Self-Assembly of a Complex Fluorinated Metallacycle from Hexafluoroacetone and Acetonitrile on Aerobic Photolysis of $(HBpz_3)ReO(C_2O_4)$

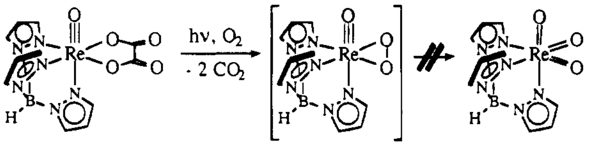
Seth N. Brown[1] and James M. Mayer*

Department of Chemistry, Box 351700, University
of Washington, Seattle, Washington 98195-1700

Received February 15, 1995

Introduction

We have previously reported that photolysis of the rhenium(V) oxo oxalate complex $(HBpz_3)ReO(C_2O_4)$ ($HBpz_3$ = hydrotris(1-pyrazolyl)borate) under oxygen yields the rhenium(VII) trioxo compound $(HBpz_3)ReO_3$.[2] Mechanistic and ^{18}O-labeling studies implicated the rhenium(V) oxo−peroxo complex $[(HBpz_3)ReO(O_2)]$ as an intermediate in this process but indicated that formation of the trioxo compound does not occur by simple cleavage of the O−O bond (eq 1). In an attempt to



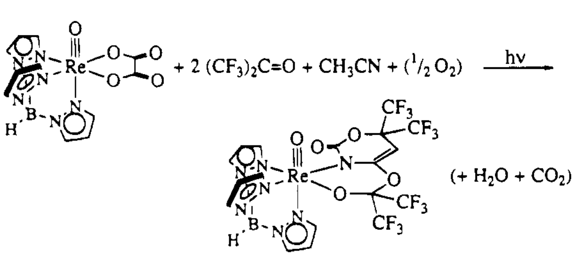
(1)

trap the peroxide intermediate, the oxalate complex was photolyzed in the presence of hexafluoroacetone, a powerful electrophile. Although trapping was not successful, photolysis formed an unusual and remarkably complex metallacycle, whose structure and construction are the subject of this note.

Results and Discussion

The oxalate complex $(HBpz_3)ReO(C_2O_4)$[2] is insoluble in neat $(CF_3)_2C{=}O$ but dissolves in mixtures of acetonitrile and hexafluoroacetone. Photolysis in this solvent system under an oxygen atmosphere results in very slow formation (ca. 4 days) of a new diamagnetic rhenium complex, as well as traces of $(HBpz_3)ReO_3$. The new air-stable complex may be purified by chromatography on silica gel and isolated as violet crystals in 24% yield. The presence of O_2 is essential, as none of the product is formed in its absence.

X-ray crystallographic analysis indicates that this photoproduct has incorporated not only *two* molecules of hexafluoroacetone but also a molecule of acetonitrile and part of the original oxalate ligand (eq 2). The structure of the complex is illustrated



(2)

in Figure 1, and crystallographic and structural details are supplied in Tables 1 and 2, respectively. The tris(pyrazolyl)borate and terminal oxo ligand ($d[Re{\equiv}O]$ = 1.684(6) Å) are unexceptional, but photolysis has assembled from smaller molecules a new chelate of surprising complexity. The chelate is formally a dianion, with the rhenium bound to an alkoxide oxygen derived from hexafluoroacetone and to the deprotonated nitrogen of an *N*-vinylcarbamate (derived from CH_3CN). Including the rhenium atom, the chelate forms two fused six-membered rings. The ligand, excluding the trifluoromethyl groups, is roughly planar (rms deviation from the plane is 0.19 Å). The rhenium is 1.21 Å above this plane and the rhenium−oxo bond canted toward it by 26°. This allows the carbonyl oxygen O(5) to rest in the cleft between the two pyrazoles *cis* to N(1).

