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Preliminary communication

Syntheses and structures of σ-pyridine, quinoline, and isoquinoline complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NC_xH_y)]^+CF_3SO_3^-$

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Abstract

Reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ with pyridine, quinoline, and isoquinoline gives the title complexes in high yields. The crystal structure of the isoquinoline complex is determined, and exhibits unexpected features.

We have had an ongoing interest in complexes of the chiral rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ and unsaturated organic ligands such as monosubstituted alkenes [1], aldehydes [2], and methyl ketones [3]. One of two possible diastereomeric adducts can usually be obtained with high stereoselectivity. Further, these adducts commonly undergo highly stereoselective nucleophilic attack. We sought to extend these synthetic and structural studies to complexes of unsaturated nitrogen-containing ligands such as imines and aromatic heterocycles. In this communication, we report (1) efficient syntheses of pyridine, quinoline, and isoquinoline complexes of the general formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NC_xH_y)]^+$ TfO^- ($TfO^- = CF_3SO_3^-$), (2) selected spectroscopic and physical properties, and (3) a crystal structure of the isoquinoline complex that shows an unexpected Re–N conformation [4*].

The methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**) [5] and TfOH were combined in toluene at −41 °C. The triflate complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ (**2**) was generated as previously described [6]. Then pyridine, quinoline, and isoquinoline were added (5.0 equiv., Scheme 1). The reactions with pyridine and isoquinoline were complete after several hours at room temperature, but that with quinoline required heating (1 h, 110 °C). Workup gave σ-heteroarene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NC_xH_y)]^+$ TfO^- (**3**, NC_xH_y = pyridine; **4**, quinoline; **5**, isoquinoline) as orange powders in 88–96% yields. In all cases, crystals could be obtained from CH_2Cl_2/hexanes.

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

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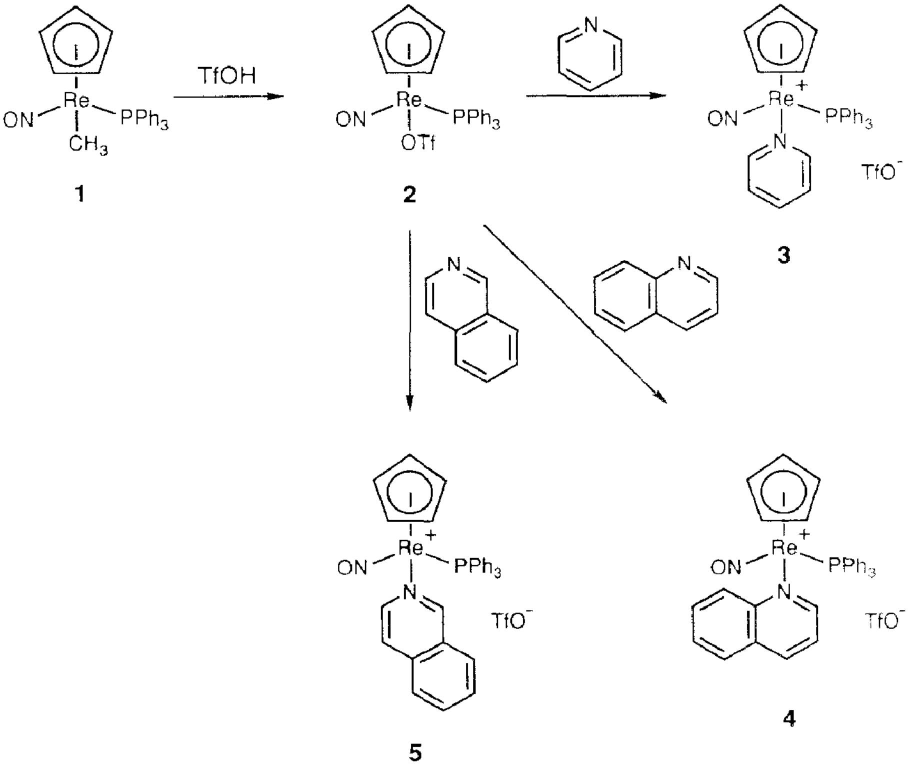
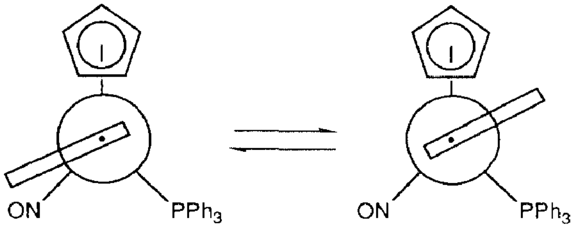


Scheme 1. Synthesis of heteroarene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NC_xH_y)]^+$ TfO^-.

