 °C [20].

Finally, oxidative addition products such as $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)(C_6H_5)]^+BF_4^-$ (**19**) or $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)(C_6H_4Cl)]^+BF_4^-$ (**20**) might also

form under the conditions of Scheme 2 or upon warming. As exemplified previously [4], such square pyramidal compounds can exist as three diastereomers. For example, the dihydride complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)_2]^+BF_4^-$ exists as a 40 : 60 equilibrium mixture of *cis/trans* isomers at room temperature, with ^{31}P NMR resonances of 19.9 and 11.6 ppm [4]. The benzyl hydride complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)(CH_2C_6H_5)]^+BF_4^-$ is a single isomer with a ^{31}P NMR resonance at 16.5 ppm [4].

Most of the unassigned ^{31}P NMR resonances in Fig. 1A–C are in a region (15–21 ppm) consistent with oxidative addition products. Also, some of the IR ν(NO) in warmed samples of **5** (1741–1765 cm^{-1}) are in a region commonly found for such cationic five-coordinate complexes (1750–1770 cm^{-1}) [4,24]. Further, the pentamethylcyclopentadienyl dichloromethane complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (^{31}P NMR, 16.3 ppm) undergoes carbon–chlorine bond oxidative addition at $-35\,^\circ C$ to give the chloromethyl chloride complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(Cl)(CH_2Cl)]^+BF_4^-$ (^{31}P NMR, 10.1 ppm; IR ν(NO) 1739 cm^{-1}) [2]. However, note that in this case an upfield shift of the PPh_3 resonance is observed.

Regardless of exact composition, all of the species represented in Fig. 1A must be configurationally stable on the time scales of the reactions in Scheme 4. In each case, Lewis base adducts form with overall retention of configuration at rhenium from optically active methyl complex (+)-(*S*)-**1**. The conversion of **1** to dichloromethane complex **2** has previously been shown to proceed with retention of configuration [4]. We therefore assume that the optically active chlorobenzene complex **5** also forms with retention of configuration. Note that the absolute configuration of the chlorine-ligated isomer is opposite to that of any η^2-arene isomer (see Scheme 4) [15].

Although the species that give rise to the resonances in Fig. 1C react much more slowly with Lewis bases, they nonetheless retain chemical integrity as functional equivalents of the Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$. In fact, future reports will describe high-yield reactions with weak donor ligands at temperatures as high as $80\,^\circ C$! [22] We therefore presume that any oxidative additions to chlorobenzene are reversible. Indeed, many examples of reagent or Lewis base-promoted reductive eliminations are known [23].

Several studies of other researchers are particularly relevant to our work. First, Milstein and Osborn have recently described the first catalytic carbonylations and formylations of chlorobenzene [24,25]. Both groups employ palladium catalysts with bulky phosphine ligands, and propose key carbon–chlorine bond oxidative addition steps. Second, Strauss has isolated a number of complexes of silver and saturated chlorocarbons, and reported detailed structural and spectroscopic data [3]. His results indicate that although chlorocarbons have traditionally been considered very weak donor ligands, a rich and characterizable coordination chemistry can be anticipated.

In summary, this study has resulted in a new, easily generated functional equivalent of the chiral transition metal Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$, and provided the first direct evidence for a η^1 transition metal/chlorobenzene binding interaction. Additional reactions of **5** with alkynes [22], ketones [26], cycloalkenes [27], and other donor ligands will be described in the near future.

Experimental section

General data

All reactions were carried out under a dry N_2 atmosphere. FT-IR spectra were recorded on a Mattson Polaris spectrometer. NMR spectra were recorded on Varian XL-300 spectrometers: ^{31}P, referenced to external 85% H_3PO_4; ^1H, referenced to $CDHCl_2$ (δ 5.32) or $(CH_3)_4Si$ (δ 0.00). Optical rotations were measured in $CHCl_3$ (purified by filtration through basic alumina) in thermostated cells on a Perkin Elmer 241 MC polarimeter. Microanalyses were conducted by Atlantic Microlab, Norcross, GA. Melting points were determined in evacuated capillaries and were not corrected.