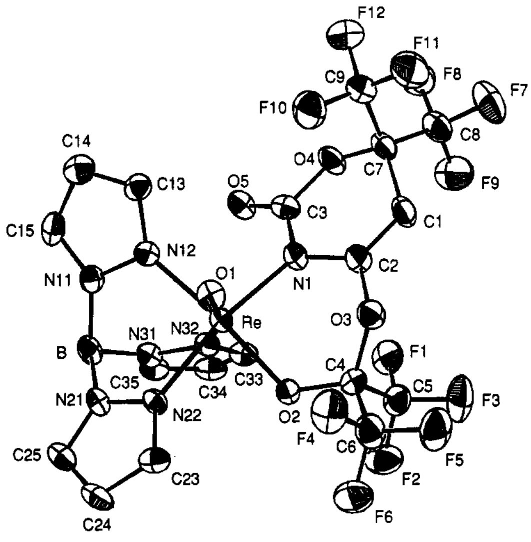


Figure 1.

Table 1. Crystal Data for $(HBpz_3)ReO(C_9HF_{12}NO_4){\cdot}C_6H_6$

a = 9.492(3) Å
b = 11.752(4) Å
c = 15.174(3) Å
α = 93.56(2)°
β = 103.62(2)°
γ = 104.70(3)°
Z = 2
μ = 40.16 cm^{-1}
R = 0.052^a
goodness of fit = 1.294

formula $C_{24}H_{17}BF_{12}N_7O_5Re$
fw 908.44
space group $P\bar{1}$
T = 25 °C
λ = 0.710 73 Å
V = 1578 (2) Å^3
ϱ_{calc} = 1.912 g cm^{-3}
transm coeff = 0.4128−0.9989
R_w = 0.066^b

$^a\ R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b\ R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Spectroscopic analysis of this compound is consistent with its solid-state structure. Its mass spectrum shows a parent ion at m/z = 831, confirming the molecular formula of the complex as $(HBpz_3)ReO(C_9HF_{12}NO_4)$. Above the mass of $(HBpz_3)Re$ (m/z = 400) are observed three major fragment ions at m/z = 665 ($[M - (CF_3)_2CO]^+$), 596 ($[M - (CF_3)_2CO, -CF_3])^+$, and 458 ($[HBpz_3]ReO(NCO)^+$). ^1H NMR spectra show three sets of pyrazole resonances, and $^{13}C\{^1H\}$ NMR spectra show four distinct CF_3 resonances, indicating the absence of symmetry in the molecule. The lone proton in the new fluorinated ligand (δ 5.01 in $CDCl_3$) is replaced with deuterium if the reaction is performed with CD_3CN. The infrared spectrum, in addition to the bands expected for the $(HBpz_3)ReO$ fragment[2] (e.g., ν_{BH} = 2523 cm^{-1} and ν_{ReO} = 985 cm^{-1}), shows strong bands at 1758 cm^{-1} ($\nu_{C=O}$) and 1694 cm^{-1} ($\nu_{C=C}$ of the vinylurethane). One noteworthy spectroscopic feature is the appearance in the $^{13}C\{^1H\}$ NMR of the coupling of one of the pyrazole carbons to the fluorines of a single CF_3 group (q, J_{CF} = 2.4 Hz). This long-range coupling (at least six bonds) is presumably from F(1)−F(3) to C(33), as these are rather close (F(1)−C(33) is

---

[1] Current address: Department of Chemistry, 164-30, California Institute of Technology, Pasadena, CA 91125. Electronic mail: snbrown@cco.caltech.edu.

[2] Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091−4100.

0020-1669/95/1334-3560$09.00/0 © 1995 American Chemical Society

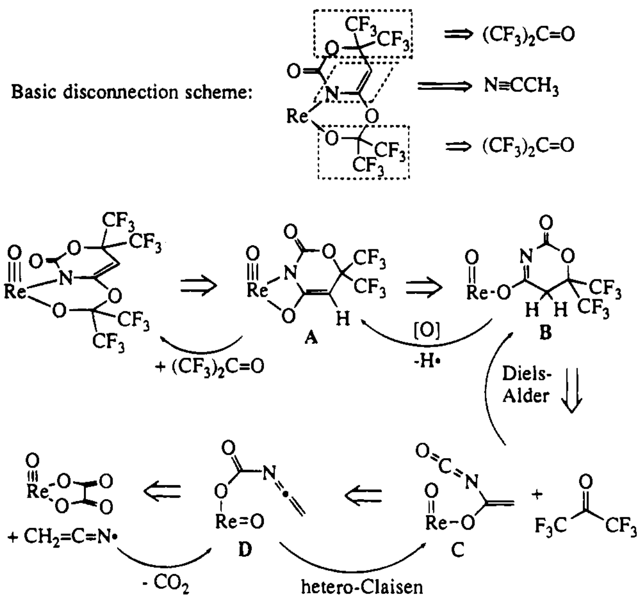
Table 2. Selected Bond Distances (Å) and Angles (deg) in $(HBpz_3)ReO(C_9HF_{12}NO_4)\cdot C_6H_6$

