3026 *Inorg. Chem.* 1994, *33*, 3026–3027

A Versatile Synthon for the Preparation of Chiral Rhenium(I)–Amine Complexes and Synthesis of an η^2-Benzaldehyde Species

Stephen D. Orth, Joseph Barrera, Michal Sabat, and W. Dean Harman*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

Received March 18, 1994

At present, the pentaammineosmium(II) moiety is unparalleled in its ability to form η^2-coordinated complexes with unsaturated organic ligands such as aldehydes, ketones,[1] arenes,[2] and aromatic heterocycles.[3] For aromatic ligands in particular, these complexes have proven to be valuable synthons for organic systems.[4] The combination of an electron-rich heavy metal and an octahedral ligand environment lacking strong π-acids provides a system showing properties common to both classical coordination and organometallic chemistry. It is our expectation that isoelectronic Re(I) in a suitable octahedral amine ligand environment may show properties similar to those of the pentaammineosmium system.

Re(I) chemistry is currently dominated by compounds which contain organic π-acids such as CO and CNR, ligands that greatly stabilize the low oxidation state of the metal through back-bonding interactions. Our synthetic approach to Re(I)–amine systems relies on the observation made by Chatt and Dilworth that benzoylhydrazide was an effective agent for the conversion of Re(V)–oxo species to dinitrogen species of the form $Re^I(L)_4(N_2)Cl$ in the presence of various phosphines (L).[5] Our hope was that a one-electron oxidation of an analogous amine complex would displace the dinitrogen and yield a synthon for the preparation of Re(I)-tetraamines with one open coordination site similar to $Os(NH_3)_5(OTf)_3$ (which is prepared from oxidation of $[Os(NH_3)_5(N_2)]Cl_2$).[6]

The compound $Re({=}NN{=}C(Ph)O{-})(PPh_3)_2Cl_2$, readily prepared from $Re(O)Cl_3(PPh_3)_2$,[5] undergoes a two-electron reduction of the metal when refluxed in toluene along with LL = 4,4′-di-*tert*-butyl-2,2′-bipyridine (tbpy; **1a**) or 2,2′-bipyridine (bpy; **1b**) to form the compounds $ReCl_2(-N{=}NC(O)Ph)(LL)(PPh_3)$.[7] Like their phosphine analogs,[5] these rhenium(III) complexes exhibit diamagnetic NMR spectra and characteristic $\nu_{N{=}N}$ bands ranging from 1470 to 1570 cm^{-1}. When the complex $ReCl_2(N{=}NC(O)Ph)(tbpy)(PPh_3)$ (**1a**) is refluxed in benzene along with MeOH and ampy (Figure 1), reduction to Re(I) occurs with elimination of methyl benzoate, and $[Re(N_2)(ampy)(tbpy)PPh_3]Cl$ (**2**) is obtained in 71% yield.[8] Derivatives of **2** such as $[Re(N_2)(ampy)_2PPh_3]Cl$ and $[Re(N_2)(tbpy)(en)PPh_3]Cl$ may be obtained by a similar reaction sequence.[9] The dinitrogen stretch for **2** occurs at 1940 cm^{-1}, which is considerably lower in energy than that for the osmium(II) analog $[Os(NH_3)_5(N_2)]^{2+}$ (2009, 2022 cm^{-1}),[10] and this observation suggests that the rhenium(I) metal center is highly electron-rich. An ORTEP diagram of **2** (Figure 2)[11] shows that the ampy ligand, the phosphorus, and a nitrogen from tbpy lie in a common plane, perpendicular to the Re–N_2 bond. The N–N bond length is 1.13(1) Å, approximately equal to that for $[Os(NH_3)_5(N_2)]Cl_2$ (1.12(2) Å).[12] After anion exchange of **2** with TlOTf (DME) to generate **3**,[13] oxidation of the rhenium with AgOTf results in loss of the dinitrogen, affording the Re(II) precursor $[Re(OTf)(ampy)(tbpy)PPh_3]OTf$ (**4**).[14] Reduction of **4** in 1,2-dimethoxyethane (DME) by Mg^0 in the