Solvents and reagents were purified as follows: C_6H_5Cl, distilled from P_2O_5; CH_2Cl_2, distilled from P_2O_5 or CaH_2; THF, ether, hexane, and benzene, distilled from Na/benzophenone; $CDCl_3$, CD_2Cl_2, and C_6D_6, vacuum transferred from CaH_2; $HBF_4 \cdot OEt_2$ (Aldrich), standardized as previously described [1]; C_6D_5Cl (Cambridge Isotopes), allylbenzene, $HSi(OEt)_3$, $Ph_3PEt^+Br^-$, $Ph_3PMe^+I^-$, bis-(1,8-dimethylamino)naphthalene (Aldrich), CH_3CN (spectral reagent grade), PPN^+Cl^- (Strem) [11], HBr, HI, HCl (Mallinckrodt, Fisher, Baker), used without purification; benzaldehyde (Aldrich), fractionally distilled. Optically active (−)-(*R*)- and (+)-(*S*)-*O*-acetylmandelic acids (Aldrich) were used without purification and assayed for optical purity as previously described [17]. Optically active (+)-(*S*)-2-phenylbutyric acid (Aldrich) was similarly assayed for optical purity (86.4 ± 2.7% e.e.), and converted to (−)-(*S*)-2-phenylbutyronitrile ($[\alpha]_{589}^{25}$ −34.5° ± 0.1°, *c* (EtOH) 7.0 mg/ml) by a literature method known to proceed without racemization [28].

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+BF_4^-$ (7)

A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (1; 0.131 g, 0.236 mmol) [8], C_6H_5Cl (3.5 ml), and a stir bar, and was cooled to −45°C (CH_3CN/N_2 bath). Then $HBF_4 \cdot OEt_2$ (0.039 ml, 0.24 mmol) was added with stirring. After 15 min, CH_3CN (0.060 ml, 1.15 mmol, 4.9 equiv.) was added. The resulting solution was stirred at −45°C for 1 h, and then room temperature for 2 h. Some solid precipitated. The mixture was added dropwise to rapidly stirred hexane (30 ml). A tan powder precipitated, which was collected by filtration, washed with pentane (4 × 10 ml), and dried under vacuum at 56°C to give 7 (0.144 g, 0.214 mmol, 91%) [4,29*]. Anal. Calcd for $C_{25}H_{23}BF_4N_2OPRe$: C, 44.72; H, 3.45; N, 4.17. Found: C, 44.44; H, 3.35; N, 4.04.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2C_6H_5)]^+BF_4^-$ (8)

Complex 1 (0.125 g, 0.224 mmol), C_6H_5Cl (2.5 ml), $HBF_4 \cdot OEt_2$ (0.036 ml, 0.224 mmol), and allylbenzene (0.119 ml, 0.896 mmol) were combined in a procedure similar to that given for 7. The resulting solution was stirred at −45°C for 5 min. The cold bath was removed, and the solution was stirred for 13 h. The solvent was removed under oil pump vacuum at room temperature, and the crude residue was analyzed by ^1H NMR ($CDCl_3$; δ 5.44/5.77 (70 ± 2) : (30 ± 2), (*RS,SR*)/(*RR,SS*)-**8**). The residue was dissolved in CH_2Cl_2, and the solution was added dropwise to stirred ether. A tan powder precipitated, which was collected by filtration, washed

with ether, and dried under vacuum at 56 °C to give **8** (0.138 g, 0.184 mmol, 82%) [9,29*].

