Selective Oxidation of the Alkyl Ligand in Rhenium(V) Oxo Complexes

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Abstract: Rhenium(V) oxo alkyl triflate compounds ($HBpz_3$)ReO(R)OTf [R = Me (**4**), Et (**5**), *n*-Bu (**6**); $HBpz_3$ = hydrotris(1-pyrazolyl)borate; OTf = OSO_2CF_3, triflate] are formed on sequential reaction of ($HBpz_3$)$ReOCl_2$ with dialkyl zinc reagents and AgOTf. These triflate compounds are rapidly oxidized at ambient temperatures by oxygen atom donors pyridine *N*-oxide (pyO) and dimethyl sulfoxide (DMSO) to give ($HBpz_3$)ReO_3 (**7**) and the corresponding aldehyde. In the cases of **5** and **6** this transformation is quantitative. The addition of 2,6-lutidine to a low-temperature oxidation of **5** by DMSO redirects the reaction to form *cis*-2-butene instead of acetaldehyde. These oxidation reactions do not proceed through alkoxide intermediates, as shown by independent studies of alkoxide oxidations. Reaction of **5** with pyO or DMSO at −47 °C results in the formation of intermediates which are assigned as ylide or "trapped-carbene" complexes [($HBpz_3$)ReO(OH){$CH(L)CH_3$}]OTf (L = py (**8**) or SMe_2 (**9**), respectively). Mechanistic studies and analogies with related systems suggest that oxygen atom transfer to **4**-**6** forms [($HBpz_3$)ReO_2R]$^+$. Transfer of an α-hydrogen from the alkyl group to an oxo ligand then forms an alkylidene complex which is trapped by SMe_2 or py to give the observed intermediates. Further oxidation of the ylide complex gives the aldehyde.

Introduction

The oxidation or oxygenation of alkyl and aryl ligands is likely to be a key step in organometallic oxidation processes. It is, for instance, the redox step in the Sharpless mechanism for dihydroxylation.[1] Selective oxidations of organic compounds mediated by metal compounds have long been of interest in industrial and bench-scale processes.[2] Organometallic approaches to oxidation reactions, via intermediates with metal−carbon bonds, are attractive because of the potential for high selectivity. Yet there are few examples of clean oxidation of transition metal−alkyl or aryl complexes.[3−6] Alkyl compounds of electropositive metals, both main group and transition elements, often react with dioxygen by a radical chain mechanism.[4] Such a mechanistic generalization is difficult for the scattered cases of oxidation of middle- and late-transition metal alkyl compounds,[5] such as the conversion of nickel alkyls to alkoxide complexes on treatment with nitrous oxide.[6]

Reported here are oxidations of rhenium(V) alkyl triflate complexes which convert the alkyl ligand to the corresponding aldehyde. Oxidative reactions that give aldehydes are unusual, as further oxidization to the corresponding carboxylic acid is usually facile.[7] The oxidants in these reactions are oxygen atom transfer agents, such as pyridine *N*-oxide and dimethyl sulfoxide. Use of such oxygen atom donors has become a popular route to form oxidizing metal centers,[8] as in the chemistry of metal porphyrin and related complexes.[9] Oxygen atom transfer to the rhenium(V) complexes generates considerably more reactive rhenium(VII) species in which the activation of the alkyl ligand takes place. This approach of adding an oxygen atom donor to a metal center that bears an oxidizable organic group has been valuable in the discovery of the first well-defined phenyl-to-oxo migration reaction[10] and other reactions.[11]

Experimental Section

General Considerations. All experiments were performed under an inert atmosphere using standard vacuum, Schlenk, and glovebox techniques, except where noted. Solvents were degassed and dried according to standard procedures.[12] ($HBpz_3$)$ReOCl_2$,[13] ($HBpz_3$)ReO(Et)Cl (**2**),[14] ($HBpz_3$)$ReO(OCD_2CD_3)(OTf)$,[11] $CH_3C(^{18}O)H$,[15] $Me_2S^{18}O$,[16] and

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^{15}N-pyridine *N*-oxide[17] were synthesized according to published procedures (for abbreviations see footnote 18). 2,6-Lutidine *N*-oxide was synthesized by the general procedures detailed by Ochiai.[19] ^{18}O-$(HBpz_3)Re(O)_3$ was synthesized by Dr. Seth Brown.[13b] Deutero and ^{18}O labeled solvents were purchased from Cambridge Isotope Laboratories. Other reagents were purchased from Aldrich and used as received unless otherwise noted. NEt_3 and 2,6-lutidine were degassed and dried over CaH_2 then vacuum transferred prior to use. Pyridine *N*-oxide, Me_3NO, and dimethyl sulfone were sublimed and kept under nitrogen. Me_2SO was degassed and dried over 4 Å molecular sieves. Me_2S was degassed, dried over sodium, and vacuum transferred prior to use. HCl (technical grade), NMe_2H (tech grade), N_2O, and ethylene oxide were purchased from Matheson.

NMR spectra were recorded on Bruker AC-200 (^1H, ^2H, ^{19}F) and AF-300 (^1H, ^{13}C) Fourier transform spectrometers. All spectra were recorded at ambient temperatures unless otherwise noted. Peaks in the ^1H and ^{13}C spectra were referenced to solvent resonances. ^{19}F spectra were referenced to neat $CF_3C(O)OH$. ^2H spectra were referenced to a spike of deutero solvent injected into the protio solvent. Low-temperature ^1H and $^{13}C\{^1H\}$ NMR spectra utilized a Bruker B-VT 1000 temperature controller. The controller was calibrated by Seth Brown by use of the ^1H chemical shifts for methanol.[20] Peak positions are reported in ppm and coupling constants in Hz. The pyrazole protons always have a $J_{HH} = 2$ Hz, which is not included in the spectral descriptions below. IR spectra, reported below in cm^{-1}, were recorded using a Perkin-Elmer 1600 FTIR with samples prepared as Nujol mulls or evaporated films on NaCl plates. The pyrazole bands are relatively constant and therefore the following common bands are not repeated in each of the spectral lists below: 3112 (m), 1503 (m), 1409 (s), 1312 (s), 1212 (s), 1116 (s), 1072 (m), 1051 (vs), 987 (w), 762 (s), 715 (s), 657 (m), 615 (m). Electron impact mass spectra were recorded using a Kratos Analytical mass spectrometer using a direct probe technique with samples packed into glass capillaries and heated typically to 100 °C. GC−MS were recorded using a Kratos Analytical MS and a 5890 Hewlett Packard GC−MS equipped with cooling units. Elemental analyses were performed by Canadian Microanalytical Services Ltd.