Complexes **3–5** were characterized by microanalysis, and IR and NMR (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}) spectroscopy [7]. Spectroscopic features resembled those previously reported for σ-ketone complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(R)CH_3)]^+$ X^- (**6**) [3]. The ambient temperature ^{13}C NMR spectrum of pyridine complex **3** exhibited three pyridine carbon resonances (156.3, 137.4, 126.3 ppm), indicative of rapid rotation about the Re–NC_5H_5 bond on the NMR time scale. No decoalesence or significant broadening was observed in spectra recorded at −90 °C (CD_2Cl_2). Similar behavior was exhibited by the related neutral phenyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C_6H_5)$ (7) [8].

Quinoline, unlike pyridine, has a carbon substituent *ortho* to the donor nitrogen. We thought that this increased bulk might lead to higher Re–NC_xH_y rotational barriers in **4**, allowing the observation of rotamers of the general types I and II [9*]. Hence, NMR spectra (^{1}H, ^{31}P, ^{13}C) were recorded at −90 °C (CD_2Cl_2). Resonances broadened and shifted somewhat (e.g., C_5H_5: δ 5.62, 20 °C; δ 5.52, −90 °C). However, no decoalesence was observed except for some PPh_3 carbon resonances. Similar broadening, but no PPh_3 carbon decoalesence, was observed with isoquinoline complex **5**.



