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Syntheses of cyclic imine complexes of the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ by hydride ion abstraction from amido complexes *

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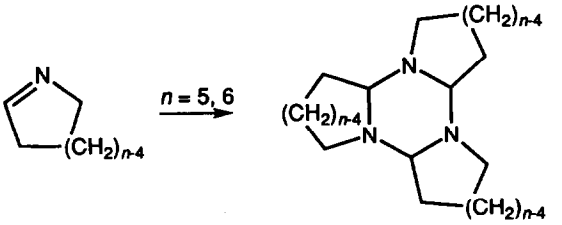
Abstract

Reactions of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ and the cyclic amines $HN\overline{CH_2CH_2CH_2(CH_2)_{n-4}}$ give adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HN\overline{CH_2CH_2CH_2(CH_2)_{n-4}})]^+$ TfO^- (**3a–e**$^+$ TfO^-; n = **a**, 3; **b**, 4; **c**, 5; **d**, 6; **e**, 7) in 98–88% yields. Reactions of **3a–e**$^+$ TfO^- and $^tBuO^-$ K^+ give the labile amido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{NCH_2CH_2CH_2(CH_2)_{n-4}})$ (**4a–e**), which are characterized *in situ* at −20°C. Subsequent reactions of **4b–e** with Ph_3C^+ PF_6^-, and metatheses with NH_4^+ PF_6^-, give the cyclic imine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}\overline{N{=}CHCH_2CH_2(CH_2)_{n-4}})]^+$ PF_6^- (**5b–e**$^+$ PF_6^-). However, **5d,e**$^+$ PF_6^- are difficult or impossible to separate from byproducts (up to 30%). In order to circumvent these and other complications, **3a–e**$^+$ TfO^- and NH_4^+ PF_6^- are first allowed to react to give **3a–e**$^+$ PF_6^- (94–76%). Additions of $^tBuO^-$ K^+ and then Ph_3C^+ PF_6^- give, under carefully optimized conditions, **5b–e**$^+$ PF_6^- of > 98% purities. All attempts to prepare the three-membered cyclic imine complex **5a**$^+$ PF_6^-, and phenyl-substituted analogs, are unsuccessful. The IR and NMR properties of the preceding compounds are analyzed in detail.

Key words: Rhenium; Cyclicimine; Chirality

1. Introduction

The ability of transition metals to stabilize reactive organic compounds has been extensively documented, and has in numerous cases opened up new realms of chemistry. However, there have been few applications in the area of organo-nitrogen molecules. For example, certain cyclic imines rapidly trimerize as shown in eqn. (1) [1,2]. Such compounds can be studied as transient species in the gas phase, and condensed at low temperatures into solutions [1]. Nonetheless, stable metal complexes could potentially lead to valuable applications in organic synthesis. In particular, there is much current interest in the development of auxiliary-based methodologies for the enantioselective functionalization of small and medium-sized nitrogen heterocycles [3,4].



(1)

Several years ago, we began an extensive study of complexes of the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**) and unsaturated nitrogen-containing organic molecules. In initial efforts, we synthesized adducts of **I** and (a) aromatic nitrogen heterocycles, and (b) acyclic imines in both racemic and optically active forms [5,6]. Each class of compounds underwent highly diastereoselective addition reactions [7,8]. Hence, we set out to prepare the corresponding parent cyclic imine complexes, as detailed in the narrative below. Complementary efforts involving more highly unsaturated cyclic imine complexes derived from isoquinoline, pyrrole and indole are described separately [7,9].

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* Dedicated with admiration and respect to Professor Dr. Helmut Werner on the occasion of his 60th birthday.

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2. Results

2.1. Cyclic amine complexes

In earlier work, the triflate complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ (**1**) [10,11*] was shown to react with amines and aromatic nitrogen heterocycles (L) to give adducts of the formulae $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+$ TfO^- [5,12]. Thus, **1** was generated from the methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**2**) and TfOH in toluene at −45°C as previously described. In separate experiments, the three to seven-membered cyclic amines aziridine, azetidine, pyrrolidine, piperidine, and perhydroazepine [11b*] were then added (1.0 equiv; Scheme 1). Workups gave the corresponding adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HNCH_2CH_2CH_2(CH_2)_{n-4}]^+$ TfO^- (**3a–e**$^+$ TfO^-; n = **a**, 3; **b**, 4; **c**, 5; **d**, 6; **e**, 7) in 98–88% yields as analytically pure orange or yellow powders.

Complexes **3a–e**$^+$ TfO^-, and all new compounds isolated below, were characterized by microanalysis and IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy, as summarized in Table 1 and the experimental section. Although the pyrrolidine complex **3c**$^+$ TfO^- was reported earlier [12], data are presented again for comparison purposes. The IR ν_{NO} values (1695–1682 cm^{-1}) were similar to those of acyclic amine complexes of **I** (1698–1676 cm^{-1}) [12]. The PPh_3 ^{31}P NMR chemical shifts (19.2–14.3 ppm) were close to those of acyclic secondary amine complexes of **I** (19.1–15.2 ppm). The NH protons gave broad ^1H NMR resonances at δ 6.9–4.2. Complexes **3a–e**$^+$ TfO^- could be kept as solids in air for six months without detectable decomposition. However, $CDCl_3$ (but not CD_2Cl_2) solutions darkened over the course of several hours. When NMR spectra were subsequently recorded, no new products were apparent.

In order to optimize procedures described below, hexafluorophosphate salts of **3a–e**$^+$ TfO^- were also sought. Thus, excesses of NH_4^+ PF_6^- were added. Complexes **3a–e**$^+$ PF_6^- were subsequently isolated in 94–76% yields. Analytical and spectroscopic data are given in the experimental section. Some ^1H NMR chemical shifts differed slightly from those of **3a–e**$^+$ TfO^- (Table 1). Also, **3d**$^+$ PF_6^- showed several couplings that were not resolved in **3d**$^+$ TfO^-. These effects may be due to dynamic equilibria involving N···H···OTf hydrogen bonding in **3a–e**$^+$ TfO^-. Related triflate salts exhibit similar hydrogen bonding in the solid state [9,12].

2.2. Cyclic amido complexes

We have previously shown that acyclic primary and secondary amine complexes of **I** undergo *N*-deprotonation when treated with ^nBuLi or $^tBuO^-$ K^+ [13]. This generates labile amido complexes, which can be isolated in a few cases. Interestingly, the basicities and nucleophilicities of the nitrogen lone pairs in such compounds are greater than those of model organic amines. Thus, **3a–e**$^+$ TfO^- were treated with $^tBuO^-$ K^+ (1.0–1.6 equiv.) at −100°C in THF or THF-d_8 (Scheme 2). The corresponding cyclic amido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}CH_2CH_2CH_2(CH_2)_{n-4})$ (**4a–e**) formed in quantitative yields, as assayed by ^{31}P NMR at −100 or −80°C [14*].