$(HBpz_3)ReO(Me)Cl$ (1). $(HBpz_3)ReOCl_2$ (575 mg, 1.183 mmol) was placed in a 500 mL round bottom flask with a stir bar. C_6H_6 (350 mL) was vacuum transferred in, and the solid was dissolved. To an attached addition funnel charged with a solution of $ZnCl_2$ (83.5 mg, 0.604 mmol) in Et_2O (40 mL) was added MeLi (1.2 mL of 1.0 M in Et_2O, 1.2mmol) via syringe. This solution was mixed and allowed to stand for 30 min, with precipitation of LiCl. This $ZnMe_2$ solution was added slowly to the solution of $(HBpz_3)ReOCl_2$, and the reaction was stirred for 3 days. The flask was opened to air and the volatiles were removed, leaving a brown residue. The product was purified by chromatography on silica gel, eluting with toluene, then recrystallized from CH_2Cl_2/pentane, yielding 197.2 mg (36%) of purple crystals. ^1H NMR (C_6D_6): δ 8.03, 7.64, 7.02, 6.96, 6.85, 6.64 (each d, 1H, pz); 5.92 (s, 3H, ReCH_3); 5.66, 5.57, 5.29 (each t, 1H, pz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.0, 144.2, 138.6, 137.4, 133.7, 129.2, 108.5, 107.7, 105.7 (pyrazoles); 14.3 (ReCH_3). IR: 3126 (w); 2495 (w; ν_{BH}); 1389 (w); 995 (s,ν_{ReO}); 889 (w); 789 (w); 650(w). DIPMS: $m/z = 465$ (M^+). Anal. Calcd for $C_{10}H_{13}BClN_6ORe$: C, 25.79; H, 2.81; N, 18.05. Found: C, 25.96; H, 2.74; N, 17.85.

$(HBpz_3)ReO(n\text{-}Bu)Cl$ (3). $(HBpz_3)ReOCl_2$ (465 mg, 0.957 mmol) was placed in a 500 mL round bottom flask with a stir bar. C_6H_6 (300 mL) was vacuum transferred in, and the solid was dissolved. The solution was then cooled to 10 °C. To an attached addition funnel charged with a solution of $ZnCl_2$ (66.7 mg, 0.498 mmol) in Et_2O (40 mL) was added *n*-BuLi (1.4 M in Et_2O, 0.70 mL, 1.0 mmol) via syringe. This solution was mixed and allowed to stand for 40 min, with LiCl precipitating out of solution. This solution was added very slowly to the prechilled solution of $(HBpz_3)ReOCl_2$, and stirring was continued for 5 h at 10 °C. The flask was opened to air and the volatiles were removed, leaving a brown residue. The product was purified by chromatography on silica gel, by eluting with toluene, then recrystallized from CH_2Cl_2/pentane, yielding 155.6 mg (32%) of purple crystals. ^1H NMR (C_6D_6): δ 8.34, 7.62, 7.25, 7.13, 7.12, 6.73 (each d, 1H, pz); 7.76, 6.35 (each d of t, 1H, ReC*HH*′CH_2−, $J_{HH} = 11$, $J_{HH'} = 5$); 5.79, 5.70, 5.30 (each t, 1H, pz); 2.87 (m, 2H, $ReCH_2CHH'CH_2CH_3$); 1.70 (m, 2H, $ReCH_2CH_2CH_2CH_3$); 1.11 (t, 3H, $Re(CH_2)_3CH_3$, $J_{HH} = 6$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.0, 146.7, 144.2, 138.5, 137.3, 133.7, 108.4, 107.7, 105.7 (pyrazoles); 44.6 ($ReCH_2CH_2$−); 39.8 ($ReCH_2CH_2CH_2CH_3$); 29.8 ($ReCH_2CH_2CH_2CH_3$); 14.4 ($ReCH_2CH_2CH_2CH_3$). IR: 2512 (w; ν_{BH}); 1114.3 (w); 975 (s,ν_{ReO}). DIPMS: $m/z = 508$ (M^+). Anal. Calcd for $C_{13}H_{19}BClN_6ORe$: C, 30.75; H, 3.77; N, 16.55. Found: C, 30.69; H, 3.75; N, 16.44.

$(HBpz_3)ReO(Me)OTf$ (4). $(HBpz_3)ReO(Me)Cl$ (176 mg, 0.379 mmol) and AgOTf (102 mg, 0.382 mmol) were placed in a 100 mL round bottom flask with a magnetic stir bar. The assembly was attached to the vacuum line and evacuated. C_6H_6 (30 mL) was vacuum transferred in, and the flask was wrapped in foil. The solution was allowed to stir for 3 days, forming a deep purple solution with a lavender precipitate. The solution was then filtered, and all but 5 mL of the solvent was removed under vacuum. Hexane (25 mL) was then vacuum transferred into the flask and the solution kept in an ice bath. The dark purple solid was filtered away from the solution and collected. The solid was recrystalized multiple times from hexane/toluene, then washed with 2 × 5 mL of pentane. The solid was then dried *in vacuo*. Yield: 160 mg (73%). ^1H NMR (C_6D_6): δ 8.37, 7.35, 7.25, 7.14, 7.09, 6.70 (each d, 1H, pz); 5.75, 5.72, 5.31 (each t, 1H, pz); 5.60 (s, ReCH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.9, 146.6, 143.7, 139.9, 137.5, 134.2; 109.1, 108.5, 106.4 (pyrazoles); 16.7 (ReCH_3). ^{19}F NMR (CD_2Cl_2): δ −1.76 (s). IR: 2523 (w; ν_{BH}); 1220 (w, ν_{OTf}); 1028 (m, ν_{OTf}); 967 (m, ν_{ReO}). DIPMS: $m/z = 580$ (M^+). Anal. Calcd for $C_{11}H_{13}BF_3N_6O_4ReS$: C, 22.80; H, 2.26; N, 14.51. Found: C, 22.60; H, 2.24; N, 14.74.

$(HBpz_3)ReO(Et)OTf$ (5) was prepared from **2** (220 mg, 0.460 mmol) and AgOTf (118 mg, 0.462 mmol), according to the procedure for **4**. Precipitation, multiple recrystalizations with pentane/toluene, and washing with pentane gave 113 mg of **5** (41.4%). ^1H NMR (C_6D_6): δ 8.09, 7.62, 7.06, 6.97, 6.91, 6.67 (each d, 1H, pz); 7.94, 6.61 (each d of q, 1H, ReC*HH*′CH_3, $J_{HH} = 6$, $J_{HH'} = 11$); 5.63, 5.60, 5.34 (each t, 1H, pz); 2.14 (t, 3H, ReCHH′CH_3, $J_{HH} = 6$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 148.1, 147.4, 143.8, 139.9, 137.3, 134.5, 108.7, 108.3, 106.5 (pyrazoles); 35.6 ($ReCH_2CH_3$); 26.3 ($ReCH_2CH_3$). ^{19}F NMR (C_6D_6): δ −1.37 (s). IR: 2523 (w, ν_{BH}); 1215 (m, ν_{OTf}); 1020 (s, ν_{OTf}); 978 (s, ν_{ReO}). DIPMS: $m/z = 594$ (M^+). Anal. Calcd for $C_{12}H_{15}BF_3N_6O_4ReS$: C, 24.29; H, 2.54; N, 14.17. Found: C, 24.59; H, 2.54; N, 14.14.