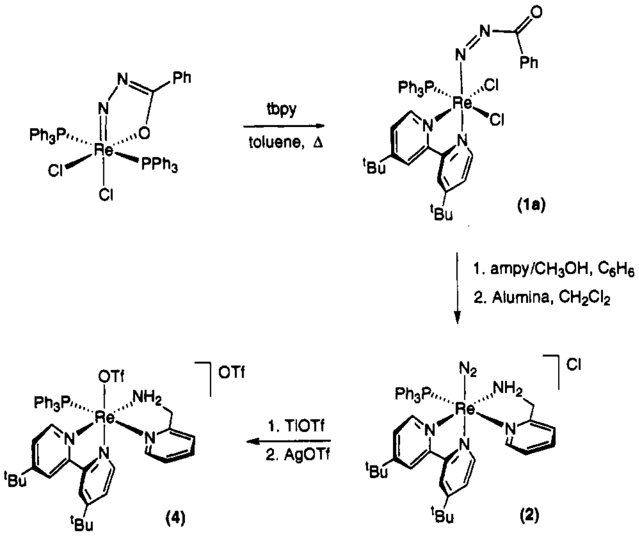

Figure 1. Reaction scheme for the synthesis of $[Re(OTf)(ampy)(tbpy)PPh_3]OTf$ (**4**).

---

(1) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223. Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439.

(2) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883. Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725.

(3) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969. Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 2896.

(4) Kopach, M. E.; Kelsh, L. P.; Stork, K.; Harman, W. D. *J. Am. Chem. Soc.* **1993**, *115*, 5322. Gonzalez, J.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1993**, *115*, 8857. Hodges, L. M.; Koontz, J. I.; Gonzalez, J.; Myers, W. H.; Harman, W. D. *J. Org. Chem.* **1993**, *58*, 4788. Kopach, M. E.; Gonzalez, J.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 8972. Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969.

(5) Chatt, J.; Dilworth, J. R.; Leigh, G. J.; Gupta, V. D. *J. Chem. Soc. A* **1971**, 2631. Chatt, J.; Dilworth, J. R.; Leigh, G. J. *Chem. Commun.* **1969**, 687.

(6) Lay, P. A.; Taube, H.; Magnuson, R. H. *Inorg. Synth.* **1986**, *24*, 269.

(7) Synthesis of $ReCl_2(N{=}NC(O)Ph)tbpy(PPh_3)$ (**1a**): $Re({=}NN{=}C(Ph)O)(PPh_3)_2Cl_2$ (1.05 g, 1.26 mmol) and tbpy (0.371 g, 1.38 mmol) were suspended in toluene (40 mL); the mixture was refluxed for 7.5 h. ^1H NMR ($CDCl_3$): δ 9.47 (d, 1H), 8.67 (d, 1H), 8.10 (d, 2H), 7.85 (d, 2H), 7.52 (t, 1H), 7.38 (m, 9H), 7.18 (m, 9H), 6.92 (d, 1H), 1.39 (s, 9H), 1.37 (s, 9H). CV (DMA/TBAH; 100 mV/s): $E_{p,a} = 0.68$ V, $E_{p,c} = -1.32$ V, $E_{p,c} = -1.53$ V vs NHE. IR (KBr): $\nu_{NN} = 1475$ cm^{-1}. Anal ($ReC_{43}H_{44}N_4Cl_2OP$) C, H, N.

