Pyrrolyl-N and pyrrolyl-C complexes of the chiral rhenium fragment [(.eta.5-C5H5)Re(NO)(PPh3)]+: synthesis, protonation, and rearrangement chemistry

Todd J. Johnson, Atta M. Arif, and J. A. Gladysz

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Pyrrolyl-*N* and Pyrrolyl-*C* Complexes of the Chiral Rhenium Fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$: Synthesis, Protonation, and Rearrangement Chemistry

Todd J. Johnson, Atta M. Arif, and J. A. Gladysz*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

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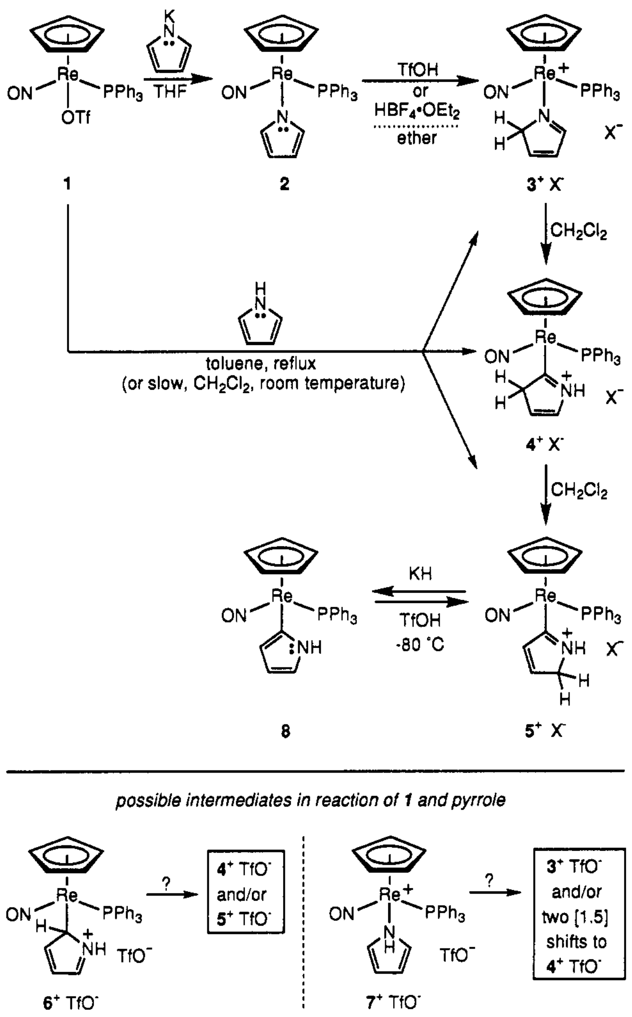
Summary: The pyrrolyl-N complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NC_4H_4)$ *and TfOH or* $HBF_4{\cdot}OEt_2$ *react to give 2H-pyrrole complexes* $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{N{=}CHCH{=}CHCH_2})]^+X^-$*. These rearrange to the carbon-ligated species* $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{C{=}NHCH_2CH{=}CH})]^+X^-$*, which is characterized crystallographically and treated with KH to give the pyrrolyl-C complex* $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{C{=}CHCH{=}CHNH})$*.*

Many transition-metal pyrrolyl-*N* complexes, $L_nMNC_4H_4$, have been synthesized.[1] However, despite the importance of the pyrrole moiety in natural products, materials, and hydrodenitrogenation chemistry, there do not appear to be any studies of ligand-based reactions. Although pyrrole undergoes attack by electrophiles at the 2-position,[2] pyrrolyl ligands should be further activated. There would be the potential for altered regiochemistry[3] and, in adducts of chiral metal fragments, control of the configurations of new stereocenters. Hence, we set out to prepare σ-pyrrolyl complexes of the chiral rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ and study their reactions with electrophiles. In this communication, we report that additions of protic acids to pyrrolyl-*N* complexes can trigger remarkable metal–carbon bond-forming rearrangements.