The amido complexes **4a–e** were characterized *in situ* by IR and NMR (^1H, ^{31}P) spectroscopy, as summarized in the experimental section. Importantly, the byproducts K^+ TfO^- and ^tBuOH were also present, although the latter presumably volatilizes upon solvent removal as described below. The IR ν_{NO} values (1639–1628 cm^{-1}) were similar to those of other amido complexes of **I** [13], but lower than those of **3a–e**$^+$ X^-. The ^1H NMR spectrum of aziridinyl complex **4a** showed a narrow multiplet for the four $ReN(CH_2)_2$ protons (δ 1.35, THF-d_8, −20°C), slightly upfield from the corresponding resonance of free aziridine (δ 1.63, $CDCl_3$). Nitrogen inversion followed by Re–N bond rotation can exchange each pair of *trans* hydrogens. An analogous inversion/rotation sequence occurs with a barrier of only 7.8 kcal/mol in the corresponding dimethyl amido complex [13]. However, since the *cis* hydrogens of **4a** remain inequivalent, there must be a near-degeneracy of chemical shifts in the high temperature limit.

Amido complexes **4a–d** were stable for at least 1 h in THF under nitrogen at 0°C, as assayed by ^{31}P NMR. However, PPh_3 dissociated from perhydroazepinyl complex **4e** above −20°C (−4.6 ppm). A solution of azetidinyl complex **4b** (21.5 ppm) was warmed to room temperature. Small quantities of PPh_3 formed (−4.7 ppm). The sample was then kept at 60°C for 10 min. Small amounts of a new species were detected (15.0 ppm, 8%). However, after 12 h at 60°C, only PPh_3 was present. Complexes **4a,c,d** behaved similarly. Although the rhenium-containing products were not investigated, the dimethylamido complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}(CH_3)_2)$ cleanly extrudes PPh_3 to give the dimeric bridging bis(dimethylamido) complex *cis*-$[(\eta^5\text{-}C_5H_5)Re(NO)(\mu\text{-}N(CH_3)_2)]_2$ [13]. Finally, as a check on structure, the aziridinyl complex **4a** and TfOH were combined at −80°C. Workup gave the aziridine complex **3a**$^+$ TfO^- in 65% yield.

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

2.3. Cyclic imine complexes

The trityl cation, Ph_3C^+, has been frequently utilized to abstract hydride ions from the α positions of ethers [15] and related heteroatomic compounds [16]. Thus, **4a–e** were generated as described above at −100°C, and volatiles were removed under oil pump

TABLE 1. Spectroscopic characterization of new rhenium cyclic amine and imine complexes

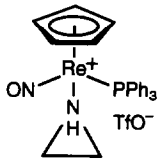
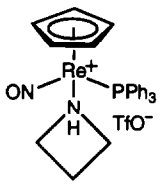
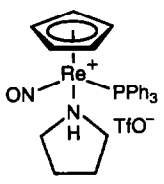
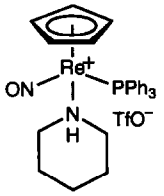
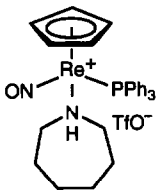
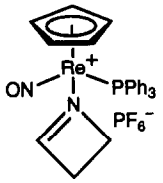
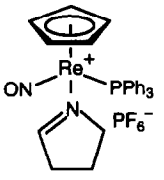
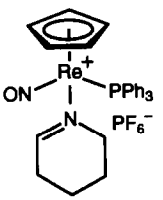
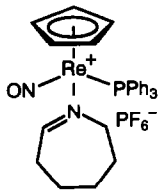
Complex	^{1}H NMR (δ) [a]	^{13}C{^{1}H} NMR (ppm) [b,c]	^{31}P{^{1}H} NMR (ppm) [d] / IR ν_{NO} (cm^{-1}) [e]
 **3a**$^+$ TfO$^-$	7.56–7.49 (m, 9H of 3Ph), 7.48–7.37 (m, 6H of 3Ph), 5.44 (s, C_5H_5), 4.16 (br t, J = 6.0, NH), $N(CH_2)_2$ at 2.82 (apparent q, J = 6.8, 1H), 1.81 (apparent dq, J = 6.3, 0.8, 1H), 1.73 (apparent q, J = 6.1, 1H), 1.51 (apparent q, J = 6.2, 1H). [f]	PPh at 133.7 (d, J = 11.0, *o*), 133.1 (d, J = 55.3, *i*), 131.3 (d, J = 2.5, *p*), 129.1 (d, J = 10.7, *m*); 91.9 (d, J = 1.4, C_5H_5), $N(CH_2)_2$ at 37.7 (d, J = 1.9), 30.2 (s).	15.8 (s) 1683 vs
 **3b**$^+$ TfO$^-$	7.52–7.47 (m, 9H of 3Ph), 7.41–7.33 (m, 6H of 3Ph), 6.88 (br t, J = 7.2, NH), 5.34 (s, C_5H_5), $N(CH_2)_3$ at 4.15–4.04 (m, 1H), 3.89 (apparent quintet, J = 8.9, 1H), 3.39 (apparent quintet, J = 8.9, 1H), 2.83–2.60 (m, 2H), 1.97–1.85 (m, 1H). [f]	PPh at 134.3 (d, J = 54.7, *i*), 133.6 (d, J = 10.9, *o*), 131.3 (d, J = 2.3, *p*), 129.2 (d, J = 10.7, *m*); 91.7 (s, C_5H_5), $N(CH_2)_3$ at 67.8 (s), 59.4 (s), 23.7 (s).	14.3 (s) 1682 vs
 **3c**$^+$ TfO$^-$	7.55–7.49 (m, 9H of 3Ph), 7.37–7.30 (m, 6H of 3Ph), 5.45 (s, C_5H_5), 5.33 (br s, NH), $N(CH_2)_4$ at 3.40–3.28 (m, 1H), 2.96–2.70 (m, 2H), 2.56–2.41 (m, 1H), 1.89–1.42 (m, 4H). [f]	PPh at 134.4 (d, J = 54.3, *i*), 133.6 (d, J = 10.8, *o*), 131.3 (d, J = 2.4, *p*), 129.3 (d, J = 10.6, *m*); 92.2 (s, C_5H_5), $N(CH_2)_4$ at 65.4 (s), 61.6 (d, J = 1.4), 25.5 (s), 25.2 (s).	16.6 (s) 1686 vs
 **3d**$^+$ TfO$^-$	7.59–7.52 (m, 9H of 3Ph), 7.35–7.27 (m, 6H of 3Ph), 5.56 (s, C_5H_5), 4.42 (br t, J = 10.1, NH), $N(CH_2)_5$ at 3.36–3.27 (m, 1H), 3.01–2.71 (m, 1H), 1.68–1.18 (m, 5H), 0.94–0.78 (m, 1H). [f]	PPh at 133.3 (d, J = 10.5, *o*), 132.4 (d, J = 54.2, *i*), 131.7 (d, J = 2.3, *p*), 129.6 (d, J = 10.6, *m*); 92.2 (s, C_5H_5), $N(CH_2)_5$ at 64.7 (s), 61.6 (s), 28.9 (s), 28.3 (s), 21.8 (s).	18.7 (s) 1695 vs
 **3e**$^+$ TfO$^-$	7.61–7.53 (m, 9H of 3Ph), 7.34–7.24 (m, 6H of 3Ph), 5.57 (s, C_5H_5), 4.51 (br s, NH), $N(CH_2)_6$ at 3.56–3.43 (m, 1H), 3.35–3.20 (m, 1H), 3.06–2.90 (m, 1H), 2.81–2.68 (m, 1H), 1.73–1.05 (m, 7H), 0.62–0.44 (m, 1H). [f]	PPh at 132.9 (d, J = 10.7, *o*), 131.9 (d, J = 54.6, *i*), 131.6 (d, J = 2.2, *p*), 129.7 (d, J = 10.7, *m*); 92.3 (s, C_5H_5), $N(CH_2)_6$ at 67.6 (s), 61.1 (s), 30.5 (s), 30.2 (s), 25.5 (s), 24.8 (s).	19.2 (s) 1695 vs

