ORGANOMETALLICS

Synthesis and reactivity of chiral rhenium amine and amide complexes of the formulas [(.eta.5-C5H5)Re(NO)PPh3)(NHRR')]+TfO- and (.eta.5C5H5)Re(NO)(PPh3)NRR')

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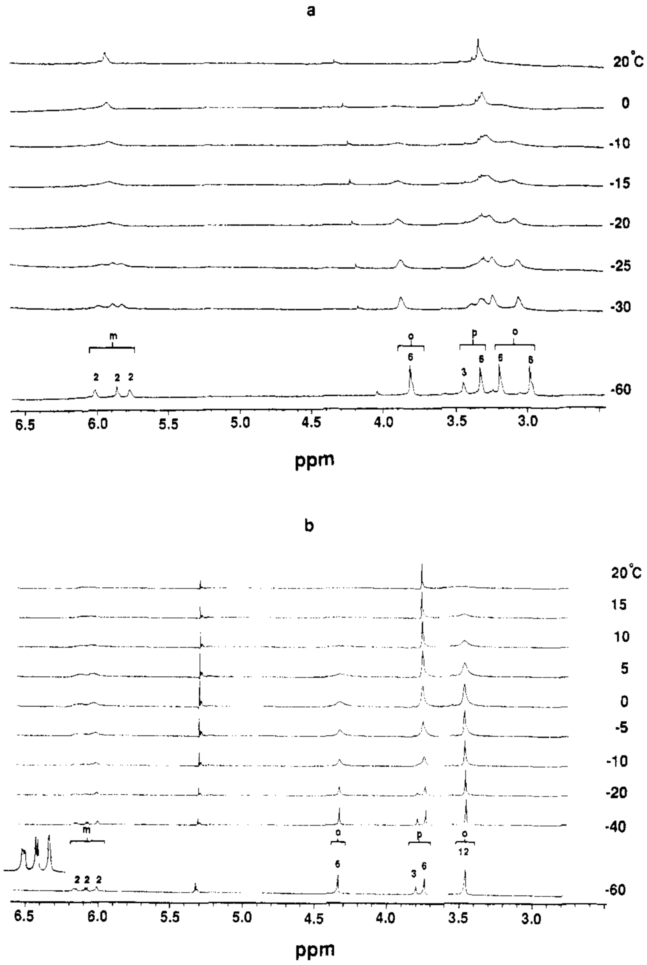

Figure 2. Variable-temperature ^{1}H NMR spectra of Mo$(CO)_3P[C_6(OMe)_3H_2]_3$ in (a) toluene-d_8 (500 MHz) and (b) CD_2Cl_2 (300 MHz; the signal at ~5.3 ppm is due to CD_2Cl_2 solvent impurity and interstitial CH_2Cl_2) (m = meta, o = ortho, p = para).

in Figure 1 shows, $Mo(CO)_3$(TMPP) possesses a distorted-octahedral geometry with two of the coordination sites being occupied by oxygens from *o*-methoxy substituents on two separate phenyl rings. This bonding mode has previously been noted in the structure of $[Rh(TMPP)_2](BF_4)_2$.[1f] The chelation effect provided by weakly interacting pendant methoxy groups accounts for the ease of isolation and moderate stability of 1. The distortion of the coordination geometry about the Mo atom is evidenced most dramatically by the acute angles P(1)-Mo(1)-O of 71.6 (2) and 74.8 (2)° for O(4) and O(9), respectively. These deviations from 90° are a consequence of the formation of the five-membered rings Mo-P-C-C-O. All other angles within the molecule are also nonideal but to a lesser degree (see Figure 1 caption). The high degree of flexibility of the TMPP ligand in achieving the observed bonding mode is apparent from an examination of the disparate Mo(1)-P(1)-C angles; these vary from 104.8 (3)° for C(4), which is involved in a metallacycle, to 120.8 (3)° for C(22) on the lone free ring. Other metric parameters within the molecule are typical for carbonyl-phosphine complexes. The Mo-O distances of 2.363 (6) and 2.337 (7) Å are long, which is to be expected for metal-ether interactions. The Mo-C distances are inequivalent (see Figure 1 caption), with Mo-C(2) distance trans to the phosphorus being the longest (1.97 (1) Å).