In a reaction similar to those used to access other pyrrolyl-*N* complexes,[1a–d] the triflate complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ (**1**)[4] and the pyrrolide salt KNC_4H_4 (1.5 equiv)[5] were combined in THF at room temperature (Scheme I). Workup gave crystalline, air-stable $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NC_4H_4)$ (**2**) in 88% yield. Complex **2**, and other new compounds isolated below, were characterized by microanalysis and IR and NMR ($^1H/^{13}C/^{31}P$) spectroscopy.[6] The ^1H and ^{13}C NMR chemical shifts of the NCH=CH moiety (δ 6.39, 5.76; 137, 108 ppm) were comparable to those of other pyrrolyl-*N* complexes.[1a,f]

Scheme I. Synthesis of Pyrrolyl-*N* and Pyrrolyl-*C* Complexes 2 and 8 and Reactions with Acids



In separate experiments, TfOH and $HBF_4{\cdot}OEt_2$ were added to ether solutions of **2** (Scheme I). The adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{N{=}CHCH{=}CHCH_2})]^+X^-$ ($\mathbf{3}^+X^-$)—which can be viewed as complexes of the unisolable pyrrole tautomer 2*H*-pyrrole[2]—precipitated as analytically pure yellow powders in 96–83% yields.[6] They exhibited IR ν_{NO} values (1681–1683 cm^{-1}) and downfield CH=N ^1H and ^{13}C NMR resonances (δ 8.1 br s; 178 ppm d, $^2J_{CP}$ = 1.8 Hz) similar to those of the corresponding acyclic imine complexes.[7] The CH_2 ^{13}C NMR chemical shift (78 ppm) was characteristic of 2*H*-pyrrole derivatives and downfield of the range for 3*H*-pyrroles.[2] The =CH ^{13}C resonances were within 6 ppm of those of the 2*H*-pyrrole salt $[\overline{HN{=}CHCH{=}CHCH_2}]^+HSO_4^-$,[8] and the

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[6] Full characterization of new compounds is provided in the supplementary material. NMR spectra were recorded in CD_2Cl_2.

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carbon connectivity was verified by a 2D INADEQUATE pulse sequence.[9]

In CH_2Cl_2 or CD_2Cl_2, 3^+X^- sequentially rearranged to two isomers (4^+X^-, 5^+X^-), as assayed by NMR (3^+TfO^-, slow, −40 °C; $3^+BF_4^-$, slower). The yields of 4^+TfO^- and $4^+BF_4^-$ reached maxima of ca. 84% and 34% (6 h, room temperature). After 4 days, workups of preparative reaction mixtures gave 5^+X^- (90–96%), which were assigned as the *carbon*-ligated N-protonated iminoacyl complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{C{=}NHCH_2\text{-}CH{=}C}H)]^+X^-$.[6] The structure was evidenced by a downfield C=N ^{13}C NMR resonance (221 ppm d, $^2J_{CP} = 8$ Hz), supported by numerous decoupling experiments, and confirmed by the crystal structure shown in Figure 1. The Re–C bond length was similar to that in the related formyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}O)$ (2.046(3) vs 2.055(10) Å), but the ReC=X bond was longer (1.314(4) vs 1.220(12) Å).[10,11a] The distance between one triflate oxygen (O3) and the C=NH proton (H25), 2.31 Å, was within the range associated with N···H···O hydrogen bonds.[12]