(8) Synthesis of $[ReN_2(ampy)(tbpy)PPh_3]Cl$ (**2**): Compound **1a** (1.37 g, 1.49 mmol) was suspended in C_6H_6 (15 mL) and CH_3OH (15 mL). Ampy (2 mL) was added, and the reaction mixture was refluxed 4 h. Yield: 71%. X-ray-quality crystals were obtained from CH_2Cl_2/hexanes. ^1H NMR (CD_2Cl_2): δ 9.46 (d, 1H), 8.68 (d, 1H), 8.33 (br m, 1H), 7.81 (d, 1H), 7.70 (d, 1H), 7.51 (m, 1H), 7.42 (d, 1H), 7.22 (m, 10H), 7.02 (m, 7H), 6.85 (dd, 1H), 6.80 (m, 2H), 5.12 (dd, 1H), 4.24 (m, 1H), 4.10 (m, 1H), 1.41 (s, 9H), 1.23 (s, 9H). IR (KBr): $\nu_{N_2} = 1940$ cm^{-1}. CV (DMA/TBAH; 100 mV/s): $E_{1/2} = -0.02$ V, $E_{1/2} = -1.61$ V vs NHE. Anal ($ReC_{42}H_{47}N_6PCl$) C, H, N.

(9) Orth, S. D.; Barrera, J.; Dubois, R.; Harman, W. D. Manuscript in preparation.

(10) Allen, A. D.; Stevens, J. R. *Chem. Commun.* **1967**, 1147.

(11) Crystallographic data: $[C_{42}H_{47}N_6PRe]Cl\cdot CH_2Cl_2\cdot 0.5CH_3(CH_2)_4CH_3$; $M = 1016.53$; triclinic, space group $P\bar{1}$ (No. 2); $a = 14.582(4)$ Å, $b = 15.573(4)$ Å, $c = 10.656(3)$ Å, $\alpha = 96.73(2)°$, $\beta = 109.57(2)°$, $\gamma = 81.12(2)°$, $V = 2247(2)$ Å^3, $Z = 2$, $d_{calcd} = 1.50$ g cm^{-3}. The structure was solved by direct methods using TEXSAN 5.0. Full-matrix least-squares refinement gave $R(F) = 0.046$ and $R_w(F) = 0.056$ for 4600 absorption-corrected reflections with $I > 3\sigma(I)$ measured up to $2\theta = 46°$ on a Rigaku AFC6S diffractometer at −120 °C (Mo Kα radiation, $\lambda = 0.710\,69$ Å). The CH_2Cl_2 solvent molecule was found disordered between two orientations with the population parameters 0.6 and 0.4, respectively.

(12) Fergusson, J. E.; Love, J. L.; Robinson, W. T. *Inorg. Chem.* **1972**, *11*, 1662.

(13) $[ReN_2(ampy)(tbpy)PPh_3]OTf$ (**3**): yield 90%. CV (DMA/TBAH; 100 mV/s): $E_{1/2} = 0.00$ V, $E_{1/2} = -1.63$ V vs NHE.

0020-1669/94/1333-3026$04.50/0

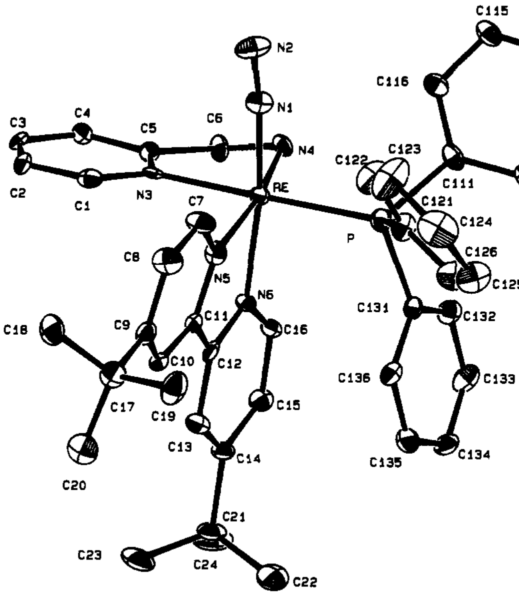

Figure 2. ORTEP drawing for the cation $[ReN_2(ampy)(tbpy)PPh_3]^+$ (**2**). Selected bond distances (Å) and angles (deg) are as follows: Re–N1 = 1.906(9), Re–N3 = 2.157(8), Re–N4 = 2.193(7), Re–N5 = 2.067(7), Re–N6 = 2.106(7), N1–N2 = 1.13(1); Re–N1–N2 = 174.2(2), N1–Re–N6 = 170.4(3), N4–Re–N5 = 166.2(3); N3–Re–N4 = 76.1(3); N3–Re–N5 = 92.1(3).