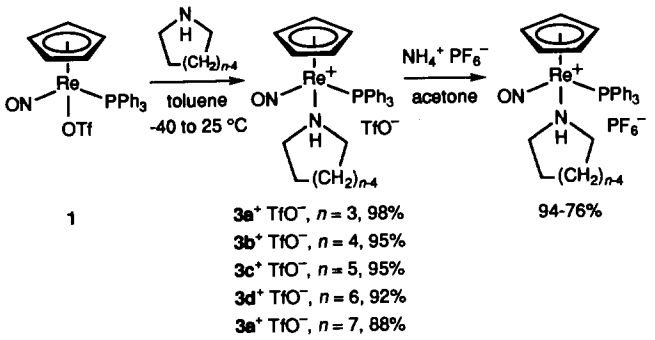
TABLE 1. (*continued*)

Complex	^{1}H NMR (δ) [a]	^{13}C{^{1}H} NMR (ppm) [b,c]	^{31}P{^{1}H} NMR (ppm) [d] IR ν_{NO} (cm^{-1}) [e]
 **5b**$^+$ PF_6^-	7.98 (s, HC=N), 7.56–7.53 (m, 9H of 3Ph), 7.30–7.22 (m, 6H of 3Ph), 5.54 (s, C_5H_5), $N(CH_2)_2$ at 4.01 (ddd, J = 11.4, 4.3, 1.9, 1H), 3.89 (ddd, J = 11.3, 4.2, 2.0, 1H), 3.49 (dm, J = 17.2, 1H), 3.28 (dm, J = 17.2, 1H).	195.8 (d, J = 2.8, C=N), PPh at 133.3 (d, J = 10.9, *o*), 131.7 (d, J = 2.5, *p*), 131.4 (d, J = 55.9, *i*), 129.4 (d, J = 10.9, *m*); 92.0 (s, C_5H_5), $N(CH_2)_2$ at 68.7 (s), 37.9 (s).	16.9 (s) 1691 vs
 **5c**$^+$ PF_6^-	7.56 (t, J = 1.8, HC=N), 7.55–7.49 (m, 9H of 3Ph), 7.28–7.17 (m, 6H of 3Ph), 5.50 (s, C_5H_5), $N(CH_2)_3$ at 3.96–3.74 (m, 2H), 3.13–2.97 (m, 1H), 2.50–2.36 (m, 1H), 1.89–1.75 (m, 1H), 1.69–1.53 (m, 1H).	184.4 (d, J = 2.5, C=N), PPh at 133.3 (d, J = 10.9, *o*), 131.5 (d, J = 2.4, *p*), 131.3 (d, J = 55.3, *i*), 129.3 (d, J = 10.7, *m*); 92.0 (s, C_5H_5), $N(CH_2)_3$ at 72.8 (s), 37.6 (s), 21.3 (s).	18.3 (s) 1686 vs
 **5d**$^+$ PF_6^-	7.84 (br s, HC=N), 7.58–7.50 (m, 9H of 3Ph), 7.29–7.21 (m, 6H of 3Ph), 5.56 (s, C_5H_5), $N(CH_2)_4$ at 3.80–3.56 (m, 2H), 2.92–2.75 (m, 1H), 2.01–1.84 (m, 1H), 1.71–1.32 (m, 4H).	185.1 (d, J = 3.4, C=N), PPh at 133.5 (d, J = 10.7, *o*), 131.4 (d, J = 2.4, *p*), 131.3 (d, J = 55.2, *i*), 129.3 (d, J = 10.7, *m*); 92.2 (s, C_5H_5), $N(CH_2)_4$ at 64.3 (s), 31.4 (s), 23.9 (s), 15.8 (s).	19.6 (s) 1686 vs
 **5e**$^+$ PF_6^-	7.82 (t, J = 5.7, HC=N), 7.62–7.49 (m, 9H of 3Ph), 7.33–7.22 (m, 6H of 3Ph), 5.48 (s, C_5H_5), $N(CH_2)_5$ at 3.88 (apparent quintet, J = 3.1, 2H), 2.30–2.11 (m, 2H), 1.72 (apparent quintet, J = 5.9, 2H), 1.61–1.39 (m, 2H), 1.36–1.22 (m, 2H). [g]	187.2 (d, J = 3.2, C=N), PPh at 133.8 (d, J = 10.6, *o*), 131.9 (br s, *p*), 131.5 (d, J = 56.5, *i*), 129.6 (d, J = 10.7, *m*); 92.6 (s, C_5H_5), $N(CH_2)_5$ at 68.8 (s), 33.7 (s), 30.0 (s), 25.2 (s), 22.3 (s). [g]	18.5 (s) 1691 vs

[a] At 300 MHz in $CDCl_3$ at ambient probe temperature and referenced to internal $SiMe_4$ unless noted; all couplings (J) are in Hz.
[b] At 75 MHz in $CDCl_3$ at ambient probe temperature and referenced to residual $CDCl_3$; all couplings (J) are to ^{31}P and are in Hz. Assignments of resonances to PPh carbons were made as described in W.E. Buhro, S. Georgiou, J.M. Fernández, A.T. Patton, C.E. Strouse and J.A. Gladysz, *Organometallics, 5* (1986) 956.
[c] The triflate anion resonances of **3a–e**$^+$ TfO^- were observed at 120.3–120.7 ppm (q, J_{CF} = 318.2–320.8 Hz).
[d] At 32 MHz in $CDCl_3$ and referenced to external H_3PO_4.
[e] In CH_2Cl_2 (**3a–e**$^+$ TfO^-) or KBr (**5b–e**$^+$ PF_6^-).
[f] NMR data for **3a–e**$^+$ PF_6^- are given in the Experimental section.
[g] In CD_2Cl_2.