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(THF)]^+BF_4^-$ (9)

Complex **1** (0.127 g, 0.227 mmol), C_6H_5Cl (5 ml), $HBF_4 \cdot OEt_2$ (0.039 ml, 0.306 mmol) and THF (3 ml) were combined in a procedure similar to that given for **7**. The cold bath was removed, and the mixture was allowed to slowly warm to room temperature. After 2 h, hexane was added. A pink powder precipitated, which was collected by filtration, washed with hexane and dried under vacuum to give **9** (0.142 g, 0.202 mmol, 89%) [10.29*]. Anal. Calcd for $C_{27}H_{28}BF_4NO_2PRe$: C, 46.16; H, 4.02. Found: C, 45.95; H, 3.96.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)$ (3)

A. Complex **1** (0.208 g, 0.372 mmol), C_6H_5Cl (6 ml), $HBF_4 \cdot OEt_2$ (0.048 ml, 0.372 mmol), and solid PPN^+Cl^- (0.533 g, 0.928 mmol) were combined in a procedure similar to that given for **7**. The cold bath was removed, and the mixture was allowed to slowly warm to room temperature. After 1 h, the solvent was removed under oil pump vacuum. The resulting residue was extacted with benzene. The extract was filtered through a fritted-glass funnel containing a 2-cm layer of Celite. The solvent was removed from the filtrate by rotary evaporation. This gave a red-pink powder that was dissolved in CH_2Cl_2 and filtered through a fritted-glass funnel containing a 1-cm layer of silica. The silica was eluted with additional CH_2Cl_2. Solvent was removed from the filtrate by rotary evaporation. The resulting red powder was crystallized from CH_2Cl_2/hexane. Red prisms formed, which were collected by filtration, washed with hexane, and dried under vacuum to give **3** (0.180 g, 0.311 mmol, 84%) [12,29*]. Anal. Calcd for $C_{23}H_{20}ClNOPRe$: C, 47.71; H, 3.48. Found: C, 47.65; H, 3.52.

B. A Schlenk flask was charged with **1** (0.107 g, 0.191 mmol), C_6H_5Cl (15 ml), and a stir bar and was cooled to −45 °C. Then 37% aqueous HCl (0.037 mL, 0.44 mmol) was added. The mixture was stirred for 0.5 h at 0 °C, and 0.5 h at room temperature. The mixture was then filtered through a fritted-glass funnel containing a 1-cm layer of silica. The silica was eluted with chlorobenzene. Solvent was removed from the filtrate under vacuum. The resulting red powder was crystallized as in *A* to give **3** (0.092 g, 0.159 mmol, 83%). Anal. Found: C, 47.65; H, 3.49.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Br)$ (10)

A. Complex **1** (0.160 g, 0.286 mmol), C_6H_5Cl (6 ml), $HBF_4 \cdot OEt_2$ (0.037 ml, 0.286 mmol) and $Ph_3PEt^+Br^-$ (0.212 g, 0.572 mmol) were combined in a procedure similar to *A* for **3**. An identical workup gave red prisms of **10** (0.155 g, 0.249 mmol, 87%) [12,29*]. Anal. Calcd for $C_{23}H_{20}BrNOPRe$: C, 44.31; H, 3.23. Found: C, 44.21; H, 3.24.

B. Complex **1** (0.105 g, 0.190 mmol), C_6H_5Cl (15 ml), and 48% aqueous HBr (0.059 ml, 0.53 mmol) were combined in a procedure similar to *B* for **3**. An identical workup gave red prisms of **10** (0.098 g, 0.157 mmol, 83%). Anal. Found: C, 44.29; H, 3.27.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (11)

A. Complex **1** (0.165 g, 0.295 mmol), C_6H_5Cl (6 ml), $HBF_4 \cdot OEt_2$ (0.038 ml, 0.295 mmol) and $Ph_3PMe^+I^-$ (0.238 g, 0.589 mmol) were combined in a procedure

similar to *A* for **3**. An identical workup gave purple prisms of **11** (0.163 g, 0.243 mmol, 82%) [12,29*]. Anal. Calcd for $C_{23}H_{20}INOPRe$: C, 41.20; H, 3.01; N, 2.09; I, 18.93. Found: C, 41.18; H, 2.96.