presence of a variety of ligands results in a new series of Re(I)–amine complexes of the form $[Re(ampy)(tbpy)(PPh_3)(L)]^+$ where L = N_2, ethene, benzaldehyde, *tert*-butyl isocyanide, or CO.[15] The most notable of these is the benzaldehyde complex, **5** (Figure 3), similar in nature to the more conventional organometallic system $\{ReCp(NO)PPh_3\}$,[16] prepared by Gladysz et al. The aldehyde proton resonance of **5** occurs at 5.98 ppm (indicative of η^2-coordination) and is split into a doublet by the phosphorus (J_{HP} = 9.2 Hz).[17] $^{13}C\{^1H\}$ NMR and HETCOR data allow the assignment of the aldehyde carbon at 85.81 ppm (d, J_{CP} = 1.7 Hz), a value similar to that reported by Gladysz,[18] and suggest that **5** is formed as a single diastereomer (de > 97%). Judging from modeling studies, the two possible diastereomers resulting from η^2-aldehyde coordination each have only one energetically reasonable conformer, provided that the ampy, bpy, and phosphine ligands remain in the same orientation as that for **2**.[19] Strong NOE interactions between the ortho-PPh_3 hydrogens (6.98 ppm) and the aldehyde proton (5.98 ppm) as well as between an ampy amine proton (6.27 ppm) and the phenyl ring of benzaldehyde are most consistent with the diastereomer shown in Figure 3.

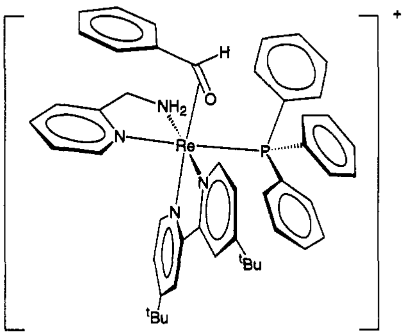

Figure 3. Proposed structure of $[Re(PhC(O)H)(ampy)(tbpy)PPh_3]^+$ (**5**).

Remarkably, the cyclic voltammogram of the benzaldehyde complex **5** shows a *reversible* (II/I) potential with $E_{1/2}$ = –0.07 V at 100 mV/s (NHE; DMA/TBAH). Given the large difference expected in reduction potential for an η^1- and η^2-bound aldehyde,[1] this observation suggests that the η^2-aldehyde dication is also moderately stable. Notably, the II/I oxidation potential for **5** is considerably negative of the III/II couple of similar pentaammineosmium species (~0.5 V),[1] and the greater reducing nature of the rhenium may be responsible for the increased kinetic stability of the d^5 system. That the $[Re(ampy)(tbpy)(PPh_3)]^+$ system is highly electron-rich is also supported by the observation that the compound $[Re(ampy)(tbpy)(PPh_3)(CO)]^+$ has a ν_{CO} of 1799 cm^{-1}. This absorption is of considerably lower energy than that for $[ReCpNo(PPh_3)CO]^+$ (2001 cm^{-1}),[20] or the pentaammineosmium(II) analog (1894 cm^{-1}),[21] and is similar to that for the *neutral* species ReCl(diphos)CO (1820 cm^{-1}).[22]

Reduction of **4** in the presence of acetone, furan, benzene, naphthalene, or *N*-methylpyrrole fails to produce detectable amounts of any material bearing these ligands. Possibly, the hindered environment about the labile coordination site prevents stable binding in these cases; however, preliminary evidence suggests that the ampy ligand in this system may be unstable with respect to β-hydride elimination. Despite the limitations of this ligand set, the synthetic approach to Re(I)–amine precursors, explicitly outlined for **4**, appears to be highly versatile, allowing independent selection both of bidentate amine ligands and possibly of the phosphine. This approach should allow for the convenient adjustment of both steric and electronic factors in $[Re^IL_5]$ systems—systems which may eventually surpass osmium(II) in their ability to *dearomatize* organic substrates.[4]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (PRF Grant 26027-AC), the Camille and Henry Dreyfus Foundation, and the National Science Foundation (NSF Young Investigator Program) for generous support of this work.