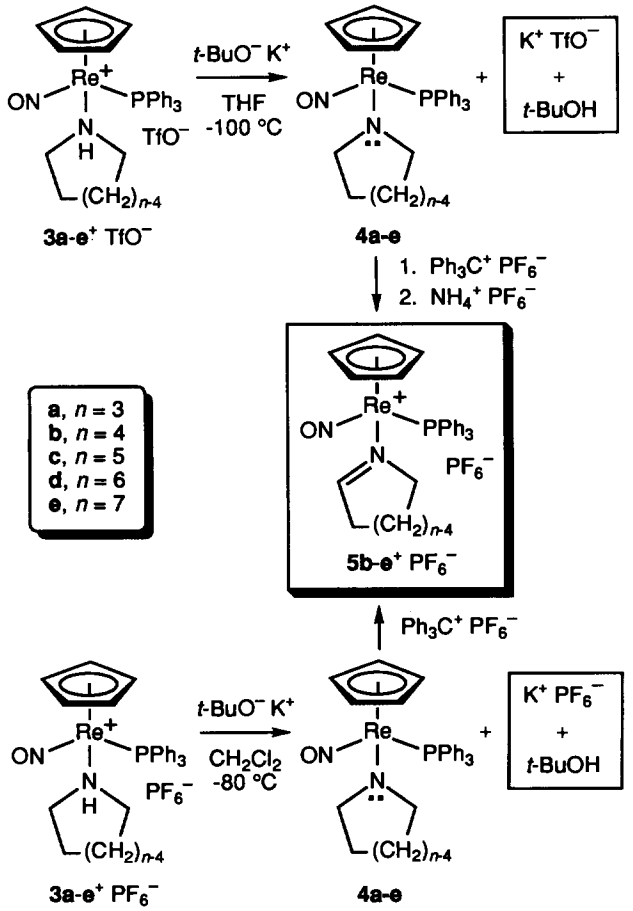
vacuum at 0°C. The residues were cooled to −80°C and dissolved in CH_2Cl_2. Then Ph_3C^+ PF_6^- (1.0 equiv.) was added to each sample (Scheme 2, top).

In the cases of **4b,c**, workups gave the crude four- and five-membered cyclic imine complexes **5b,c**$^+$ X^- in *ca.* 80–90% yields. However, two salts were present, **5b,c**$^+$ TfO^- and **5b,c**$^+$ PF_6^-, as judged by characteristic IR absorptions of the anions. Hence, excesses of NH_4^+



Scheme 1. Preparation of cyclic amine complexes.

PF_6^- were added. Crystalline, analytically pure **5b,c**$^+$ PF_6^- were subsequently isolated in 62–49% yields. Complexes **5b,c**$^+$ PF_6^- were characterized by IR and NMR spectroscopy, as summarized in Table 1. Properties were similar to those of analogous acyclic imine complexes [6]. In particular, downfield HC=N ^1H and ^{13}C NMR resonances were observed at δ 7.98–7.56 (t or br s) and 195.8–184.4 ppm (d, $^3J_{CP}$ = 2.8–2.5 Hz).



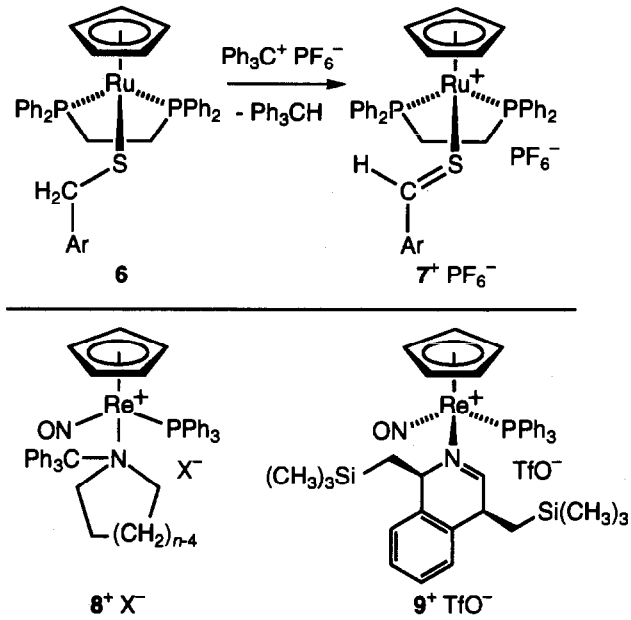
Scheme 2. Preparation of cyclic amido and imine complexes.

In the case of **4d**, it was possible to isolate the six-membered cyclic imine complex **5d**$^+$ PF_6^- in spectroscopically pure form. However, the reproducibility was poor. In particular, the NH_4^+ PF_6^- treatments gave variable amounts of a material that cocrystallized with **5d**$^+$ PF_6^- (acetone/hexane, CH_2Cl_2/heptane). This species could not be detected in the crude product. In the case of **4e**, the crude seven-membered cyclic imine complex **5e**$^+$ X^- reproducibly contained, prior to any NH_4^+ PF_6^- treatments, 25–30% of the precursor amine complex **3e**$^+$ X^- [17*]. Inverse Ph_3C^+ PF_6^- additions, modified reaction stoichiometries, and substitution of the stronger base ^{n}BuLi for ^{t}BuO$^-$ K^+ gave similar results. We were unable to remove the **3e**$^+$ X^-, even after metathesis steps.

In an effort to circumvent these problems, **4a–e** were similarly generated from **3a–e**$^+$ PF_6^- (Scheme 2, bottom), and then treated with Ph_3C^+ PF_6^-. Under these triflate-free conditions, spectroscopically pure **5b, d**$^+$ PF_6^- were easily isolated in 87–65% yields. Crude **5c**$^+$ PF_6^- contained 10% of an unidentified impurity that was readily removed by crystallization. Complex **5e**$^+$ PF_6^- contained 1–2% of **3e**$^+$ PF_6^-, which as above could not be separated by crystallization. Nonetheless, a correct microanalysis was obtained. Importantly, all of these recipes required individual optimization. For example, **5b,c**$^+$ PF_6^- were best prepared utilizing slight (1.3-fold) excesses of Ph_3C^+ PF_6^-, and 20 min reaction times. However, **5d,e**$^+$ PF_6^- required larger (5-fold) excesses of Ph_3C^+ PF_6^-, and 1–6 h reaction times.

Under none of the preceding conditions was any evidence obtained for the generation of significant quantities of the three-membered cyclic imine complex **5a**$^+$ X^-. In all cases, a multitude of products was obtained upon workup. When **4a** (generated from **3a**$^+$ TfO^-) and Ph_3C^+ PF_6^- were combined in CD_2Cl_2 at −80°C in a NMR tube, numerous new ^{31}P and cyclopentadienyl ^1H resonances appeared. A ^1H resonance at δ 7.82 (t, J = 7.3 Hz) was provisionally attributed to traces of **5a**$^+$ X^-. A preparative reaction of **4a** (generated from **3a**$^+$ PF_6^-) and Ph_3C^+ PF_6^- gave a 13:70:17 mixture of **3a**$^+$ PF_6^- and two new products (^{31}P NMR (ppm, CD_2Cl_2): 16.1, 14.6, 14.5 ppm). Downfield ^1H resonances were also associated with the new products (δ, major/minor: 6.33/6.15, d/d, J = 8/8 Hz).