$(HBpz_3)ReO(n\text{-}Bu)OTf$ (6) was prepared from **3** (156 mg, 0.307 mmol) and AgOTf (81.6 mg, 0.316 mmol) following the procedure for **4**, yielding 130 mg (68%). ^1H NMR (CD_2Cl_2): δ 8.11, 7.91, 7.88, 7.74, 7.57, 7.49 (each d, 1H, pz); 7.91, 6.86 (each d of t, 1H, ReC*HH*′CH_2−, $J_{HH} = 11$, $J_{HH'} = 5$); 6.56, 6.50, 6.08 (each t, 1H, pz); 2.26, 1.64 (each m, 1H, $ReCH_2CHH'CH_2$−); 1.44 (m, 2H, $ReCH_2CH_2CH_2CH_3$); 0.90 (t, 3H, $Re(CH_2)_3CH_3$, $J_{HH} = 7$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 148.4, 147.4, 143.6, 141.4, 138.4, 135.7, 109.4, 108.6, 106.7 (pyrazoles); 44.6 ($ReCH_2CH_2$−); 43.7 ($ReCH_2CH_2CH_2CH_3$); 29.7 ($ReCH_2CH_2CH_2CH_3$); 13.9 ($ReCH_2CH_2CH_2CH_3$). ^{19}F NMR (CD_2Cl_2): δ −1.86 (s). IR: 2521 (w; ν_{BH}); 1391 (w); 1351 (w); 1163 (w, ν_{OTf}); 1027 (m, ν_{OTf}); 977 (m, ν_{ReO}); 632 (m). DIPMS: $m/z = 622$ (M^+). Anal. Calcd for $C_{14}H_{19}BF_3N_6O_4ReS$: C, 27.06; H, 3.08; N, 13.53. Found: C, 27.10; H, 3.14; N, 13.44.

General Procedure for NMR Tube Experiments. Many of the experiments examined were done in sealed NMR tubes. A typical procedure for this is illustrated in the reaction between $(HBpz_3)ReO(Et)OTf$ (**5**) and pyO. In the glovebox, 6.3 mg of **5** (0.011 mmol) was placed in a sealable NMR tube attached to a ground glass joint. pyO (3.2 mg, 0.034 mmol) was added, and the contents were dissolved in C_6D_6 (0.4 mL). A needle valve with a Teflon plug was attached to the tube, and the apparatus was placed on the vacuum line. The tube subjected to three freeze−pump−thaw cycles, then frozen at −77 °C

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(18) Abbreviations: $(HBpz_3)$ = hydrotris(1-pyrazolyl)borate; OTf = CF_3SO_3; pz = pyrazole; pyO = pyridine *N*-oxide; DMSO = Me_2SO, dimethyl sulfoxide; DMS = Me_2S, dimethyl sulfide; Me = methyl, CH_3; Et = ethyl, CH_2CH_3.
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and sealed with a torch. The tube was then thawed with an acetone rinse. $(Me_3Si)_2O$ was sometimes added as an internal standard.

[(HBpz$_3$)Re(O)(OH){CH(py)CH$_3$}]OTf (8). A sealable NMR tube was charged with **5** (5.3 mg, 0.009 mmol), pyO (2.6 mg, 0.028 mmol), and $(Me_3Si)_2O$ (<1 μL). The tube was chilled to −77 °C, and CD_2Cl_2 (0.4 mL) was vacuum transferred in. The tube was sealed with a torch, and the contents were mixed at −77 °C. The ^{1}H NMR spectrum was examined starting at −80 °C and while slowly warming the sample. After 4 h at −47 °C all of **5** had converted to **8**. ^{1}H NMR (CD_2Cl_2; −47 °C): δ 8.55 (q, 1H, J_{HH} = 5.3); 8.06, 7.91, 7.88, 7.46 (each d, 1H, pz; two of the pyrazole doublets were not located due to overlapping peaks); 6.53, 6.34, 6.07 (each t, 1H, pz); 2.06 (d, 3H, J_{HH} = 5.5). ^{13}C{^{1}H} NMR (CD_2Cl_2; −47 °C): δ 142.5, 142.0, 140.8, 139.9, 135.2, 134.4, 132.2, 129.1, 126.7 (pyrazoles and pyridine); 108.0, 107.7, 106.3 (pyrazoles); 50.2 (Re*C*HCH$_3$); 24.9 (ReCH*C*H$_3$).

[(HBpz$_3$)Re(O)(OH){CH(SMe$_2$)CH$_3$}]OTf (9). A sealable NMR tube was charged with **5** (6.2 mg, 0.010 mmol) and $(Me_3Si)_2O$ (<1 μL). CD_2Cl_2 (0.4 mL) was vacuum transferred in. Me_2SO (2.3 μL, 0.011 mmol, 1.1 eq) was added at −77 °C via syringe. The tube was freeze−pump−thawed three times, then the tube was sealed with a torch and the contents were mixed at −77 °C. The ^{1}H NMR spectrum was examined starting at −82 °C and while slowly warming the sample. After 6 h at −43 °C, **5** was no longer observed while **9a**,**b** were present; the solution was lavender at this point. ^{1}H NMR (CD_2Cl_2; −43 °C). **9a**: δ 7.98, 7.92, 7.75, 7.63 (each d, 1H, pz); 7.51 (d, 2H, pz); 6.49, 6.48, 6.11 (t, 1H, pz); 5.84 (q, 1H, J_{HH} = 7, ReC*H*CH$_3$); 3.03, 2.68 (each s, 3H, S[C*H*$_3$][C*H*′$_3$]); 1.95 (d, 3H, J_{HH} = 7, ReCHC*H*$_3$). **9b**: δ 8.12, 7.97, 7.93, 7.91, 7.86, 7.51 (each d, 1H, pz); 6.56, 6.46, 6.07 (each t, 1H, pz); 5.83 (q, 1H, J_{HH} = 7, ReC*H*CH$_3$); 3.03, 2.84 (each s, 3H, S[C*H*$_3$][C*H*′$_3$]); 1.67 (d, 3H, J_{HH} = 7, ReCHC*H*$_3$). There is also a small broad peak at 15.25 ppm. Decoupling experiments showed coupling between the doublet at 1.95 ppm and the quartet at 5.84 ppm in **9a**, and similarly between the 1.67 and 5.83 ppm resonances in **9b**. ^{13}C{^{1}H} NMR for the mixture of **9a**,**b** (CD_2Cl_2; −49 °C): δ 148.0, 146.4, 144.5, 144.3, 144.1, 143.0, 139.1, 138.7, 138.0, 135.7, 135.4, 108.9, 108.1, 108.0, 107.7, 106.4, 105.9 (pyrazoles); 45.1, 41.8 (Re*C*HCH$_3$); 28.5, 24.8 (ReCH*C*H$_3$); 22.0, 21.5, 20.8, 20.3 (S[*C*H$_3$]-[*C*′H$_3$]).