Re−O(1)	1.684(6)	Re−N(12)	2.091(7)
Re−O(2)	1.966(5)	Re−N(22)	2.079(6)
Re−N(1)	2.073(7)	Re−N(32)	2.228(7)
O(2)−C(4)	1.366(11)	C(4)−O(3)	1.417(11)
O(3)−C(2)	1.366(11)	C(2)−C(1)	1.294(13)
C(1)−C(7)	1.530(14)	C(7)−O(4)	1.419(12)
O(4)−C(3)	1.361(11)	C(3)−N(1)	1.404(12)
N(1)−C(2)	1.391(12)	C(3)−O(5)	1.185(12)
C(4)−C(5)	1.526(14)	C(4)−C(6)	1.589(15)
C(7)−C(8)	1.548(17)	C(7)−C(9)	1.511(16)
C(5)−F(1)	1.331(12)	C(8)−F(7)	1.352(17)
C(5)−F(2)	1.323(13)	C(8)−F(8)	1.330(15)
C(5)−F(3)	1.294(13)	C(8)−F(9)	1.233(16)
C(6)−F(4)	1.317(14)	C(9)−F(10)	1.323(14)
C(6)−F(5)	1.299(13)	C(9)−F(11)	1.323(15)
C(6)−F(6)	1.328(14)	C(9)−F(12)	1.324(14)
O(1)−Re−O(2)	107.7(3)	O(2)−Re−N(1)	85.2(3)
O(1)−Re−N(1)	101.6(3)	O(2)−Re−N(12)	163.6(2)
O(1)−Re−N(12)	88.4(3)	O(2)−Re−N(22)	84.0(3)
O(1)−Re−N(22)	94.2(3)	O(2)−Re−N(32)	84.4(3)
O(1)−Re−N(32)	165.2(3)	N(1)−Re−N(12)	95.1(3)
N(12)−Re−N(22)	91.7(3)	N(1)−Re−N(22)	163.0(3)
N(12)−Re−N(32)	79.3(3)	N(1)−Re−N(32)	87.2(3)
N(22)−Re−N(32)	78.2(2)		
Re−O(2)−C(4)	122.4(5)	Re−N(1)−C(2)	118.9(5)
O(2)−C(4)−O(3)	116.3(7)	Re−N(1)−C(3)	123.2(6)
C(4)−O(3)−C(2)	120.5(8)	C(2)−N(1)−C(3)	117.5(7)
O(3)−C(2)−C(1)	117.2(9)	N(1)−C(3)−O(5)	125.4(9)
O(3)−C(2)−N(1)	116.1(8)	N(1)−C(3)−O(4)	116.3(10)
C(3)−O(4)−C(7)	125.6(8)	O(4)−C(3)−O(5)	118.3(9)
O(4)−C(7)−C(1)	109.8(9)	C(2)−C(1)−C(7)	116.8(9)
C(5)−C(4)−C(6)	109.8(9)	C(8)−C(7)−C(9)	115.9(10)
O(2)−C(4)−C(5)	110.4(9)	O(4)−C(7)−C(8)	102.6(10)
O(2)−C(4)−C(6)	107.5(8)	O(4)−C(7)−C(9)	106.3(10)
O(3)−C(4)−C(5)	110.6(9)	C(1)−C(7)−C(8)	108.9(10)
O(3)−C(4)−C(6)	101.9(9)	C(1)−C(7)−C(9)	112.8(11)