We thought that a phenyl C=N substituent might stabilize three-membered cyclic imine complexes. Thus, a 2-phenylaziridine complex of **I** was prepared in crude form. A ^{31}P NMR spectrum suggested a 72:28 mixture (16.7, 15.5 ppm) of Re,C or Re,N configurational diastereomers. Subsequent reaction with ^{t}BuO$^-$ K^+ gave a single amido complex resonance (19.7 ppm), but



Scheme 3. Other relevant compounds and reactions.

addition of Ph_3C^+ PF_6^- gave a mixture of products that we were unable to purify. Finally, the free imine 3-phenyl-2*H*-azirine was prepared. However, reaction with the triflate complex **1** under conditions analogous to those used for **3a–e**$^+$ TfO^- in Scheme 1 gave a purple powder with seven ^{31}P NMR resonances between 20 and 16 ppm. Similar results were obtained with the chlorobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+$ BF_4^-, which is another functional equivalent of **I** [18].

3. Discussion

As summarized in Scheme 2, four to seven-membered cyclic imine complexes of the chiral rhenium Lewis acid **I** are readily accessed via hydride ion abstraction from the corresponding amido complexes. To our knowledge, these constitute the first such syntheses of imine complexes. However, Schenk has previously shown that Ph_3C^+ PF_6^- can abstract hydride from ruthenium thiolate complexes to give the corresponding σ thioaldehyde complexes, as illustrated for **6** and **7**$^+$ PF_6^- in Scheme 3 [16a]. Furthermore, Ph_3C^+ X^- has been demonstrated to abstract hydride from organic amines [16b,c]. In unpublished work, we have found that alkoxide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OR)$ give mixtures of hydride and alkoxide abstraction products upon reactions with Ph_3C^+ X^-.

We have previously employed Ph_3C^+ X^- to abstract hydride from the α and β positions of alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R)$ [19]. In these cases, excellent evidence has been acquired for an initial electron transfer step [20] – a plausible event in Scheme 2 as well. We have also observed the addition of Ph_3C^+ X^- to C_β and C_γ of nucleophilic vinyl and allyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CHR)$ and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH{=}CHR)$, giving cationic products with new carbon–carbon bonds [21]. Thus, Ph_3C^+ X^- might add to the nitrogen lone pairs of **4b–e**, affording amine complexes as exemplified by **8**$^+$ X^- in Scheme 3. Such adducts could undergo subsequent 1,2 elimination of Ph_3CH to give **5b–e**$^+$ X^-. Alternatively, they might form reversibly and be non-productive with regard to HC=N bond formation.

As detailed above, byproducts are obtained under some reaction conditions. At the outset of this study, we were particularly concerned about the possibility of abstraction of the N=CHCH_2 protons of **5b–e**$^+$ X^- by the basic amido complex precursors **4b–e**. Similar deprotonations have been observed with functionalized cyclic imine complexes of **I** [22], and analogous reactions of **5b–e**$^+$ X^- are presently under investigation [23]. Although this may be the origin of some of the amine complex byproducts, we were unable to identify any deprotonation products in the crude reaction mixtures. We were also unable to prepare three-membered cyclic imine (2*H*-azirine) complexes of **I**, either by hydride abstraction from **4a** or from free 2*H*-azirines. Reactions of 2*H*-azirines with transition metal electrophiles often give ring-opened products [24]. As would be expected from hybridization considerations, the basicity of 2*H*-azirine is much lower than that of other cyclic imines [1,25]. However, metal 2*H*-azirine complexes have been isolated [26].

In complementary, independent efforts, we have also synthesized functionalized six-membered cyclic imine complexes derived from sequential nucleophilic and electrophilic additions to isoquinoline, as exemplified by **9**$^+$ TfO^- in Scheme 3 [7,22]. The crystal structures of **9**$^+$ TfO^- and a diastereomer have been determined [7,22]. Similarly, more highly unsaturated and functionalized derivatives of **5c**$^+$ X^- have been generated by electrophilic additions to N-pyrrolyl and N-indolyl complexes of **I** [9].

Although suitably substituted five and six-membered cyclic imines are stable [27], the availability of **5c,d**$^+$ PF_6^- should facilitate the development of the chemistry of the parent ring system. Furthermore, the triflate complex **1** is easily obtained in enantiomerically pure form [10], and has been converted to a variety of amine and imine complexes with retention of configuration at rhenium [5–7,12]. Thus, it should be possible to extend the preceding methodology to the synthesis of non-racemic **5b–e**$^+$ PF_6^-. In this context, reactions of **5b–e**$^+$ PF_6^- and nucleophiles are under investigation and will be described in future reports [23].

4. Experimental details

4.1. General data

General procedures were identical with those in a previous paper [6]. NMR spectra were recorded on Varian instruments as outlined in Table 1. Reagents were obtained as follows: aziridine and 3-phenyl-2*H*-azirine, prepared by published methods [28,29]; azetidine, $^tBuO^-$ K^+ (Fluka), pyrrolidine, piperidine, perhydroazepine, NH_4^+ PF_6^-, 1.0 M $^tBuO^-$ K^+ in THF, TfOH (Aldrich) [11*], used as received; Ph_3C^+ PF_6^- (Aldrich), crystallized from CH_2Cl_2/hexane.

4.2. $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HNCH_2CH_2)]^+$ X^- (**3a**$^+$ X^-)

(a) A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**2** [30], 3.160 g, 5.657 mmol), toluene (80 mL), and a stir bar and cooled to −45°C (CH_3CN/CO_2). Then TfOH (0.501 mL, 5.66 mmol) was added dropwise with stirring to generate $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ (**1**) [10]. After 5 min, aziridine (0.244 g, 5.66 mmol) was added and the cold bath was removed. Over the course of 15 min, the solution clouded. After another 45 min, hexane (140 mL) was added with stirring. The resulting yellow-brown powder was collected by filtration, washed with hexane, and dried under oil pump vacuum to give **3a**$^+$ TfO^- (4.079 g, 5.544 mmol, 98%), mp 201–203°C dec. Anal. Calcd for $C_{26}H_{25}F_3N_2O_4PReS$: C, 42.45; H, 3.42. Found: C, 42.30; H, 3.38.