[(HBpz$_3$)ReO(Et)(py)][OTf] and **[(HBpz$_3$)ReO(*n*-Bu)(py)][OTf]** were formed quantitatively (^{1}H NMR) upon addition of pyridine (1 eq) to **5** in CD_2Cl_2 or **6** in $CDCl_3$, respectively. For [(HBpz$_3$)ReO(Et)(py)][OTf]: ^{1}H NMR (CD_2Cl_2): δ 8.12, 7.99, 7.93, 7.71, 7.62, 7.07 (each d, 1H, pz); 6.64, 6.61, 6.20 (each t, 1H, pz); 8.11 (d, 2H, 2-py); 8.10 (m, 1H, 4-py); 7.96 (t, 2H, 3-py); 7.22 (m, 1H, ReC*H*H′CH$_3$); 5.97 (m, 1H, ReCH*H*′CH$_3$); 1.98 (t, 3H, ReCH-H′C*H*$_3$, J_{HH} = 6). For [(HBpz$_3$)ReO(*n*-Bu)(py)][OTf]: ^{1}H NMR ($CDCl_3$): δ 8.1 (m, 5H, pyridine); 8.07, 7.95, 7.87, 7.65, 7.61, 7.04 (each d, 1H, pz); 7.04, 6.32 (each t of d, 1H, ReC*HH*′CH$_2$−, J_{HH} = 12, $J_{HH'}$ = 5); 6.61, 6.58, 6.17 (each t, 1H, pz); 2.30, 1.62 (each m, 1H, ReCH$_2$C*HH*′CH$_2$−); 1.40 (m, 2H, Re(CH$_2$)$_2$C*H*$_2$CH$_3$); 0.92 (t, 3H, Re(CH$_2$)$_3$C*H*$_3$, J_{HH} = 7).

Oxygen Labeling Experiments. (HBpz$_3$)ReO(Et)OTf (4.6 mg, 0.008 mmol) was placed in a flame dried 10 mL round bottom flask and dissolved in $CDCl_3$ (0.5 mL). $Me_2S^{18}O$ (1.8 μL, 0.024 mmol) was added via microliter syringe. The flask was freeze−pump−thawed and allowed to stand for 30 min. The volatiles were then vacuum transferred to a flame-dried 5 mL collection flask. The flask's needle valve was replaced by a septum. GC−MS were recorded from three runs at a column temperature of 30 °C. The small sample of the residue remaining in the reaction flask was packed into a capillary and volatilized into the mass spectrometer at 130 °C. The observed fragmentation patterns were analyzed using the nonlabeled fragmentation and isotope patterns for each species to determine the amount of label incorporation.

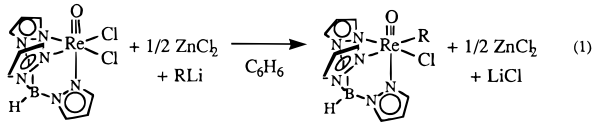
X-ray Structure Determination of (HBpz$_3$)ReO(*n*-Bu)Cl (3). Slow diffusion of pentane layered on a solution of **3** in benzene at ca. 10 °C deposited dark blue rhombohedral crystals. A crystal was glued to the tip of a glass fiber in air and data were collected on an Enraf-Nonius CAD4 diffractometer (Table 1). A semiempirical absorption correction was applied and the structure was solved by direct methods using the SHELXTL PC program. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in calculated positions.

Table 1. Crystallographic Data for (HBpz$_3$)ReO(*n*-Bu)Cl (**3**)

empirical formula	$C_{13}H_{19}BClN_6ORe$
crystal size (mm)	0.25 × 0.25 × 0.35
space group	$P2_1/n$
unit cell dimens	a = 7.880(2) Å
	b = 16.270(3) Å
	c = 13.980(3) Å
	β = 105.10(3)°
volume (Å^3)	1730.5(7)
Z	4
density (g/cm^3, calcd)	1.949
absorption coefficient (cm^{-1})	71.88
transmission factors	0.941−0.838
radiation	Mo Kα (λ = 0.710 73 Å)
monochromator	highly oriented graphite crystal
temperature (K)	183
2θ range (deg)	2.0 to 50.0
index ranges	$0 \le h \le 9$, $0 \le k \le 19$, $-16 \le l \le 16$
no. of reflns colld	3270
no. of independent reflns	3038
no. of obsd reflns ($F > 4\sigma(F)$)	2490
no. of params	204
final R, R_w (obsd data)	3.34%, 3.79%
goodness of fit	1.19

Results

Synthesis of (HBpz$_3$)ReO(R)(Cl) and (HBpz$_3$)ReO(R)-(OTf). Dialkyl zinc reagents react with (HBpz$_3$)ReOCl$_2$[13] in benzene to replace one of the chlorides by an alkyl ligand, forming (HBpz$_3$)ReO(R)Cl (R = Me, Et, *n*-Bu; eq 1).[18] Dialkyl

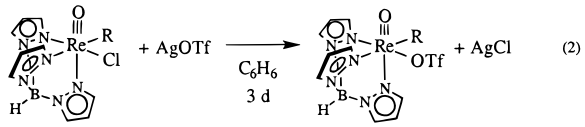


(1)

R = Me(**1**), *n*-Bu(**3**)

compounds are not observed. This preparation, generating the zinc reagents in situ from 2RLi + $ZnCl_2$, is an extension of the previously reported synthesis of (HBpz$_3$)ReO(Et)Cl (**2**) with commercial $ZnEt_2$.[14] Low yields are obtained (25−36%) apparently because reduction of the rhenium is competitive with alkylation. The use of alkyllithium or Grignard reagents rather than ZnR_2 leads only to decomposition, presumably because these are stronger reductants. Reduction is a common problem in the alkylation of even mildly oxidizing metal centers and necessitates the approach used here of alkylation at rhenium(V) followed by oxidation to rhenium(VII). The reaction with 2MeLi/$ZnCl_2$ requires 3 days at room temperature, while the more active 2*n*-BuLi/$ZnCl_2$ is best done with slow addition to a cooled solution of (HBpz$_3$)ReOCl$_2$. Syntheses of analogous *tert*-butyl and isopropyl compounds were not successful. Compounds **1**−**3** are purified by chromatography on silica gel and are isolated as purple, air stable solids.