I **II**

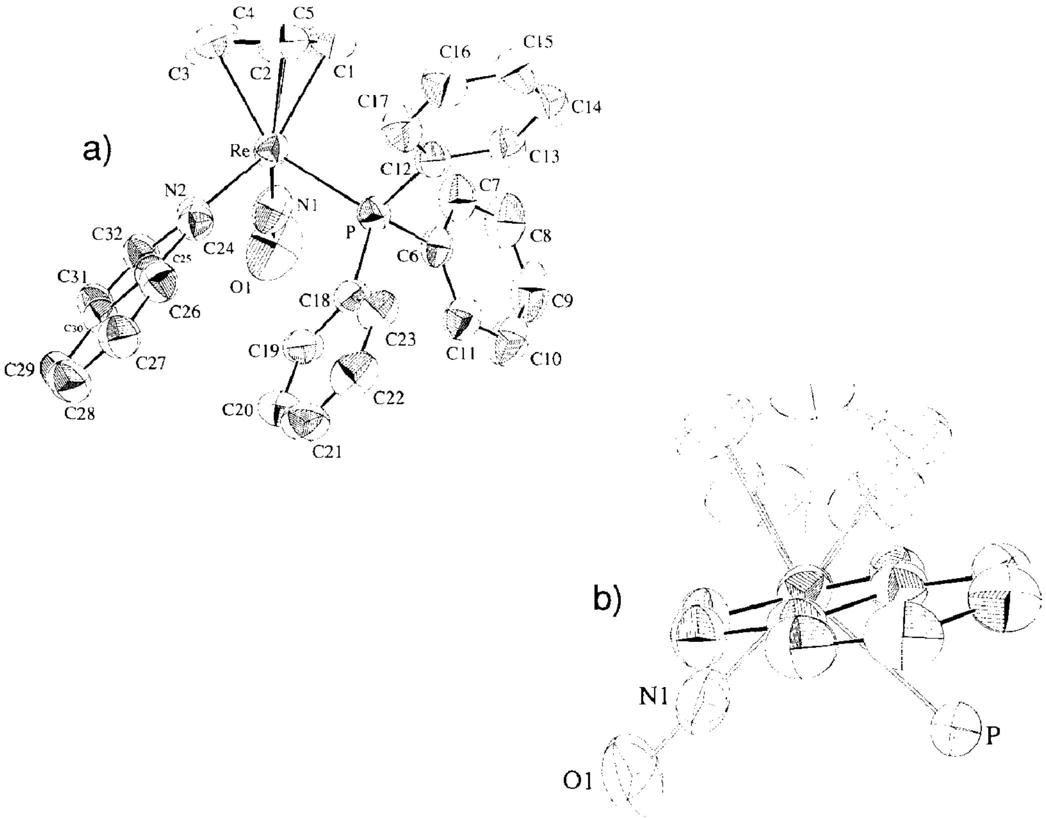


Fig. 1. Structure of the cation of isoquinoline complex **5**: (a) Numbering diagram; (b) Newman-type projection down the N2–Re bond. Selected bond lengths (Å) and angles (°): Re–N2 2.147(3), N2–C24 1.328(5), N2–C32 1.385(5), Re–N1 1.756(4), Re–P 2.378(1), N1–O1 1.195(5); Re–N2–C24 124.0(3), Re–N2–C32 118.2(3), P–Re–N1 90.0(1), N1–Re–N2 94.1(2), P–Re–N2 91.65(8), Re–N1–O1 177.1(4).

We next sought to structurally characterize one of the σ-heteroarene complexes. Accordingly, X-ray data were collected on a rectangular prism of **5** in a manner analogous to previous studies [10]. Refinement yielded the structures shown in Fig. 1 [11*]. The Re–NC$_9$H$_7$ (Re–N2) bond (2.147(3) Å) was about the same length as the Re–C$_\alpha$ bond in phenyl complex **7** (2.139(6) Å) [8], but longer than the Re–O bond in cationic σ-ketone complexes **6** (2.099(5)–2.080(5) Å) [3a]. A search of the Cambridge crystallographic data base revealed only two other structurally characterized isoquinoline complexes, both of copper(II) [12*].

To help describe the Re–N2 conformation, the least squares plane of the isoquinoline ligand was calculated. The rhenium was displaced from this plane by 0.08 Å. The Re–NO and Re–PPh$_3$ bonds made angles of 33.6 and 55.7° with the plane, respectively. These values are close to the N–Re–O–C and P–Re–O–C torsion angles found in σ-ketone complexes **6** [3a]. The most striking feature, however, is that the Re–N2 conformation belongs to the general type II. This places the benzenoid ring of the isoquinoline in the interstice between the bulky PPh$_3$ ligand and medium-sized cyclopentadienyl ligand (Fig. 1b), as opposed to the region between the cyclopentadienyl and small nitrosyl ligand. Also, the plane of the isoquinoline ligand is roughly parallel to that of the C18–C23 PPh$_3$ phenyl ring (angle 16.7°), with a distance of 3.1 Å to C19.

Although pyridine complexes are ubiquitous [4], quinoline and isoquinoline complexes of metals in lower oxidation states are scarce [13*,14*]. We speculate that complexes of quinoline, isoquinoline, and related heterocycles will exhibit rich structural diversity (e.g., σ vs. π binding) and ligand-based reactivity. The latter should have utility in organic synthesis, particularly in cases where the metal fragment is chiral and new stereocenters can be efficiently generated. In summary, this study has established the ready availability of σ-heteroarene complexes **3**–**5**, and structural properties that will aid in the interpretation of their reactions. Future reports will describe (a) the synthesis, structure, and unusual properties of analogous amine and imine complexes, and (b) highly diastereoselective nucleophilic additions to **5** [15].

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References

1 (a) G.S. Bodner, J.M. Fernández, A.M. Arif, J.A. Gladysz, J. Am. Chem. Soc., 110 (1988) 4082; (b) G.S. Bodner, T.-S. Peng, A.M. Arif, J. A. Gladysz, Organometallics, in press.

2 (a) J.M. Fernández, K. Emerson, R.D. Larsen, J.A. Gladysz, J. Am. Chem. Soc., 108 (1986) 8268; (b) C.M. Garner, J.M. Fernández, J.A. Gladysz, Tetrahedron Lett., 30 (1989) 3931.