The solution properties of $Mo(CO)_3$(TMPP) attest to its high reactivity, as it easily converts to $Mo(CO)_3(NCCH_3)_3$ in acetonitrile and is extremely air-sensitive. The ^{1}H NMR spectrum of 1 revealed that an intramolecular exchange process involving the *o*-methoxy groups is occurring at room temperature. Variable-temperature ^{1}H NMR data were obtained in toluene-d_8 and CD_2Cl_2 over the range +20 to -60 °C, and the results clearly indicate that all three rings are participating in a low-energy fluxional process. The low-temperature limiting spectrum at -60 °C in toluene-d_8 (Figure 2) exhibits eight distinct resonances, which can be integrated in accordance with the magnetically inequivalent meta, ortho, and para groups observed in the solid-state structure.[12] Above -60 °C the spectral features broaden and gradually collapse in a nonsymmetrical manner due to a dynamic exchange of interacting and noninteracting *o*-methoxy groups. Concomitantly the para and meta regions broaden and eventually coalesce at ca. -15 °C. Similar behavior is observed in CD_2Cl_2, although in this solvent the low-temperature limiting spectrum shows only one broad resonance for the noninteracting *o*-methoxy groups at $\delta = +3.49$ ppm.[12] Attempts to obtain spectra at higher temperatures were thwarted by the thermal instability of the complex.

The title complex represents a unique phosphine derivative of molybdenum tricarbonyl. Our future interest in this molecule centers around its reactivity with small molecules. The solution lability of the metal-ether interactions is expected to provide the requisite open coordination sites for binding substrates.

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Supplementary Material Available: Tables of crystallographic parameters, equivalent isotropic displacement parameters, bond distances and angles, and anisotropic thermal parameters (10 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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[12] (a) ^{1}H NMR (δ, toluene-d_8): *m*, 6.01, 5.86, 5.77; *o*, 3.81, 3.19, 2.80; *p*, 3.44, 3.33. (b) ^{1}H NMR (δ, CD_2Cl_2): *m*, 6.15, 6.07, 6.02; *o*, 4.36, 3.49; *p*, 3.82, 3.77.

Synthesis and Reactivity of Chiral Rhenium Amine and Amide Complexes of the Formulas $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NHRR')]^+TfO^-$ and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}RR')$

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Summary: Reactions of racemic and optically active $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ with primary and secondary amines give the amine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NHRR')]^+TfO^-$ with retention of configuration at rhenium. These react with *n*-BuLi to give amide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}RR')$ that contain an unusually basic and nucleophilic nitrogen.

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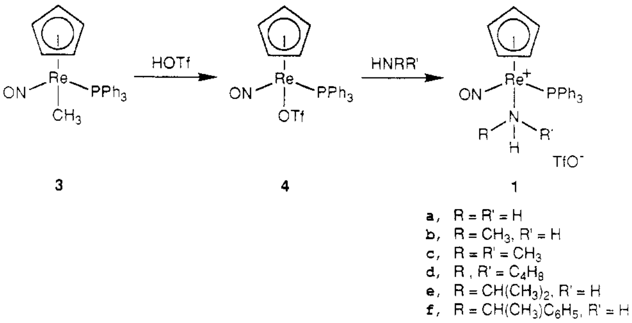
Complexes of the chiral rhenium fragment $[(\eta^5\text{-}C_5H_5)\text{Re}(NO)(PPh_3)]^+$ and unsaturated organic ligands such as alkenes,[2] aldehydes,[3] and ketones[4] exhibit a rich chemistry, including highly stereoselective binding modes and nucleophile additions. We sought to extend these studies to complexes of unsaturated nitrogen-containing ligands such as imines (RR'C=NR'') and aromatic heterocycles. Preliminary work has established the ready availability of both classes of complexes.[5,6] However, reactivity studies have uncovered unexpected properties of derived cationic amine complexes $[(\eta^5\text{-}C_5H_5)\text{Re}(NO)(PPh_3)(NHRR')]^+X^-$ (**1**) and neutral amide complexes $(\eta^5\text{-}C_5H_5)\text{Re}(NO)(PPh_3)(\ddot{N}RR')$ (**2**).[6,7] Thus, we initiated an independent study of these compound types. In this communication, we report efficient syntheses of racemic and optically active primary and secondary amine complexes of the formula **1** ($X^- = TfO^-$ (triflate)) and deprotonations to the highly basic and nucleophilic amide complexes **2**. Additional transformations are described in the following paper.[8]