Complex 4^+X^- gave NMR data similar to those for 5^+X^- [6] and in accord with analogous decoupling experiments was assigned as the tautomer $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{C{=}NHCH{=}CHC}H_2)]^+X^-$. We next sought to probe the mechanisms of these unusual rearrangements. We first considered the possibility that 3^+TfO^- might be kinetically unstable with respect to triflate complex 1 and free pyrrole. Subsequent electrophilic attack of 1 at the 2-position of pyrrole would give 6^+TfO^- (Scheme I), which could convert via proton shifts to 4^+TfO^- and 5^+TfO^-. Indeed, the reaction of 1 and excess pyrrole in refluxing toluene gave 5^+TfO^- in 92% yield after workup. NMR experiments established the intermediacy of 4^+TfO^- and the formation of some 3^+TfO^- (5 min, 65% conversion; $3^+TfO^-/4^+TfO^-/5^+TfO^-$ = 4/24/72). Pyrrole (1 equiv) and 1 were then combined in CD_2Cl_2. The reaction was monitored by ^1H and ^{31}P NMR at room temperature and the rate compared to that of the disappearance of 3^+X^- under identical conditions. After 24 h, only 18% of 1 had been consumed ($3^+TfO^-/4^+TfO^-/5^+TfO^-$/other species[13] = 6/33/6/55), but 96–92% of 3^+X^- had isomerized. Hence, 1 and pyrrole react *too slowly* to be viable intermediates in the conversion of 3^+X^- to 5^+X^-. The appearance of some 3^+TfO^- in reactions of 1 and pyrrole suggests the intermediacy of the 1*H*-pyrrole complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{NHCH{=}CHCH{=}C}H)]^+TfO^-$ (7^+TfO^-; Scheme I). In fact, 7^+TfO^- may—instead of 6^+TfO^-—constitute the primary reaction channel.[14]

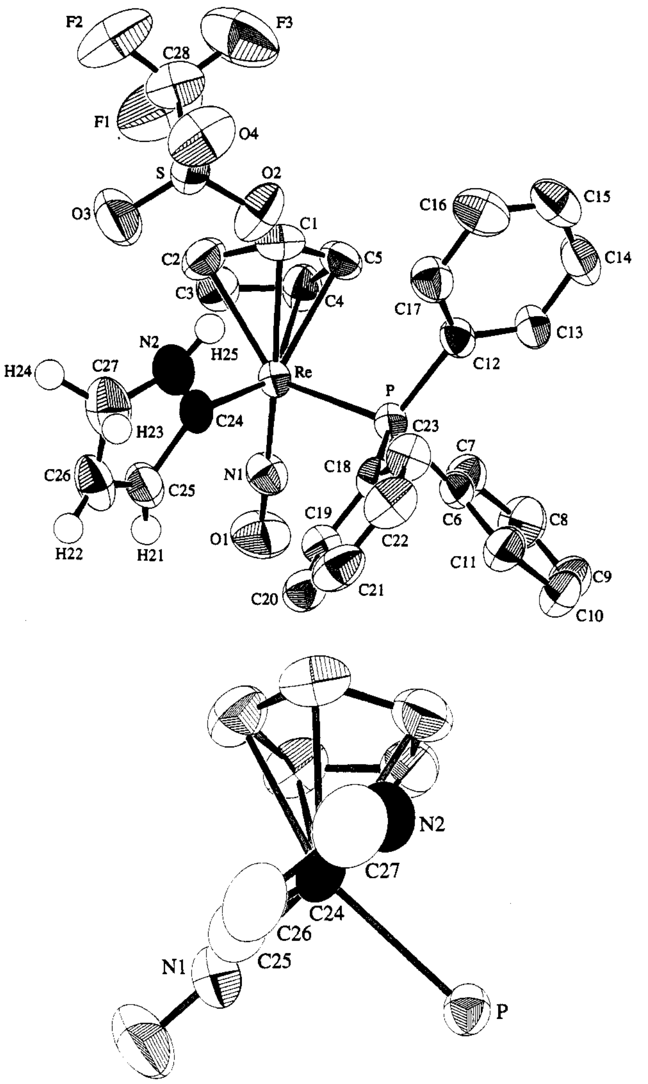

Figure 1. Structure of 5^+TfO^-: (top) numbering diagram; (bottom) Newman-type projection down the C24–Re bond with phenyl rings omitted. The C=N linkage is darkened to illustrate the discussion in footnote 10. Selected bond lengths (Å) and angles (deg): Re–C24 = 2.046(3), C24–N2 = 1.314(4), N2–C27 = 1.453(4), C24–C25 = 1.476(4), C25–C26 = 1.323(5), C26–C27 = 1.469(6), Re–N1 = 1.763(3), Re–P = 2.3854(7), N1–O1 = 1.182(3), O2–H25 = 2.31, O3–H25 = 2.77; Re–C24–N2 = 129.3(2), P–Re–N1 = 92.4(1), N1–Re–C24 = 93.6(1), P–Re–C24 = 92.5(1), Re–N1–O1 = 175.8(2), N2–C24–C25 = 105.1(3), C24–C25–C26 = 109.5(3), C25–C26–C27 = 110.2(3), N2–C27–C26 = 101.2(3), C24–N2–C27 = 114.0(3), O2–H25–N2 = 162.2.