B. Complex **1** (0.126 g, 0.225 mmol), C_6H_5Cl (15 ml), and 47% aqueous HI (0.135 ml, 0.744 mmol) were combined in a procedure analogous to *B* for **3**. An identical workup gave purple prisms of **11** (0.128 g, 0.191 mmol, 85%). Anal. Found: C, 41.28; H, 3.07.

C. Complex (+)-(*S*)-**1** (0.200 g, 0.358 mmol), C_6H_5Cl (4 ml), and 47% aqueous HI (0.140 ml, 0.771 mmol) were combined in a procedure analogous to *B*. The mixture was filtered through a plug of silica (ca. 1.5 cm, bottom) and Na_2SO_4 (0.5 cm, top) with aspirator suction. The plug was rinsed with CH_2Cl_2 (ca. 30 ml), and the filtrate was concentrated to 2–4 ml by rotary evaporation. The solution was added dropwise to rapidly stirred hexane (30 ml). A purple powder precipitated, which was collected by filtration, rinsed with hexane and pentane, and dried under vacuum at 56°C to give (+)-(*R*)-**11** (0.216 g, 0.322 mmol, 90%), $[\alpha]_{589}^{25}$ 224° ± 6°, 221° ± 3°. Crystallization from CH_2Cl_2/pentane gave large, dark violet hexagonal plates (ca. 85% recovery), m.p. 230–232°C dec, $[\alpha]_{589}^{25}$ 233° ± 2° (lit [12]: 233°) *c* ($CHCl_3$) 1.29 mg/ml. Anal. Found: C, 41.09; H, 3.05; N, 2.06; I, 18.86.

*Preparation of (η^5-C_5H_5)Re(NO)(PPh_3)(H) (**12**)*

Complex **1** (0.154 g, 0.276 mmol), C_6H_5Cl (5 ml), $HBF_4 \cdot OEt_2$ (0.035 ml, 0.276 mmol), and $HSi(OEt)_3$ (0.2 ml, 1.08 mmol) were combined in a procedure similar to that given for **7**. The mixture was stirred at −45°C for 10 min. The cold bath was removed, and the mixture was slowly allowed to warm to room temperature. After 2 h, the volatiles were removed under vacuum. The residue was dissolved in CH_2Cl_2 and chromatographed on a silica column with 80:20 (v/v) hexane/ethyl acetate. Solvent was removed from a yellow band by rotary evaporation, and the residue was dried under vacuum to give **12** (0.111 g, 0.204 mmol, 74%) that was spectroscopically pure. Crystallization from CH_2Cl_2/hexane gave a yellow microcrystalline solid that was collected by filtration, washed with hexane, and dried under vacuum (0.105 g, 0.193 mmol, 70%) [13,29*].

*Preparation of (+)-(SS)-[(η^5-C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]$^+BF_4^-$ ((+)-(SS)-**13**)*

A. A 5 mm NMR tube was charged with (+)-(*S*)-**1** (0.032 g, 0.058 mmol), C_6D_5Cl (0.6 ml), capped with a septum, and cooled to −45°C. Then $HBF_4 \cdot OEt_2$ (0.009 ml, 0.056 mmol) was added via syringe. After 5 min, (−)-(*S*)-2-phenylbutyronitrile (0.070 ml, 0.470 mmol, 86.4 ± 2.7% e.e) was added. The tube was kept at −45°C for 3 min, and was then allowed to warm to room temperature. A ^{31}P NMR spectrum showed complete conversion to nitrile complexes (+)-(*SS*)-**13** and (+)-(*SR*)-**13** [4,16], which exhibited baseline-resolved resonances (15.5, 15.7 ppm, (94 ± 2):(6 ± 2) area ratio, 88% d.e.). A ^1H NMR spectrum showed (after resolution enhancement) baseline-resolved cyclopentadienyl resonances (δ 5.34, 5.32) in an identical area ratio.