The chloride ligand of compounds **1**−**3** is cleanly removed by 1.05 equiv of AgOTf[18] to give the alkyl triflate complexes (HBpz$_3$)ReO(R)(OTf) (R = Me (**4**), Et (**5**), *n*-Bu (**6**); eq 2).



(2)

OTf = OSO_2CF_3 R = Me(**4**), Et(**5**), *n*-Bu(**6**)

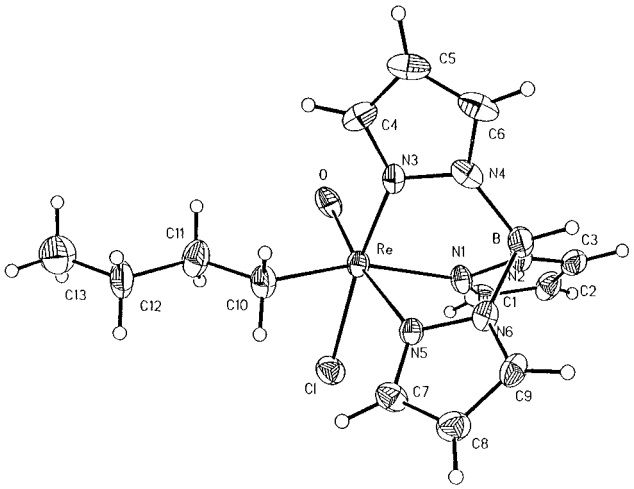


Figure 1. ORTEP drawing of (HBpz$_3$)ReO(*n*-Bu)Cl (**3**).

Table 2. Bond Lengths (Å) and Angles (deg) for (HBpz$_3$)ReO(*n*-Bu)(Cl) (**3**)

Re−Cl	2.342(2)	Re−O	1.705(5)
Re−N(1)	2.114(6)	Re−N(3)	2.104(6)
Re−N(5)	2.280(5)	Re−C(10)	2.112(8)
C(10)−C(11)	1.540(11)	C(11)−C(12)	1.524(12)
C(12)−C(13)	1.498(13)		
O−Re−Cl	103.4(2)	C(10)−Re−Cl	85.7(2)
O−Re−C(10)	101.4(3)	C(10)−Re−N(1)	157.1(3)
O−Re−N(1)	101.5(2)	C(10)−Re−N(3)	90.5(3)
O−Re−N(3)	91.1(2)	C(10)−Re−N(5)	80.6(3)
O−Re−N(5)	167.7(2)	Re−C(10)−C(11)	112.2(5)
C(10)−C(11)−C(12)	113.7(6)	C(11)−C(12)−C(13)	115.2(7)

The reactions require 3−5 days, but excess AgOTf cannot be used because of subsequent separation problems. The triflate compounds are air sensitive and do not survive chromatography but can be isolated as pure dark purple (**4**), dark blue (**5**), or lavender (**6**) solids after multiple recrystallizations with pentane/toluene.

The composition and stereochemistry of **1**−**6** are indicated by their NMR, IR, and mass spectra, elemental analyses, and an X-ray crystal structure of (HBpz$_3$)ReO(*n*-Bu)Cl (**3**). The ^{1}H NMR spectra all indicate molecular C_1 symmetry, showing three inequivalent pyrazole rings. The protons on the alkyl α-carbon appear significantly down field at δ 5−8 ppm. IR bands and ^{19}F chemical shifts of **4**−**6** suggest a coordinated, rather than ionic, triflate ligand.[21] Compound **3** crystallizes as discrete molecules in the monoclinic space group $P2_1/n$ (Figure 1, Tables 1 and 2). The short rhenium−oxo bond distance (1.705(5) Å) and large trans influence (Re−N1, N3 = 2.114(6), 2.104(6) Å vs Re−N5 = 2.280(5) Å) are typical of related compounds.[22] The butyl group shows no evidence of disorder, apparently because the butyl groups of neighboring molecules are nestled in between the pyrazole rings of each other (Figure 2), which effectively "locks" them in place.

The alkyl chloride compounds (**1**−**3**) are fairly robust, decomposing only on prolonged exposure to silica gel or over more than a week at 80 °C in benzene solution. The alkyl triflate compounds (**4**−**6**) are considerably more reactive, decomposing in air in under 1 min while in solution and within a few minutes as a solid. Neither **5** nor **6** shows any evidence,

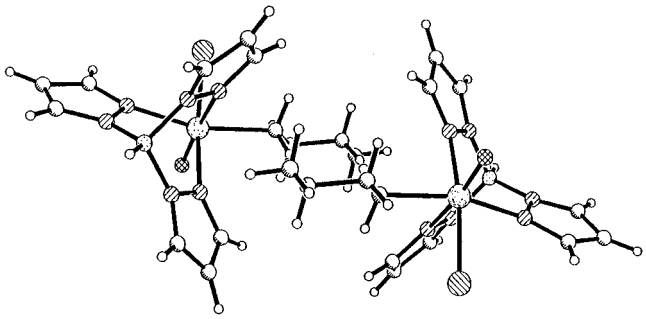
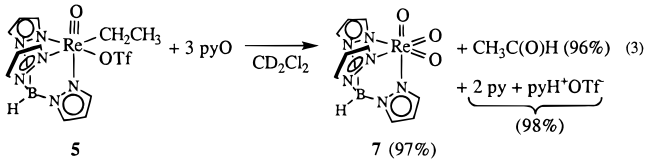


Figure 2. ORTEP drawing of two molecules of (HBpz$_3$)ReO(*n*-Bu)-Cl (**3**) showing the packing of the two butyl groups.

by ^{1}H NMR, of β-hydrogen elimination on thermolysis. The triflate ligands are easily displaced by coordinating solvents, such as THF, CH_3CN, and pyridine, and by chloride. The addition of ^{n}Bu$_4$NCl to a CD_3CN solution of **5**, for instance, results in the formation of **2** as indicated by ^{1}H NMR.