3.36 Å in the crystal) and through-space interactions are often significant in long-range coupling to ^{19}F.[3]

To probe the mechanism of this transformation, the photoreaction was carried out with $(HBpz_3)ReO(C_2O_4)$ that was ^{18}O-enriched in the oxalate ligand (44.5% per oxygen). Mass spectrometry of the product indicates slight but significant enrichment of the parent ion and all three significant fragment ions above the mass of $(HBpz_3)Re$ ($m/z = 400$). In fact, within experimental error all four observed fragments are equally enriched, with 8.5 ± 1.1% of an oxygen-18 atom per molecule. Since even the ion of mass 458 with composition $(HBpz_3)ReO(NCO)^+$ has this same degree of enrichment, this shows that the terminal oxo and the carbonyl oxygen are the only oxygens that can be significantly enriched. Some of the label is definitely in the oxo ligand, as the IR spectrum of the enriched compound shows a weak new band at 935 cm^{-1} (calcd for $\nu_{\mathrm{Re}^{18}\mathrm{O}} = 933$ cm^{-1}). No new bands are apparent in the carbonyl stretching region (or elsewhere in the spectrum), but given the low enrichment, this does not rule out some incorporation in the carbonyl oxygen as well. The poor retention of label is not surprising, as the large excess of the electrophilic hexafluoroacetone is likely to engage in some exchange reactions, especially given the long reaction time.

Scheme 1. Suggested Pathway for Formation of $(HBpz_3)ReO(C_9HF_{12}NO_4)$



To attempt to understand the steps involved in the construction of the new chelate, one can work backward from its final structure (Scheme 1). The alkoxide oxygen and its attached $C(CF_3)_2$ group are almost certainly due to addition of hexafluoroacetone to the enolate oxygen in a compound such as **A**. Next arises the central puzzle of the entire mechanism, namely the origin of the other six-membered ring, and in particular the only new carbon−carbon bond, that between C(1) and C(7). A reasonable solution is suggested if one imagines that **A** might have been formed by oxidative removal of a hydrogen atom from **B**. The oxidant needed for this step might be molecular oxygen or a photogenerated radical. Inspection of **B** reveals that it is the Diels−Alder adduct of hexafluoroacetone and the vinyl isocyanate **C**. Such hetero-Diels−Alder reactions are well precedented,[4] and the observed orientation of the $(CF_3)_2CO$ is consistent with connection of its electron-poor carbonyl with the electron-rich carbon of the enol ether in **C**. Rearrangement of **C** to ketenimine **D** allows one to recover the oxalate and acetonitrile fragments in recognizable form. Participation of oxo ligands in pseudo-Claisen rearrangements has been seen in other systems.[5] Complex **D** might arise from attack of the CH_2CN radical on the oxalate complex to form a nitrogen−carbon bond and expel CO_2; radicals are known to add to oxalyl chloride.[6] The initial photoevent is likely not the usual photofragmentation of the oxalate ligand, since one carbon of the oxalate is certainly retained in the product and since no $[(HBpz_3)_2Re_2(O)_2(\mu\text{-}O)(\mu\text{-}pz)]ReO_4$ and only traces of $(HBpz_3)ReO_3$ are produced.[2] Instead, the event that likely initiates this cascade of reactions is probably excitation of the hexafluoroacetone ($\lambda_{\max} = 302$ nm, $\epsilon = 17$ M^{-1} cm^{-1}) and hydrogen atom abstraction from acetonitrile by the triplet ketone (or photoproduced trifluoromethyl radicals).[7]

This skein of unusual reactions must surely be thought fanciful, were it not for the fact that it renders comprehensible an otherwise inexplicable transformation. It is also consistent with the appearance of the ^{18}O label from the oxalate ligand in the oxo group of the product. Many questions about the details

---

(3) Hilton, J.; Sutcliffe, L. H. *Prog. NMR Spectrosc.* **1975**, *10*, 27−39.