B. Complex (+)-(*S*)-**1** (0.358 g, 0.640 mmol), C_6H_5Cl (7.0 ml), $HBF_4 \cdot OEt_2$ (0.103 ml, 0.643 mmol), and (−)-(*S*)-2-phenylbutyronitrile (0.290 ml, 1.95 mmol, 86.4 ± 2.7% e.e.) were combined in a procedure similar to that given for **7**. The amber solution was stirred for 24 h at room temperature, and then added dropwise

to rapidly stirred hexane (40 ml). A yellow powder precipitated, leaving a colorless supernatant. The powder was collected by filtration, washed with pentane, and dried under vacuum at 56 °C to give (+)-(*SS*)-**13** (0.461 g, 0.595 mmol, 93%), 86% d.e. [4,16,29*]. Anal. Calcd for $C_{33}H_{31}BF_4N_2OPRe$: C, 51.10; H, 4.03; N, 3.61. Found: C, 50.86; H, 4.06; N, 3.59. The powder was chromatographed on silica gel in CH_2Cl_2/acetone (0–10% acetone gradient). This gave (+)-(*SS*)-**13** as a bright yellow-orange microcrystalline powder, 86% d.e.

Preparation of (+)-(RR)-(η^5-C_5H_5)Re(NO)(PPh_3)(O(C=O)CH(OAc)C_6H_5) ((+)-(RR)-14)

Complex (+)-(*S*)-**1** (0.123 g, 0.220 mmol), C_6H_5Cl (2 ml), and $HBF_4 \cdot OEt_2$ were combined in a procedure analogous to that given for **7**. Then a solution of (−)-(*R*)-*O*-acetylmandelic acid (0.115 g, 0.592 mmol, > 99.5% e.e.) in C_6H_5Cl (2 ml) was added. The resulting solution was stirred for 10 min at −45 °C, and then 10 min at room temperature. A solution of bis(1,8-dimethylamino)naphthalene (0.132 g, 0.616 mmol) in C_6H_5Cl (1 ml) was added, and the solution was stirred for 1.5 h at room temperature. Hexane (6 ml) was added to the resulting orange solution. A white powder precipitated (amine salts), and the mixture was filtered through Celite. The Celite was rinsed with benzene and pentane, and volatiles were removed under oil pump vacuum. The resulting crude orange oil-foam was analyzed by ^{1}H NMR (no (+)-(*RS*)- or (−)-(*SR*)-**14** detected) [17], and then flash chromatographed on silica gel (12 g, 17 mm diameter column, 230–400 mesh). A faint yellow band eluted prior to the orange product band. Fractions were concentrated to give (+)-(*RR*)-**14** (0.138 g, 0.188 mmol, 86%) as an orange solid, $[\alpha]_{589}^{25}$ 369° ± 2° (lit [17]: 361° ± 7°), *c* ($CHCl_3$) 1.2 mg/ml [29*].

Preparation of (+)-(RS)-[(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-O=CHC_6H_5)]$^+BF_4^-$ ((+)-(RS)-15$^+BF_4^-$.

Complex (+)-(*S*)-**1** (0.437 g, 0.781 mmol), C_6H_5Cl (5.5 ml), $HBF_4 \cdot OEt_2$ (0.125 ml, 0.781 mmol), and benzaldehyde (0.400 ml, 3.61 mmol) were combined in a procedure analogous to that given for **7**. The cold bath was removed, and the solution was stirred for 5 h. Hexane (5 ml) and then ether (5 ml) were added. A precipitate formed, which was collected by filtration, washed with ether, and dried under vacuum at 56 °C to give (+)-(*RS*)-**15**$^+BF_4^-$ (0.536 g, 0.728 mmol, 93%) as a dull yellow powder, $[\alpha]_{589}^{25}$ 315° ± 2° (lit [17]: 316° ± 3°), *c* ($CHCl_3$) 1.0 mg/ml [29*].

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