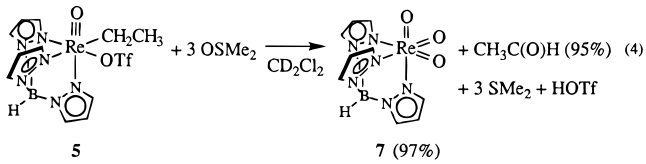
Oxidation of Alkyl Triflate Complexes. The ethyl triflate complex **5** reacts swiftly with 3 equiv of pyridine *N*-oxide (pyO) in C_6D_6, CD_2Cl_2, or $CDCl_3$ to give initially a light brown solution which becomes colorless in about 1 min. ^{1}H NMR spectra of the reaction mixtures show the essentially quantitative formation of (HBpz$_3$)ReO$_3$ (**7**), acetaldehyde, and pyridine/pyridinium triflate (eq 3; yields vs the internal standard Me$_3$-



(3)

SiOSiMe$_3$). Similarly, the oxidation of **6** with pyO gives **7**, *n*-butyraldehyde, and pyridine/pyridinium triflate. The rates of these reactions are unaffected by the presence of excess pyO. With less than 3 equiv of pyO, the same products are observed, though in lower yields, along with the pyridine adducts [(HBpz$_3$)ReO(R)py][OTf] (R = Et, *n*-Bu) and trace amounts of a few other HBpz$_3$ compounds. The adducts are rapidly formed when **5** and **6** are reacted with pyridine. The oxidation of **4** with pyO is less quantitative. In CD_2Cl_2 or $CDCl_3$ solution, reaction mixtures turn brown and ^{1}H NMR spectra show 85% yield of **7** but only 37% yield of formaldehyde (whose integral decreases over time). In C_6D_6, an insoluble gray oil forms along with **7**, py + pyH$^+$OTf$^-$, and a trace of formaldehyde; most of the material is not observable by ^{1}H NMR.

Reactions of **5** with 3 equiv of Me$_2$SO (DMSO) are very similar to those with pyO. In C_6D_6, CD_2Cl_2, or $CDCl_3$, there is immediate formation of a light brown solution which becomes colorless within minutes. ^{1}H NMR spectra show near quantitative formation of **7** and acetaldehyde, along with 3 equiv of SMe$_2$ and 1 equiv of triflic acid (eq 4). The products were



(4)

identified by comparison of ^{1}H NMR spectra and by spiking the reaction mixture with authentic samples. The resonance at δ 13.6 ppm grows in intensity and shifts downfield on addition of additional HOTf to the reaction mixture. This peak is assigned to triflic acid because it is close to the resonance for

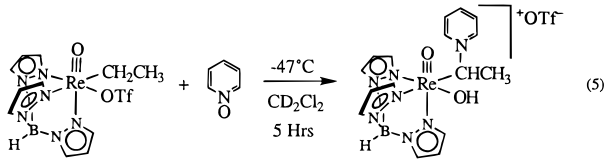
(21) (a) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17−33. (b) Conry, R. R.; Mayer, J. M. *Organometallics* **1993**, *12*, 3179−3186.

(22) References 10, 13, 14, and: (a) Herrmann, W. A.; Marz, D.; Herdtweck, E.; Schafer, W.; Kneuper, H. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 462. (b) Pearlstein, R. M.; Davidson, A. *Polyhedron* **1988**, *7*, 1981. (c) Mayer, J. M. *Inorg. Chem.* **1988**, *27*, 3899−3903.

free HOTf in CD_2Cl_2 (δ 15.3) although it is likely to be interacting with other compounds present in the solution.

Oxidation of **6** by 3 equiv DMSO gives moderate yields of **7** (73%), *n*-butyraldehyde (69%), and SMe_2 within 1 min, but the remaining products are not observed. Over the course of 5 days, the remaining mass is observed in the form of butyric acid and a new, as yet unidentified, $HBpz_3$ product with C_{3v} symmetry. During this time ~10% of the *n*-butyraldehyde is oxidized to butyric acid. The reaction of **4** with 3 equiv of DMSO in CD_2Cl_2 or $CDCl_3$ immediately forms **7**, formaldehyde, and a number of unidentified ($HBpz_3$) products. The amount of **7** continues to increase over the course of the reaction (about 8 h at room temperature) to finally form a 70−80% yield of **7**.

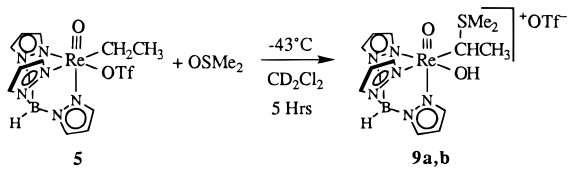
At low temperatures, an intermediate is observed in the reaction of **5** with pyO in CD_2Cl_2. Solid **5** and pyO are mixed and quickly cooled to −77 °C because the solids visibly react within 1 min at 25 °C. If cooling is too slow, small amounts of **7** and acetaldehyde are observed. At −70 °C in the NMR probe, **5** slowly decays and a new species, **8**, grows in. Conversion is complete after 4 h at −47 °C. The ^{1}H and ^{13}C NMR spectra of **8** at −47 °C show three inequivalent pyrazoles, indicating C_1 symmetry. The proton spectrum displays a doublet (J_{HH} = 5 Hz) for three hydrogens at 2.05 ppm coupled to one hydrogen (quartet, δ 8.55), indicating a $CHCH_3$ unit. In addition to these signals, there is an equivalent of pyridine that is distinct from free pyO and the averaged resonance for py + pyH^+ (there is always at least a trace of pyH^+OTf^- present from the solid-phase reaction). When ^{15}N-labeled pyO is used, the singlet in the $^{13}C\{^1H\}$ NMR spectrum corresponding to the methyne carbon (δ 50.2) becomes a doublet with J_{NC} = 9 Hz. This coupling is similar to nitrogen−carbon couplings in pyridine ylide complexes[23] and indicates the presence of a C−N bond. These data show the presence of a $CH_3CH-NC_5H_5$ unit, derived from the ethyl group in **5**. The J_{NC} is too large for a pyridine *N*-oxide adduct, rather than a pyridine complex. Complex **8** is therefore assigned as a rhenium(V) pyridine ylide−hydroxide complex, [($HBpz_3$)ReO(OH){CH(py)CH_3}]OTf (eq 5). The pyridine-ylide ligand can also be viewed as a pyridine-trapped carbene ligand (see below).



5 **8** (5)

Compound **8** is formed similarly with 1 equiv of pyO or in the presence of excess oxidant. It is stable for at least 17 h at −47 °C. On warming a solution of **8** to room temperature with at least 2 equiv of pyO, the reaction proceeds to form the expected products of **7**, acetaldehyde, and pyridine/pyridinium triflate. If the reaction is held at approximately −34 °C for 5 h or more, a trace amount of *cis*-2-butene (2−5% of the possible organic products) is also formed. Running this reaction in the presence of acetaldehyde-d_4 does not lead to any incorporation of the labeled aldehyde in to the *cis*-2-butene. Attempts to trap **8** and form a more stable ylide complex, using HCl, H_2O, and various phosphines and amines, were not successful.