Supplementary Material Available: Additional information on the synthesis and characterization of compounds **1–5** and stereochemical assignment of **5** and tables of experimental details, atomic positional parameters, thermal parameters, and bond distances and angles $[ReN_2(ampy)(tbpy)PPh_3]Cl$ (**2**) (15 pages). Ordering information is given on any current masthead page.

---

(14) Synthesis of $[Re(OTf)(ampy)(tbpy)PPh_3]OTf$ (**4**): **3** (2.93 g, 2.92 mmol) was suspended in DME (40 mL), and AgOTf (0.75 g, 2.9 mmol) was added. The reaction mixture was stirred for 3 h and then filtered through Celite; the filtrate was reduced to 10 mL and added dropwise to Et_2O/hexanes (1:1, 50 mL). The resulting solid was filtered off, washed (Et_2O), and dried; yield 2.92 g, 89%. CV (DMA/TBAH; 100 mV/s): $E_{p,a}$ = 0.73 V, $E_{p,c}$ = –0.97 V vs NHE. Anal ($ReC_{44}H_{47}N_4F_6O_6PS_2$) H, N; C: calcd, 47.05; found, 46.64.

(15) Synthesis of $[Re(PhC(O)H)(ampy)(tbpy)PPh_3]OTf$ (**5**): **4** (0.111 g, 0.099 mmol) was dissolved in DME (2 mL). Benzaldehyde (0.262 g, 2.47 mmol) and activated magnesium (0.21 g) were added; the reaction mixture was stirred for 1.5 h and then filtered through Celite. The filtrate was added dropwise to Et_2O/hexanes (1:4, 75 mL). The precipitate was isolated by filtration, washed (hexanes), and dried; yield 0.098 g, 92%. Selected resonances are as follows. ^1H NMR (CD_2Cl_2): δ 6.27 (m, 1H, NH_2), 5.98 (d, J_{HP} = 9.2 Hz, CHO, 1H), 3.95 (m, 1H, NH_2), 3.74 (m, 1H, CH_2), 3.21 (dd, 1H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 85.81 (d, J_{CP} = 9.2 Hz, CHO), 51.26 (CH_2), 31.18 (*tert*-butyl), 31.09 (*tert*-butyl). CV (DMA/TBAH; 100 mV/s): $E_{p,a}$ = 0.50 V, $E_{1/2}$ = –0.07 V, $E_{1/2}$ = –1.57 V vs NHE. Anal ($ReC_{50}H_{55}N_4F_3O_4PS$) H, N; C: calcd, 55.48; found, 56.00.

(16) Quirós Méndez, N.; Seyler, J. W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 2323.

(17) The coupling to P was confirmed with a broad-band phosphorus-decoupled ^1H NMR spectrum of **5**.

(18) Garner, C. M.; Quirós Méndez, N.; Kowalczyk, J. J.; Fernández, K. E.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 5146. Note that σ-bound aldehyde complexes exhibit carbonyl carbon resonances at ~167 ppm. See ref 16.

(19) Although this assumption has not been verified, NOE data are consistent with this assignment of ligands. Furthermore, when the precursor **4** is reduced in DME under N_2, a compound spectroscopically identical to **3** is obtained.

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

(21) Allen, A. D.; Stevens, J. R. *Can. J. Chem*, **1973**, *50*, 3093.

(22) Chatt, J.; Dilworth, J. R.; Gunz, H. P.; Leigh, G. J. *J. Organomet. Chem.* **1974**, *64*, 245.