(b) A round bottom flask was charged with **3a**$^+$ TfO^- (1.171 g, 1.592 mmol), NH_4^+ PF_6^- (0.433 g, 2.66 mmol), acetone (50 mL), and a stir bar, and was capped with a septum. The mixture was stirred for 5 min. The solvent was removed by rotary evaporation, and the residue was triturated with CH_2Cl_2 (50 mL). The mixture was filtered through silica gel, which was eluted with additional CH_2Cl_2 (250 mL). Heptane (50 mL) was added to the eluant, which was concentrated by rotary evaporation. The resulting orange powder was collected by filtration. An IR spectrum showed **3a**$^+$ PF_6^- (ν_{PF} 843 cm^{-1}), but no diagnostic bands of **3a**$^+$ TfO^- (1275, 1031, 637 cm^{-1}). The silica gel, which retained **3a**$^+$ TfO^-, was eluted with acetone (50 mL). The eluant was treated with NH_4^+ PF_6^-, and two more crops of **3a**$^+$ PF_6^- were similarly collected and then combined (0.885 g, 1.21 mmol, 76%), mp 216–218°C dec. IR (cm^{-1}, KBr) 1678 vs, 843 vs, ^1H NMR (δ, CD_2Cl_2) 7.58–7.49 (m, 9H of 3Ph), 7.41–7.34 (m, 6H of 3Ph), 5.42 (s, C_5H_5), 2.92–2.84 (m, 1H), 2.69 (br s, NH), 2.05–1.97 (m, 1H), 1.89–1.80 (m, 2H). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2) 16.1 (s). A sample was dissolved in CH_2Cl_2, and a layer of hexane was gently added. Orange needles formed, which were collected by filtration and dried under oil pump vacuum. Anal. Calcd for $C_{25}H_{25}F_6N_2OP_2Re$: C, 41.04; H, 3.44. Found: C, 40.96; H, 3.41.

4.3. $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HNCH_2(CH_2)_2)]^+$ X^- (**3b**$^+$ X^-)

(a) Complex **2** (1.676 g, 3.000 mmol), toluene (60 mL), TfOH (0.265 mL, 3.00 mmol), and azetidine (0.203 mL, 3.00 mmol) were combined in a procedure analogous to that given for **3a**$^+$ TfO^-. A similar workup gave **3b**$^+$ TfO^- as a bright yellow powder (2.141 g, 2.856 mmol, 95%), mp 196–198°C dec. Anal. Calcd for $C_{27}H_{27}F_3N_2O_4PReS$: C, 43.25; H, 3.63. Found: C, 43.10; H, 3.61.

(b) Complex **3b**$^+$ TfO^- (1.359 g, 1.812 mmol), NH_4^+ PF_6^- (0.493 g, 3.02 mmol), and acetone (50 mL) were combined in a procedure analogous to that given for **3a**$^+$ PF_6^-. A similar workup gave **3b**$^+$ PF_6^- as an orange powder (1.269 g, 1.702 mmol, 94%), mp 222–224°C dec. IR (cm^{-1}, KBr) 1687 vs, 841 vs. ^1H NMR (δ, CD_2Cl_2) 7.55–7.49 (m, 9H of 3Ph), 7.37–7.29 (m, 6H of 3Ph), 5.54 (br s, NH), 5.35 (s, C_5H_5), 4.04–3.94 (m, 1H), 3.87 (apparent quintet, $J = 9.2$, 1H), 3.60 (apparent quintet, $J = 9.3$, 1H), 3.04–2.92 (m, 1H), 2.68–2.52 (m, 1H), 2.06–1.94 (m, 1H). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2) 14.6 (s). A sample was dissolved in CH_2Cl_2, and a layer of hexane was gently added. Orange prisms formed, which were collected by filtration and dried under oil pump vacuum. Anal. Calcd for $C_{26}H_{27}F_6N_2OP_2Re$: C, 41.88; H, 3.65. Found: C, 41.62; H, 3.60.

4.4. $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HNCH_2(CH_2)_3)]^+$ X^- (**3c**$^+$ X^-)

(a) Complex **2** (1.927 g, 3.450 mmol), toluene (80 mL), TfOH (0.305 mL, 3.45 mmol), and pyrrolidine (0.288 mL, 3.45 mmol) were combined in a procedure analogous to that given for **3a**$^+$ TfO^-. A similar workup gave previously reported **3c**$^+$ TfO^- [12] as a yellow-brown powder (2.503 g, 3.277 mmol, 95%), mp 219–220°C dec.

(b) Complex **3c**$^+$ TfO^- (0.771 g, 1.01 mmol), NH_4^+ PF_6^- (0.329 g, 2.02 mmol), and acetone (50 mL) were combined in a procedure analogous to that given for **3a**$^+$ PF_6^-. A similar workup gave **3c**$^+$ PF_6^- as an orange powder (0.654 g, 0.860 mmol, 85%), mp 240–241°C dec. IR (cm^{-1}, KBr) 1688 vs, 839 vs. ^1H NMR (δ, CD_2Cl_2) 7.59–7.54 (m, 9H of 3Ph), 7.34–7.26 (m, 6H of 3Ph), 5.47 (s, C_5H_5), 4.09 (br s, NH), 3.35–3.26 (m, 1H), 2.99–2.73 (m, 2H), 2.50–2.36 (m, 1H), 1.81–1.67 (m, 2H), 1.54–1.27 (m, 2H). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2) 18.6 (s). Anal. Calcd for $C_{27}H_{29}F_6N_2OP_2Re$: C, 42.69; H, 3.85. Found: C, 42.76; H, 3.85.

*4.5. $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HN\overline{CH_2(CH_2)_4})]^+ X^-$ (**3d**$^+$ X^-)*

(a) Complex **2** (1.865 g, 3.339 mmol), toluene (80 mL), TfOH (0.295 mL, 3.34 mmol), and piperidine (0.330 mL, 3.34 mmol) were combined in a procedure analogous to that given for **3a**$^+$ TfO^-. A similar workup gave **3d**$^+$ TfO^- as a yellow-brown powder (2.398 g, 3.086 mmol, 92%), mp 222–223°C dec. Anal. Calcd for $C_{29}H_{32}F_3N_2O_4PReS$: C, 44.78; H, 4.15; N, 3.60. Found: C, 44.86; H, 4.11; N, 3.60.

(b) Complex **3d**$^+$ TfO^- (0.937 g, 1.21 mmol), NH_4^+ PF_6^- (0.393 g, 2.41 mmol), and acetone (50 mL) were combined in a procedure analogous to that given for **3a**$^+$ PF_6^-. A similar workup gave **3d**$^+$ PF_6^- as an orange powder (0.879 g, 1.14 mmol, 94%), mp 211–213°C dec. IR (cm^{-1}, KBr) 1691 vs, 840 vs. ^1H NMR (δ, CD_2Cl_2) 7.63–7.55 (m, 9H of 3Ph), 7.34–7.25 (m, 6H of 3Ph), 5.53 (s, C_5H_5), 3.93 (br t, $J = 10.7$, NH), 3.55 (dt, $J = 13.0$, 1.8, 1H), 2.94 (ddd, $J = 24.7$, 12.7, 2.6, 1H), 2.71 (br d, $J = 13.0$, 1H), 2.44 (ddd, $J = 24.7$, 12.7, 2.6, 1H), 1.60–1.10 (m, 6H). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2) 20.1 (s). Anal. Calcd for $C_{28}H_{31}F_6N_2OP_2Re$: C, 43.47; H, 4.04. Found: C, 43.27; H, 4.05.