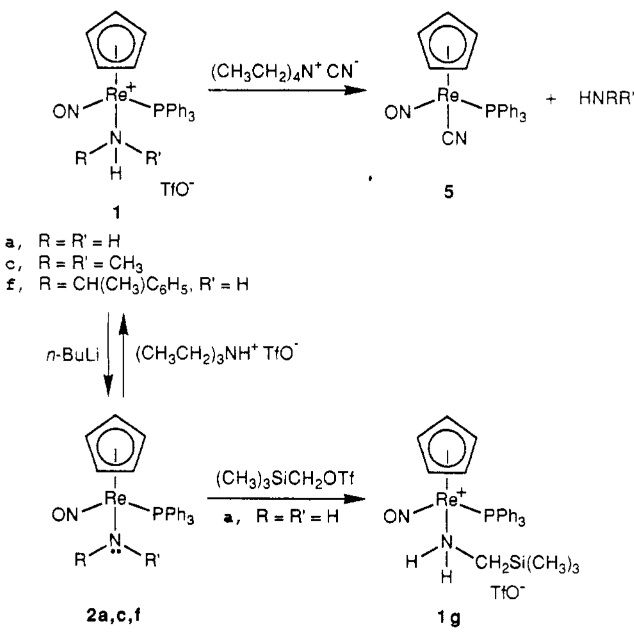
The methyl complex $(\eta^5\text{-}C_5H_5)\text{Re}(NO)(PPh_3)(CH_3)$ (**3**)[9] and TfOH were combined in toluene at −41 °C to give the triflate complex $(\eta^5\text{-}C_5H_5)\text{Re}(NO)(PPh_3)(OTf)$ (**4**).[5,10] Then excesses of (**a**) ammonia, (**b**) methylamine, (**c**) dimethylamine, (**d**) pyrrolidine, (**e**) isopropylamine, and (**f**) α-methylbenzylamine were added (Scheme I). Precipitation occurred, and workup gave the amine complexes $[(\eta^5\text{-}C_5H_5)\text{Re}(NO)(PPh_3)(NHRR')]^+TfO^-$ (**1a–f**) as analytically pure yellow powders in 80–97% yields.

Complexes **1a–f** were characterized by IR and NMR spectroscopy.[11] Features resembled those previously reported for related ether and alcohol complexes $[(\eta^5\text{-}C_5H_5)\text{Re}(NO)(PPh_3)(ROR')]^+X^-$.[12] The α-methylbenzylamine complex **1f** formed as a mixture of Re/C diastereomers (52:48 for a homogeneous reaction in CD_2Cl_2) that differed markedly in their NMR properties (^{1}H NMR C_5H_5 at δ 5.38, 4.89). In all cases, diastereotopic amine substituents exhibited distinct NMR resonances. For example, the NH_2 protons in the primary amine complexes were generally separated by ≥2 ppm.

Scheme I. Synthesis of the Amine Complexes $[(\eta^5\text{-}C_5H_5)\text{Re}(NO)(PPh_3)(NHRR')]^+TfO^-$ (1)



Scheme II. Reactions of Amine Complexes 1 and Amide Complexes 2



Amine complexes **1a–f** were indefinitely stable in solution at room temperature. However, **1c,f** readily reacted with the cyanide salt $(CH_3CH_2)_4N^+CN^-$ (25 °C, CH_2Cl_2; Scheme II). Workup gave the cyanide complex $(\eta^5\text{-}C_5H_5)\text{Re}(NO)(PPh_3)(CN)$ (**5**; 94–86%)[13] and (with **1f**) α-methylbenzylamine (60%, isolated). When $CDCl_3$ solutions of **5** were treated with the chiral NMR shift reagent (+)-Eu(hfc)$_3$ (0.5 equiv), the cyclopentadienyl ^{1}H NMR resonances of the two enantiomers exhibited base-line resolution (Δδ ≃ 0.28 ppm).[14]