A related intermediate is observed on monitoring the reaction of **5** with DMSO at low temperature. Conversion to new product (**9a**) begins to be observed on warming a solution of **5** and DMSO in CD_2Cl_2 from −77 to −65 °C. At −43 °C, **5** fully converts to two apparently isomeric species, **9a**,**b**. The two species are stable for at least 14 h at this temperature and maintain a constant 2:3 ratio. ^{1}H NMR spectra for both **9a**,**b** each show resonances for a $HBpz_3$ ligand in C_1 symmetry and a doublet/quartet pattern indicative of a $CHCH_3$ group. In addition, both species have a pair of singlets, which are assigned as diastereotopic methyls of a SMe_2 group since they are not present in reactions with DMSO-d_6. These data are consistent with assignment of **9a**,**b** as diastereomers of a hydroxide−sulfur ylide complex, [($HBpz_3$)ReO(OH){$CH(SMe_2)CH_3$}]OTf (eq 6).



5 **9a,b** (6)

Diastereomers are possible because both the rhenium and the ylide carbon are chiral centers. Again, the ylide ligand can be viewed as a dimethyl sulfide-trapped carbene group. No evidence for a second isomer is observed for **8**; perhaps the greater size of pyridine destabilizes one isomer in this case.

The formation of **9a** + **9b** consumes 1 equiv of DMSO and produces no free Me_2S. Reaction of **5** with 3.1 equiv of DMSO-d_6 and 2.7 equiv of $S(CH_3)_2$ generates **9a**,**b** initially with almost entirely protium in the SMe_2 sites, as judged from ^{1}H NMR integration. As the reaction proceeds, the intensities of the $S(CH_3)_2$ resonances in **9a**,**b** decrease, equilibrating at 70% of the expected intensity based upon the methyl and pyrazole intensities of the complex. The solution at the end of the reaction contains a total of 3.7 equiv of SMe_2, the 2.7 equiv of $S(CH_3)_2$ added initially and 1 equiv of $S(CD_3)_2$ formed from DMSO-d_6. Thus the SMe_2 is 2.7/3.7 or 73% $S(CH_3)_2$ (the rest deuterated), in very good agreement with the observed integrals for bound SMe_2 in **9a**,**b**. No protio-DMSO is observed. These data indicate that **9a**,**b** contain a bound Me_2S group, and not bound DMSO. The **9a**,**b** are formed initially with $S(CH_3)_2$ because that is the major sulfide present in solution. At the end of the reaction, the isotopic composition of **9a**,**b** is equal to that in the solution, implying that bound SMe_2 exchanges with free SMe_2 in solution. Attempts to replace the SMe_2 group in **9** with amines or phosphines were unsuccessful.

The proposed ylide structures for **8** and **9** are much more reasonable than other formulations. It is not clear how pyridine or Me_2S would coordinate to rhenium in a dioxo-alkylidene compound or an η^1- or η^2-bound acetaldehyde complex. The chemical shifts for the ReCHR group (^{1}H: δ 5−9; ^{13}C: δ 40−50) do not resemble those of alkylidene nor η^1-bound aldehyde complexes, which typically have much lower field signals.[24] An unusual alkoxide formulation, [($HBpz_3$)ReO{OCH(L)-CH_3}]$^+$ could be consistent with the spectra but would require a coordinatively unsaturated rhenium center. Unfortunately, there is no direct evidence for the presence of the proposed hydroxide ligand in **8** or **9**, as the OH proton was not observed. It could easily be masked, given the number of other signals in the spectra, or be broadened or averaged by exchange with the acidic proton of pyH^+OTf^-.

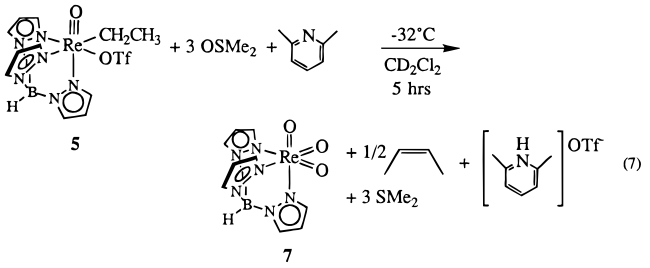
Warming **9a**,**b** in the presence of DMSO causes conversion to ($HBpz_3$)ReO_3 (**7**), acetaldehyde, HOTf, and 3Me_2S, just as observed in ambient temperature reactions. Conversion is slow at −30 °C but complete upon reaching room temperature. The solution is light brown after the tube is removed from the probe,

(23) (a) Lichter, R. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 5218. (b) Vitorge, M. C.; Chenon, M. T.; Coupry, C.; Lumbroso-Bader, N. *Org. Magn. Reson.* **1983**, *21*, 20−23.

(24) (a) Reference 2c, p 135. (b) Gladysz, J. A.; Huang, Y. H. *J. Chem. Educ.* **1988**, *65*, 298 and references therein.

turning clear after a few minutes. The presence of added Me_2S does not seem to affect the rates of formation of **9a**,**b**, but it does slow the conversion of **9** to $(HBpz_3)ReO_3$ (**7**) and acetaldehyde. Like **8** in the reaction of **5** with pyO, **9a**,**b** are kinetically competent to be intermediates for the oxidation of **5** by DMSO to **7**.

The oxidation of **5** by DMSO at room temperature is not affected by the presence of 2,6-lutidine, except that 2,6-lutidinium triflate is observed instead of HOTf. When the reaction is run with lutidine at low temperatures, however, **9** is not observed and *cis*-2-butene is formed instead of acetaldehyde. Starting at −67 °C, and going to completion after 4 h at −32 °C, **5** forms **7** (89%), *cis*-2-butene (83% of the possible organic products), 4.4 equiv of DMS, and 2,6-lutidinium triflate (eq 7).



(7)

Only a trace amount of acetaldehyde (2%) is observed, and no *trans*-2-butene is detected by ^{1}H NMR. Oxidation of **6** under the same conditions gives *cis*-4-octene (80% yield), and **4** generates small amounts of ethylene. In contrast, addition of 2,6-lutidine to low-temperature pyO reactions does not affect the product distributions.