3 (a) J.M. Fernández, K. Emerson, R.D. Larsen, J.A. Gladysz, J. Chem. Soc., Chem. Commun., (1988) 37; (b) D.M. Dalton, J.A. Gladysz, J. Organomet. Chem., 370 (1989) C17.

4 Review of heterocyclic nitrogen-donor ligands: J. Reedijk In G. Wilkinson, R.D. Gilliard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, Pergamon Press, New York, 1987, Vol. 2, p. 73–97.

5 W. Tam, G.-Y. Lin, W.-K. Wong, W.A. Kiel, V.K. Wong, J.A. Gladysz, J. Am. Chem. Soc., 104 (1982) 141.

6 J.H. Merrifield, J.M. Fernández, W.E. Buhro, J.A. Gladysz, Inorg. Chem., 23 (1984) 4022.

7 Full characterization has been provided to the reviewers, and selected data are as follows: IR (cm^{-1}, KBr) 1692–1698; ^{1}H NMR (δ, $CDCl_3$) C_5H_5 5.62–5.68; ^{13}C NMR (ppm, $CDCl_3$) C_5H_5 91.2–93.0; ^{31}P NMR (ppm, $CDCl_3$) 16.0–17.4. Anal. C, H, N.

8 S.K. Agbossou, G.S. Bodner, A.T. Patton, J.A. Gladysz, Organometallics, in press.

9 Based upon the crystal structure of phenyl complex 7 [8], a third type of $Re{-}NC_xH_y$ rotamer that places the benzenoid ring in the interstice between the nitrosyl and PPh_3 ligands must also be considered accessible.

10 C.H. Winter, W.R. Veal, C.M. Garner, A.M. Arif, J.A. Gladysz, J. Am. Chem. Soc., 111 (1989) 4766.

11 Data: triclinic, $P\bar{1}$, a 10.961(2) Å, b 15.770(2) Å, c 10.159(1) Å, α 87.65(2)°, β 109.88(2)°, γ 101.27(2)°, $Z = 2$. Atomic coordinates have been deposited with the Cambridge crystallographic data base.

12 (a) $Cu(O_2CCH_2SCH(CH_3)_2)_2(iso\text{-}NC_9H_7)_3$: Y. Sato, A. Ouchi, Y. Yukawa, T. Takeuchi, Chem. Lett., (1982) 1495; (b) $[Cu(OH_2)_2(iso\text{-}NC_9H_7)_2]^{2+}$ $(ClO_4^-)_2$: K. Al Sarraj, J. Gouteron, S. Jeannin, Y. Jeannin, Acta Cryst. C, 43 (1987) 1261.

13 A CAS-online structure search located many quinoline and isoquinoline complexes of metals in +2 or higher oxidation states, but very few of metals in lower oxidation states: (a) Rh^{I}: R. Uson, L.A. Oro, C. Claver, M.A. Garralda, J. Organomet. Chem., 105 (1976) 365; (b) Rh^{I}: G.K.N. Reddy, B.R. Ramesh, ibid., 87 (1975) 347; (c) Ru, Os: C.M. Eisenstadt, C.M. Giandomenico, M.F. Frederick, R.M. Laine, Organometallics, 4 (1985) 2033; (d) Mo^{0}: E.C. Aleya, A. Somogyvari, Trans. Met. Chem., 12 (1987) 310; Can. J. Chem., 66 (1988) 397.

14 For recent studies of monocyclic heteroarene complexes, see: (a) B. Chaudret, F.A. Jalon, J. Chem. Soc., Chem. Commun., (1988) 711; (b) D.R. Neithamer, L. Párkányi, J.F. Mitchell, P.T. Wolczanski, J. Am. Chem. Soc., 110 (1988) 4421; (c) R. Cordone, W.D. Harman, H. Taube, ibid., 111 (1989) 5969; (d) S.G. Davies, M.R. Shipton, J. Chem. Soc., Chem. Commun., (1989) 995.

15 (a) M.A. Dewey, J.M. Bakke, J.A. Gladysz, submitted; (b) M.A. Dewey, J.A. Gladysz, manuscripts in preparation.