*4.6. $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HN\overline{CH_2(CH_2)_5})]^+ X^-$ (**3e**$^+$ X^-)*

(a) Complex **2** (1.390 g, 2.488 mmol), toluene (50 mL), TfOH (0.220 mL, 2.49 mmol), and perhydroazepine (0.280 mL, 2.49 mmol) were combined in a procedure analogous to that given for **3a**$^+$ TfO^-. A similar workup gave **3e**$^+$ TfO^- as an orange powder (1.737 g, 2.194 mmol, 88%), mp 201–202°C dec. Anal. Calcd for $C_{30}H_{33}F_3N_2O_4PReS$: C, 45.51; H, 4.20. Found: C, 45.44; H, 4.21.

(b) Complex **3e**$^+$ TfO^- (1.298 g, 1.640 mmol), NH_4^+ PF_6^- (0.535 g, 3.28 mmol), and acetone (50 mL) were combined in a procedure analogous to that given for **3a**$^+$ PF_6^-. A similar workup gave **3e**$^+$ PF_6^- as an orange powder (1.162 g, 1.476 mmol, 90%), mp 116–117°C dec. IR (cm^{-1}, KBr) 1691 vs, 840 vs. ^1H NMR (δ, CD_2Cl_2) 7.62–7.57 (m, 9H of 3Ph), 7.33–7.25 (m, 6H of 3Ph), 5.49 (s, C_5H_5), 4.38 (br s, NH), 3.67–3.57 (m, 1H), 3.28–3.15 (m, 1H), 2.77–2.52 (m, 2H), 1.75–1.08 (m, 7H), 0.44–0.35 (m, 1H). $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2) 133.4 (d, $J = 10.8$, *o*-Ph), 132.2 (d, $J = 2.1$, *p*-Ph), 132.0 (d, $J = 55.1$, *i*-Ph), 130.2 (d, $J = 10.6$, *m*-Ph), 92.5 (s, C_5H_5), 68.6 (s), 61.2 (s), 31.2 (s), 31.0 (s), 26.1 (s), 25.1 (s). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2) 19.3 (s). Anal. Calcd for $C_{29}H_{33}F_6N_2OP_2Re$: C, 44.22; H, 4.22. Found: C, 44.02; H, 4.26.

*4.7. $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{NCH_2CH_2})$ (**4a**)*

An NMR tube was charged with **3a**$^+$ TfO^- (0.009 g, 0.012 mmol) and $^tBuO^-$ K^+ (0.0021 g, 0.019 mmol) and was evacuated. The lower half of the tube was immersed in liquid N_2, and THF-d_8 (*ca.* 0.6 mL) added by vacuum transfer. The sample was gradually warmed to *ca.* −80°C, and transferred to a −80°C NMR probe, which was gradually warmed. NMR (THF-d_8, −20°C): ^1H (δ) 7.58–7.51 (m, 6H of 3Ph), 7.46–7.37 (m, 9H of 3Ph), 5.24 (s, C_5H_5), 1.35 (narrow m, $N(CH_2)_2$); $^{31}P\{^1H\}$ (ppm) 19.0 (s). IR (cm^{-1}, THF) ν_{NO} 1639 vs [31*].

*4.8. $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{NCH_2(CH_2)_2})$ (**4b**)*

Complex **3b**$^+$ TfO^- (0.010 g, 0.014 mmol) and $^tBuO^-$ K^+ (0.0023 g, 0.021 mmol) were combined in a procedure analogous to that given for **4a**. NMR (THF-d_8, −20°C): ^1H (δ) 7.53–7.46 (m, 6H of 3Ph), 7.43–7.39 (m, 9H of 3Ph), 5.23 (s, C_5H_5), 3.54 (apparent q, $J = 6.7$, 2H), 3.47 (apparent q, $J = 6.6$, 2H), 2.04 (apparent quintet, $J = 6.7$, 2H); $^{31}P\{^1H\}$ (ppm) 21.0 (s). IR (cm^{-1}, THF) ν_{NO} 1640 vs [31*].

*4.9. $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{NCH_2(CH_2)_3})$ (**4c**)*

This complex was generated as previously described [13].

*4.10. $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{NCH_2(CH_2)_4})$ (**4d**)*

Complex **3d**$^+$ TfO^- (0.015 g, 0.020 mmol), THF (3 mL), and $^tBuO^-$ K^+ (0.020 mL, 0.020 mmol, 1.0 M in THF) were combined in a procedure analogous to that given for **4c**. NMR (THF-d_8, −20°C): ^1H (δ) 7.60–7.24 (m, 3Ph), 5.13 (s, C_5H_5), 2.93–2.68 (m, 4H), 1.51–1.00 (m, 6H); $^{31}P\{^1H\}$ (ppm) 19.7 (s). IR (cm^{-1}, THF) ν_{NO} 1635 vs [31*].

*4.11. $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{NCH_2(CH_2)_5})$ (**4e**)*

Complex **3e**$^+$ TfO^- (0.011 g, 0.013 mmol), THF (3 mL), and $^tBuO^-$ K^+ (0.013 mL, 0.013 mmol, 1.0 M in THF) were combined in a procedure analogous to that given for **4c**. NMR (THF-d_8, −20°C): ^1H (δ) 7.52–7.20 (m, 3Ph), 5.19 (s, C_5H_5), 3.24–3.05 (m, 4H), 1.71–1.06 (m, 8H); $^{31}P\{^1H\}$ (ppm) 19.3 (s): IR (cm^{-1}, THF) ν_{NO} 1628 vs [31*].

*4.12. Reaction of **4a** and TfOH*

A Schlenk flask was charged with **3a**$^+$ TfO^- (0.271 g, 0.368 mmol) and THF (50 mL). An IR spectrum of the suspension was recorded (ν_{NO} 1684 cm^{-1}). The flask was cooled to −80°C (acetone/CO_2), and $^tBuO^-$ K^+ was added (0.368 mL, 0.368 mmol, 1.0 M in THF) to generate **4a**. After 5 min, an IR spectrum of the wine red solution was recorded (1633 cm^{-1}). Then TfOH was added (0.33 mL, 0.37 mmol). An IR spectrum of the yellow-brown solution was recorded (1683 cm^{-1}). Solvent was removed by rotary evaporation, and the residue was extracted with CH_2Cl_2 (40 mL). The

extract was filtered through Celite, and solvent was removed from the filtrate by rotary evaporation. The brown residue was triturated with ethyl ether (30 mL) and dried under oil pump vacuum to give **3a**$^+$ TfO^- (0.177 g, 0.240 mmol, 65%). The ^1H NMR spectrum was identical with that given in Table 1.