We sought to assign configurations to the diastereomers of α-methylbenzylamine complex **1f**. Hence, the synthesis was repeated with the optically active triflate complex (+)-(*S*)-**4**.[10] Reactions with (−)-(*S*)- and (+)-(*R*)-α-methylbenzylamine (95.8% and 97.1% ee)[8] gave (+)-(*SS*)- and (+)-(*SR*)-**1f** (84% and 80% after workup, >98% de), with $[\alpha]^{25}_{589}$ = 374 ± 6° and 395 ± 5°.[15] The absolute configurations, corresponding to retention at rhenium, were assigned by analogy to closely related substitution reactions and the commonly observed correlation with the sign of $[\alpha]_{589}$ for this series of compounds.[2c,10,13] These complexes were configurationally stable for 6 days in CH_2Cl_2.

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(11) Characterization of **1a–g** and **2a,c,f** is given in the supplementary material. Selected data for **1a–g**: IR (cm^{-1}, KBr) 1703–1676; ^{1}H NMR (δ, $CDCl_3$) C_5H_5 5.50–5.38 and 4.89, NH 6.0–3.3; $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$) C_5H_5 92.4–91.1; $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$) 23.1–15.2. Anal. C, H, N. Selected data for **2a,c,f**: IR (cm^{-1}, KBr) 1637–1624; ^{1}H NMR (δ, $CDCl_3$) C_5H_5 5.23–5.04; $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$) C_5H_5 92.6–91.4; $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$) 28.1–19.7.

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(15) In diastereomeric compounds, the rhenium configuration is specified first, by *R*/*S* conventions described previously.[2,3] All [α] are recorded in CH_2Cl_2 in thermostated cells with *c* = 0.5–0.6 mg/mL.

Reactions of (+)-(*SS*)- and (+)-(*SR*)-**1f** with $(CH_3CH_2)_4N^+CN^-$ as above gave the optically active cyanide complex (+)-(*S*)-**5**, with $[\alpha]^{25}_{589} = 183 \pm 3°$.[15] The absolute configuration, corresponding to retention at rhenium, was assigned as above. Importantly, $(+)$-Eu(hfc)$_3$ analysis showed the (+)-(*S*)-**5** to be of >98% ee, thus bounding the optical purities of (+)-(*SS*)- and (+)-(*SR*)-**1f**.

We have previously shown that secondary phosphine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PHRR')]^+X^-$ can be deprotonated to the corresponding phosphido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{P}RR')$.[16] Accordingly, amine complexes **1a,c**, (+)-(*SS*)-**1f**, and (+)-(*SR*)-**1f** were treated with *n*-BuLi (1.0 equiv) in THF at −80 °C (Scheme II). Amide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}RR')$ (**2a,c**, (*SS*)-**2f**, (*SR*)-**2f**) formed in quantitative yields, as assayed by ^{31}P NMR spectroscopy. Solvent evaporation gave spectroscopically pure powders that contained the byproduct LiOTf. Further purification attempts gave decomposition. Amine complex deprotonation could also be effected with freshly sublimed $K^+(t\text{-}BuO^-)$.

Complexes **2a,c,f** were characterized by IR and NMR spectroscopy.[11] The nitrogen substituents in symmetrically substituted **2a,c** generally gave a single set of NMR resonances. However, **2c** exhibited *two* methyl ^1H NMR resonances in CD_2Cl_2/THF-d_8 at −115 °C. These coalesced at −105 °C ($\Delta G^{\ddagger}_{T_c}$ 7.8 kcal/mol). For a *pyramidal* $-\ddot{N}R_2$ moiety, both nitrogen inversion and Re–$\ddot{N}$ bond rotation are required to render the substituents equivalent.[16,17] Hence, 7.8 kcal/mol is an upper limit on any nitrogen inversion barrier. Thus, nitrogen-derived diastereomers of the unsymmetrically substituted complexes **2b,e,f** should not be observable under normal NMR conditions.