(4) (a) Schulze, A.; Goerdeler, J. *Tetrahedron Lett.* **1974**, 221−224. (b) Kniežo, L.; Kristian, P.; Imrich, J.; Ugozzoli, F.; Andreetti, G. D. *Tetrahedron* **1988**, *44*, 543−556. (c) Drobnica, Ľ.; Kristián, P.; Augustín, J. In *The Chemistry of Cyanates and Their Thio Derivatives*, Patai, S., Ed.; John Wiley & Sons: New York, 1977; Chapter 22.

(5) Chabardes, P.; Kuntz, E.; Varagnat, J. *Tetrahedron* **1977**, *33*, 1775−1783. Matsubara, S.; Okazoe, T.; Oshima, K.; Takai, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 844−849. Belgacem, J.; Kress, J.; Osborn, J. A. *J. Mol. Catal.* **1994**, *86*, 267−285 and references therein.

(6) Kharasch, M. S.; Brown, H. C. *J. Am. Chem. Soc.* **1942**, *64*, 329−333.

(7) Krespan, C. G.; Middleton, W. J. *Fluorine Chem. Rev.* **1967**, *1*, 145−196.

of the mechanism remain, but if the general sweep of Scheme 1 is correct, it provides a fascinating example of the power of a cascade of electrocyclic reactions to construct complex inorganic frameworks to supplement the examples in organic chemistry.[8]

Experimental Section

Acetonitrile was dried over 4 Å molecular sieves, followed by CaH_2, and was vacuum-transferred prior to use. $(HBpz_3)ReO(C_2O_4)$ and $(HBpz_3)ReO(C_2{}^{18}O_4)$ were prepared as previously described.[2] ^1H, ^{19}F, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian VXR-300 spectrometer at 300, 282.2, and 75.4 MHz, respectively. ^{19}F NMR spectra were referenced to external $C\mathit{F}_3COOH$ at 0 ppm. IR spectra were obtained as films evaporated onto NaCl plates on a Perkin-Elmer 1604 FT-IR spectrometer; peaks are reported in wavenumbers. Electron impact mass spectra were acquired on a Kratos Analytical mass spectrometer in the positive-ion mode. Solid samples were loaded in direct-inlet mode in melting point capillaries and were heated in vacuo to 150 °C to vaporize them for analysis. Elemental analyses were performed by Canadian Microanalytical Services, Ltd., Vancouver, BC, Canada.

$(HBpz_3)ReO(C_9HF_{12}NO_4)$. $(HBpz_3)ReO(C_2O_4)$ (74.6 mg, 0.148 mmol) and a magnetic stirbar were placed in a glass bomb with a Teflon needle valve. On a vacuum line, 6 mL of dry acetonitrile and 5 mL of dry hexafluoroacetone (Peninsular Chemresearch Inc.; volume of liquid $(CF_3)_2CO$ measured at −78 °C) were vacuum-transferred into the bomb. With this mixture at −78 °C, the bomb was filled with 1 atm of O_2. The needle valve was then closed, and the apparatus was warmed to ambient temperature. The solution was photolyzed through a Pyrex filter, with stirring, for 4.5 d. The volatiles were removed on the vacuum line, and the residue was taken up in a minimum amount of CH_2Cl_2. The product was chromatographed in the air on a short silica gel column, eluting with CH_2Cl_2. The blue fraction was collected and then rechromatographed, eluting with benzene to separate the blue fraction from $(HBpz_3)ReO_3$. Yield: 30 mg (24%). The analytical sample was recrystallized from benzene. ^1H NMR ($CDCl_3$), δ: 6.03, 6.44, 6.52 (t, 2 Hz, 1H each, pz 4-H); 7.41, 7.43, 7.70, 7.74, 7.86, 7.96 (d, 2 Hz, 1H each, pz 3-H and 5-H); 5.01 (s, 1H, metallacycle $C\mathit{H}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 106.8, 108.2, 108.6; 135.1, 137.3, 139.1; 144.5 (q, $J_{CF} = 2.4$ Hz), 145.1, 149.1 (pzs); 75.2 ($=\mathit{C}H$); 79.7 (sept, $J_{CF} = 33$ Hz; $\mathit{C}(CF_3)_2$; the other such carbon was not observed); 120.9 (q, $J_{CF} = 293$ Hz; $\mathit{C}F_3$), 121.2 (q, $J_{CF} = 286$ Hz; $\mathit{C}F_3$), 121.4 (q, $J_{CF} = 290$ Hz; $\mathit{C}F_3$), 121.7 (q, $J_{CF} = 288$ Hz; $\mathit{C}F_3$); 155.9, 157.9 (urethane $\mathit{C}=O$, quaternary vinylic $\mathit{C}=CH$). ^{19}F NMR (CD_3CN), δ: 0.49, 5.33 (q, 9 Hz, 3F each; nearer pair of $C\mathit{F}_3$); 2.03 (s, 6F; pair of $C\mathit{F}_3$ farther from Re). IR (typical $HBpz_3$ bands[2] are not included), cm^{-1}: 2523 (m, ν_{BH}), 1758 (s, $\nu_{C=O}$), 1694 (s, $\nu_{C=C}$), 1394 (m), 1356 (s), 1246 (s), 1162 (s), 985 (s, ν_{ReO}), 920 (w), 884 (w), 816 (w), 792 (w), 747 (m), 674 (w). MS: 831 (M^+), 665 ($[M - (CF_3)_2CO]^+$), 596 ($[M - (CF_3)_2CO, -CF_3]^+$), 458 ($[HBpz_3]ReO(NCO)^+$). Anal. Calcd for $C_{18}H_{11}BF_{12}N_7O_5Re$: C, 26.04; H, 1.34; N, 11.81. Found: C, 26.06; H, 1.32; N, 11.84.