*4.13. [(η^5-C_5H_5)Re(NO)(PPh_3)($\overline{N{=}CH(CH_2)_2}$)]$^+$ PF_6^- (**5b**$^+$ PF_6^-)*

(a) A Schlenk flask was charged with **3b**$^+$ TfO^- (0.450 g, 0.600 mmol), THF (20 mL), and a stir bar and cooled to −100°C. Then $^tBuO^-$ K^+ (0.601 mL, 0.601 mmol, 1.0 M in THF) was added with stirring. After 5 min, the flask was transferred to a 0°C bath. After 5 min, the solvent was removed by oil pump vacuum. The residue was cooled to −80°C, and CH_2Cl_2 (20 mL) and Ph_3C^+ PF_6^- (0.233 g, 0.601 mmol) were added. The cold bath was removed, and the solution was stirred for 0.5 h. Hexane (80 mL) was added, and the resulting yellow-brown powder was collected by filtration and dried in air (1 h) to give **5b**$^+$ X^- (0.412 g, 0.551–0.554 mmol; $X^- = TfO^-$ or PF_6^-). A portion of the sample (0.369 g) was dissolved in a degassed solution of NH_4^+ PF_6^- (1.03 g, 6.32 mmol) in acetone (50 mL). After 15 min, solvent was removed under oil pump vacuum. The residue was extracted with CH_2Cl_2 (2 × 20 mL), and the extract was filtered through Celite. Solvent was removed from the filtrate, and the yellow oil was triturated with ethyl ether (50 mL). The resulting yellow solid was cycled through the preceding metathesis procedure twice. The yellow solid was then dissolved in acetone, and a layer of hexane was gently added. Orange microcrystals of **5b**$^+$ PF_6^- formed, which were collected by filtration and dried under oil pump vacuum (0.248 g, 0.333 mmol; 62% corrected for the portion of **5b**$^+$ X^- metathesized), mp 239–240°C dec. Anal. Calcd for $C_{26}H_{25}F_6N_2OP_2Re$: C, 41.99; H, 3.39. Found: C, 41.99; H, 3.42.

(b) A Schlenk flask was charged with **3b**$^+$ PF_6^- (0.163 g, 0.218 mmol), CH_2Cl_2 (20 mL), and a stir bar and cooled to −80°C. Then $^tBuO^-$ K^+ (0.262 mL, 0.262 mmol, 1.0 M in THF) was added with stirring. After 20 min, CH_2Cl_2 (5 mL) and Ph_3C^+ PF_6^- (0.110 g, 0.284 mmol) were added. The cold bath was removed, and the solution stirred for 20 min. The mixture was filtered through silica gel, which was eluted with CH_2Cl_2 (250 mL). The eluant was concentrated to *ca.* 1 mL and added to petroleum ether (35–60°C, 100 mL) with stirring. The resulting precipitate was collected by filtration, washed with petroleum ether (3 × 15 mL), and dried under oil pump vacuum to give spectroscopically pure **5b**$^+$ PF_6^- as a yellow powder (0.105 g, 0.142 mmol, 65%).

*4.14. [(η^5-C_5H_5)Re(NO)(PPh_3)($\overline{N{=}CH(CH_2)_3}$)]$^+$ PF_6^- (**5c**$^+$ PF_6^-)*

(a) Complex **3c**$^+$ TfO^- (1.690 g, 2.212 mmol), $^tBuO^-$ K^+ (2.21 mL, 2.21 mmol, 1.0 M in THF), and Ph_3C^+ PF_6^- (0.859 g, 2.21 mmol) were combined in a procedure analogous to method (a) for **5b**$^+$ PF_6^-. An identical workup gave crude **5c**$^+$ X^- (1.424 g, 1.869–1.879 mmol), a portion of which (0.499 g) was similarly treated with NH_4^+ PF_6^- (1.074 g, 6.589 mmol; three cycles). Complex **5c**$^+$ PF_6^- was obtained as orange microcrystals from acetone/hexane (0.289 g, 0.381 mmol; 49% corrected for the portion of **5c**$^+$ X^- metathesized), mp 253–254°C dec. Anal. Calcd for $C_{27}H_{27}F_6N_2OP_2Re$: C, 42.80; H, 3.59. Found: C, 42.79; H, 3.61.

(b) Complex **3c**$^+$ PF_6^- (0.163 g, 0.215 mmol), $^tBuO^-$ K^+ (0.258 mL, 0.258 mmol, 1.0 M in THF) and Ph_3C^+ PF_6^- (0.108 g, 0.279 mmol) were combined in a procedure analogous to method (b) for **5b**$^+$ PF_6^-. A similar workup gave crude **5c**$^+$ PF_6^- as a yellow powder (0.116 g, 0.153 mmol, 71%). A ^{31}P NMR spectrum showed a 90:10 mixture of **5c**$^+$ PF_6^- and an unidentified species (17.7/17.9 ppm, CD_2Cl_2). The sample was dissolved in CH_2Cl_2, and a layer of hexanes was gently added. Orange needles of spectroscopically pure **5c**$^+$ PF_6^- formed, which were collected by filtration and dried under oil pump vacuum (0.041 g, 0.054 mmol, 25%; unoptimized).

*4.15. [(η^5-C_5H_5)Re(NO)(PPh_3)($\overline{N{=}CH(CH_2)_4}$)]$^+$ PF_6^- (**5d**$^+$ PF_6^-)*

Complex **3d**$^+$ PF_6^- (0.1064 g, 0.1375 mmol), $^tBuO^-$ K^+ (0.165 mL, 0.165 mmol, 1.0 M in THF) and Ph_3C^+ PF_6^- (0.267 g, 0.688 mmol) were combined in a procedure analogous to method (b) for **5b**$^+$ PF_6^-. After a 1 h reaction period with Ph_3C^+ PF_6^-, a similar workup gave spectroscopically pure **5d**$^+$ PF_6^- as a pale orange powder (0.093 g, 0.120 mmol, 87%), mp 255–257°C dec. A portion of the sample was dissolved in CH_2Cl_2, and a layer of hexane was gently added. Orange microcrystals formed, which were collected by filtration and dried under oil pump vacuum. Anal. Calcd for $C_{28}H_{29}F_6N_2OP_2Re$: C, 43.58; H, 3.79. Found: C, 43.67; H, 3.76.

*4.16. [(η^5-C_5H_5)Re(NO)(PPh_3)($\overline{N{=}CH(CH_2)_5}$)]$^+$ PF_6^- (**5e**$^+$ PF_6^-)*

Complex **3e**$^+$ PF_6^- (0.121 g, 0.153 mmol), $^tBuO^-$ K^+ (0.184 mL, 0.184 mmol, 1.0 M in THF) and Ph_3C^+ PF_6^- (0.297 g, 0.766 mmol) were combined in a procedure analogous to method (b) for **5b**$^+$ PF_6^-. After a 6 h reaction period with Ph_3C^+ PF_6^-, a similar workup gave crude **5e**$^+$ PF_6^- as a golden yellow powder (0.0845 g, 0.108 mmol, 70%), mp 255–256°C dec. The sample

was dissolved in CH_2Cl_2, and a layer of hexanes was gently added. Orange microcrystals formed, which were collected by filtration and dried under oil pump vacuum (0.0797 g, 0.101 mmol, 66%). A ^{31}P NMR spectrum showed a 98.4:1.6 $\mathbf{5e}^+$ PF_6^-/$\mathbf{3e}^+$ PF_6^- mixture (18.5/19.3 ppm, CD_2Cl_2). Anal. Calcd for $C_{29}H_{31}F_6N_2OP_2Re$: C, 44.33; H, 3.98. Found: C, 44.42; H, 3.96.

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