We also noted that the deprotonation of 5^+X^- might give another potential intermediate, the pyrrolyl-*C* complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{C{=}CHCH{=}CHN}H)$ (8). Thus, 5^+TfO^- and KH were combined in THF at room temperature. Workup gave 8 (68%), which exhibited a downfield ReC ^{13}C NMR resonance (286 ppm d, $^2J_{CP}$ =

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(10) The ON—Re—C=NH torsion angle in 5^+TfO^- is 177.4(4)°, indicating an *anti* arrangement of the ON—Re and C=NH moieties. The opposite Re—C conformation, which would have *anti* ON—Re and C—CH moieties, would be equivalent sterically (neglecting hydrogen bonding). Although there is presently no assurance that 5^+TfO^- has crystallized in the lower energy Re—C conformation, this feature is of interest in the context of a lively controversy involving the origin of analogous orientations of acyl and formyl ligands in complexes of the formula $(\eta^5\text{-}C_5H_5)M(XO)(PPh_3)(COR)$ (M = Fe, Re; X = C, N).[11]

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(13) Cyclopentadienyl ^1H NMR chemical shifts: $3^+TfO^-/4^+TfO^-/5^+TfO^-$ at δ 5.55/5.64/5.61; other species at δ 5.48, 5.36, 5.25, 5.01.

(14) Under acidic conditions, pyrrole undergoes H/D exchange at nitrogen much more rapidly than C2 or C3. Thus, the least basic site is the most reactive toward certain electrophiles. See ref 2, pp 305–306.

7 Hz). To our knowledge, 8 is the first pyrrolyl-*C* complex to be prepared. Subsequent reaction with TfOH in CD_2Cl_2 (−80 °C, <5 min) gave exclusively 5^+TfO^-, as assayed by ^1H and ^{31}P NMR. Hence, 8 cannot be a precursor to 4^+TfO^-.

Although the preceding data exclude several plausible mechanisms for the rearrangement of 3^+X^- to 4^+X^- and 5^+X^-, they do not in our view identify a compelling choice among the remaining possibilities. We have considered pathways that involve initial formation of 7^+X^- or the corresponding 3*H*-pyrrole complex. The requisite proton shifts might be mediated by the counteranions, accounting for the rate trend (more basic TfO^- faster than BF_4^-). From these species, either (1) series of sigmatropic shifts or (2) deprotonations of ═CH groups adjacent to nitrogen (possibly via π isomers) allow rhenium–carbon bond formation in a manner consistent with the above data. Efforts to further probe and define the reaction coordinate are in progress.

Other aspects of the preceding reactions deserve emphasis. To our knowledge, 1 is the first transition-metal electrophile observed to attack free pyrrole to give a species with a metal–carbon σ bond. However, in important related work, osmium dications have been found to add to pyrrole to give π complexes.[15] These also undergo a rich array of reactions with electrophiles. Further, the facile formation of *non*aromatic pyrrole derivatives in Scheme I suggests several means by which metals could promote ring degradation reactions that would facilitate hydrodenitrogenation processes. In this context, potentially relevant conversions of cationic thiophene to neutral 2-thienyl complexes have recently been reported.[16] Finally, extensions of the above chemistry to other aromatic heterocycles, optically active complexes, and stereoselective carbon–carbon bond-forming reactions will be described in the near future.

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Supplementary Material Available: Text giving experimental procedures and analytical data and a table of NMR and IR data for new compounds[6] and tables of crystallographic data for 5^+TfO^- (17 pages). Ordering information is given on any current masthead page.

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