X-ray Structure of $(HBpz_3)ReO(C_9HF_{12}NO_4)\cdot C_6H_6$. A large (0.2 × 0.5 × 0.5 mm) violet plate was obtained by allowing a supersaturated solution of the compound in benzene to stand at room temperature overnight. The crystal was glued to the tip of a glass fiber in the air. A total of 7302 reflections in four octans (hkl, $hk\bar{l}$, $h\bar{k}l$, $h\bar{k}\bar{l}$) with $2\theta \le 54°$ were collected at 25 °C on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation with a graphite monochromator ($\lambda = 0.710\,37$ Å). Scans of three standard reflections, measured every 160 reflections, indicated substantial decay (25.2% over the course of data collection), to account for which a linear correction was applied. An empirical absorption correction was applied ($\mu = 40.162\ cm^{-1}$; transmission factors 0.999−0.413, average 0.724). After corrections for absorption and for Lorentz and polarization effects, 6442 unique reflections were obtained, of which 4655 were judged observed ($I > 3\sigma(I)$, $R_{av} = 0.025$ on F_o). The rhenium atom was located on a Patterson map, and remaining non-hydrogen atoms were located on subsequent difference Fourier maps. All heavy atoms were refined anisotropically, except the carbon atoms of the benzene of solvation, which were refined isotropically. Hydrogens were fixed in calculated positions. Final full-matrix least-squares refinement converged at $R = 0.052$ and $R_w = 0.066$. All calculations used the SDP/VAX package of programs supplied by the Enraf-Nonius Corp. with scattering factors and anomalous dispersion terms taken from the standard compilation.[9] Crystallographic details are summarized in Table 1, and selected bond distances and angles appear in Table 2.

Acknowledgment. We thank Dr. Sue C. Critchlow for assistance with the X-ray structure determination. We are grateful to the National Science Foundation for financial support. S.N.B. acknowledges support from a National Science Foundation Predoctoral Fellowship, a Shell Graduate Fellowship, and a Howard J. Ringold Fellowship of the University of Washington Department of Chemistry.

Supplementary Material Available: Tables of data collection and refinement details, atom positional and thermal parameters, bond distances and angles, torsional angles, and least-squares planes (10 pages). Ordering information is given on any current masthead page.

IC950165M

---

(8) (a) Ziegler, F. E. In *Comprehensive Organic Synthesis*; Paquette, L. A., Ed.; Pergamon Press: New York, 1991; Vol. 5, pp 875−898. (b) Danheiser, R. L.; Gee, S. K. *J. Org. Chem.* **1984**, *49*, 1672−1674 and references therein.

(9) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974.