Chemical properties of the amide complexes **2** were briefly probed. First, **2a,c** and (*SR*)-**2f** reacted with 1.0 equiv of $(CH_3CH_2)_3NH^+TfO^-$ within 5 min in THF at −80 °C. Amine complexes **1a,c** and (+)-(*SR*)-**1f** formed quantitatively, as assayed by ^{31}P NMR spectroscopy (Scheme II). Hence, the $-\ddot{N}RR'$ nitrogens in **2** are considerably more basic than those in organic amines. Second, **2a** and $(CH_3)_3SiCH_2OTf$ (1.2 equiv) rapidly reacted in THF at −60 °C to give the amine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH_2CH_2Si(CH_3)_3)]^+TfO^-$ (**1g**; 62% after workup; Scheme II). Thus, the $-\ddot{N}RR'$ nitrogens in **2** are also highly nucleophilic.

In summary, this study has established that (1) the title compounds are readily available in both racemic and optically active forms and (2) the chemical properties of both classes of compounds are influenced by the high basicity and nucleophilicity of the amide nitrogen in **2**. Many useful applications of these compounds are readily envisioned (e.g., precursors to imine complexes, chiral LiNRR′ bases, mechanism probes) and will be reported in due course.

Acknowledgment. We thank the NSF for support of this research and the NTNF for a fellowship (J.M.B.).

Supplementary Material Available: Tables of spectroscopic data for **1a–g** and **2a,c,f** and analytical data for **1a–g** (7 pages). Ordering information is given on any current masthead page.

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Mechanism of Equilibration of Diastereomeric Rhenium Amide Complexes of the Formula $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}HCHRR')$: Rhenium vs Carbon Epimerization

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Summary: Amide complexes (*SR*)- and (*SS*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}HCH(CH_3)C_6H_5)$ epimerize at rhenium (32–60 °C) by a mechanism involving initial and rate-determining PPh_3 dissociation. Anchimeric assistance of the amide ligand lone pair and an intermediate with a *planar*, trigonal rhenium are proposed.

In studying the addition of nucleophiles to chiral imine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}RN{=}CHR')]^+X^-$, we found that the products, amide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}RCHR'Nu)$, sometimes underwent epimerization slightly above room temperature.[1] Similar behavior has been noted in the related alkoxide complexes $(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(OCHRR')$.[2] In theory, these epimerizations could occur at rhenium or carbon. Either event would be of considerable interest. For example, while a carbon-based epimerization would complicate the application of these reactions in asymmetric organic synthesis, it would represent an unusual and potentially exploitable type of C–H bond activation. Thus, we sought to probe the mechanisms of these configurational processes.

Accordingly, the diastereomeric optically active amine complexes (+)-(*SR*)- and (+)-(*SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH_2CH(CH_3)C_6H_5)]^+TfO^-$ ((+)-(*SR*)- and (+)-(*SS*)-**1f**, TfO^- = triflate)[3] were converted to the corresponding amide complexes (*SR*)- and (*SS*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}HCH(CH_3)C_6H_5)$ ((*SR*)- and (*SS*)-**2f**), as described in the preceding paper (Scheme I).[4] The solvents were replaced by THF-d_8, and ^1H NMR analyses (C_5H_5 resonances) showed that each amide complex was of >98% de.[5]

Next, a THF-d_8 solution of (*SR*)-**2f** was kept at 60 °C. Epimerization occurred over the course of 2.5 h to give a (30 ± 2):(70 ± 2) mixture of diastereomers, with the *new* diastereomer predominating (see Scheme I). An identical reaction was conducted with (*SS*)-**2f**. Epimerization occurred to give a (70 ± 2):(30 ± 2) mixture of diastereomers, with the *original* diastereomer predominating. These experiments establish that (*SS*)-**2f** is slightly more stable than (*SR*)-**2f** (K_{eq} = 2.3) and that the pyramidal rhenium fragment[6] $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ exhibits a moderate degree of chiral recognition in binding enantiomers of the $-\ddot{N}HCH(CH_3)C_6H_5$ fragment.

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