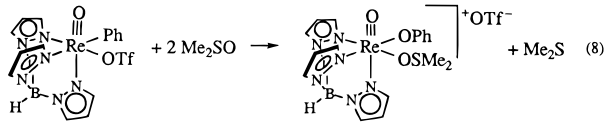
Use of $Me_2S^{18}O$ in the reaction with **5** was explored as a way to follow the mechanism of the oxidation. If the oxygen atom in the acetaldehyde product derives purely from DMSO, then 50 ± 2% labeled DMSO should give 50%-labeled CH_3-CHO, and $HBpz_3ReO_3$ (**7**) with, on average, one ^{18}O (2 × 50%). If the acetaldehyde is formed statistically from one DMSO and the original rhenium-oxo ligand, the prediction is CH_3CHO-25%-^{18}O and an average of 1.25 ^{18}O atoms in **7**. It has previously been found that the oxygen isotopomers of **7** rapidly scramble so only average enrichments are available.[13b] The results, from 11 experiments, are that the acetaldehyde is 29 ± 3% ^{18}O enriched and that the product **7** has an average of 0.91 ± 0.03 ^{18}O atoms. This is a statistical result, that all four oxygen atoms in the products have the same enrichment of 30%. There is therefore some scrambling process, and the results are not mechanisticaly informative. In addition, there is a loss of label that we cannot account for, as the average enrichment should be 50% × (3/4) = 37.5%. Control experiments run using various combinations of Me_2S, HOTf, and ^{18}O-labeled and unlabeled DMSO, acetaldehyde, and $(HBpz_3)ReO_3$ showed no label scrambling or label loss within the time scale of the experiment. Therefore loss and/or scrambling of the label does not occur by a combination of the products—it must happen during the reaction. The possibility of label loss occurring because of interaction with the glass vessel seems minimal given the consistency of results over so many runs.

Oxidations of **4**−**6** with oxygen atom donors other than pyO and DMSO were less successful. Reaction with Me_3NO produces **7** and acetaldehyde in reasonable but lower yields (63% and 45%, respectively). No reaction is observed with dimethyl sulfone (Me_2SO_2), N_2O, or dry O_2. Reaction of **5** with ethylene oxide in CD_2Cl_2 or $CDCl_3$ results in the formation of a moderately stable epoxide adduct, which will be reported elsewhere,[25] but no alkyl oxidation is observed. Similarly $OPPh_3$ merely displaces the triflate ligand in **5** to form an adduct. Reaction of **5** with 3 equiv of 2,6-lutidine *N*-oxide gives nearly quantitative formation of **7** (94%), acetaldehyde (96%), and lutidine/lutidinium triflate, but the reaction takes nearly 1 h to go to completion at ambient temperatures. During the course of the reaction starting material can still be observed along with the newly formed products, as the triflate ligand is not replaced by either 2,6-lutidine or acetaldehyde.

The ethyl chloride complex **2** is much less reactive than the triflate **5**, with either pyO or DMSO. With 3.4 equiv of pyO in $CDCl_3$ or C_6D_6 there is no apparent reaction at ambient temperatures. Heating a $CDCl_3$ solution at 81 °C for 39 h gives some **7** (29% yield) and acetaldehyde (21%) and acetic acid (18%; yields by ^{1}H NMR), along with decomposition. The reaction with DMSO is very similar, either heating **2** plus 4 equiv of DMSO in $CDCl_3$ or heating **2** in neat DMSO-d_6.

Discussion

Reaction of $(HBpz_3)ReO(Et)OTf$ (**5**) with oxygen atom donors results in oxidation of the ethyl ligand to acetaldehyde or, under certain conditions, *cis*-2-butene. The methyl and butyl derivatives behave similarly. We have previously used this approach—oxygen atom transfer to a complex containing an oxidizable group—to convert a phenyl ligand to a phenoxide and alkoxide ligands to aldehydes or ketones (*e.g.*, eqs 8 and 9; both oxidations proceed with either Me_2SO or pyO as the oxidants).[10,11] The mechanisms of these processes provide a framework for discussion the mechanism of alkyl oxidation in this system.



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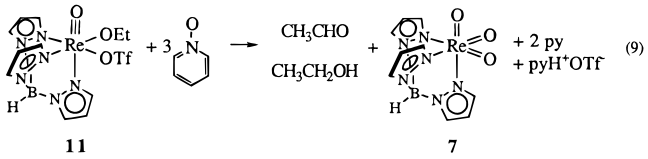
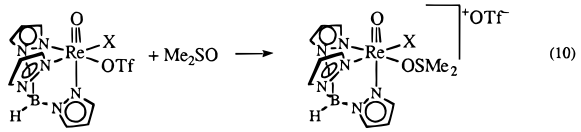
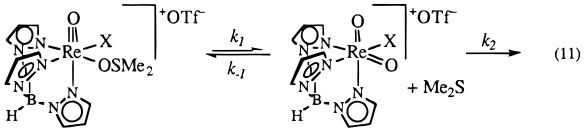


(9)

When DMSO oxidizes **10** or **11**, an initial adduct is observed with displacement of triflate (eq 10; X = Ph, OEt). The adducts are in rapid equilibrium with a rhenium(VII) dioxo cation (eq 11): k_1 = 3 s^{-1} (**10**), 8 s^{-1} (**11**) at 25 °C. It is in this dioxo cation that oxidation of the *cis* ligand occurs (k_2).



(10)



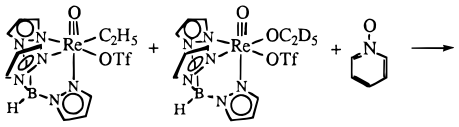
(11)

No DMSO adduct is observed on oxidation of the ethyl triflate complex **5**, but all evidence suggests that the pattern of eqs 10 and 11 holds in this case as well. Related adducts are readily

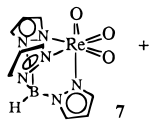
(25) DuMez, D. D.; Mayer, J. M. Work in progress.

formed by displacement of the triflate ligand in **5** by Ph_3PO and ethylene oxide. As found for **10** and **11**, **5** does not react with N_2O or O_2. Both are thermodynamically more powerful oxidants than pyO and DMSO, but are poorer ligands, apparently unable to displace triflate. Ph_3PO and Me_2SO_2 are not thermodynamically strong enough oxygen atom donors to generate a significant concentration of a rhenium(VII) dioxo complex: both are >10 kcal/mol less reactive than DMSO,[8] and the equilibrium constant for Me_2S loss from the phenyl derivative [TpReO($OSMe_2$)Ph]OTf is 10^{-5} M ($\Delta G^{\ddagger} = +6.5$ kcal/mol).[10] Use of pyO, a 15 kcal/mol more potent oxygen atom donor than DMSO, allows low-temperature observation of the dioxo phenyl complex from **10**. The greater driving force makes the dioxo complex the favored side of the equilibrium analogous to the first part of eq 11. Formation of the dioxo ethyl complex [($HBpz_3$)ReO_2(Et)]OTf (**A**) should be similar to the phenyl derivative, yet the ethyl compound is not observed. The lack of observation of either **A** or the DMSO adduct is due to the fast subsequent reaction of **A**—a large k_2 in eq 11—in the ethyl case.

Our initial mechanistic hypothesis was that the dioxo ethyl complex **A** reacts by migration of the ethyl group from rhenium to oxygen, as occurs in the phenyl derivative (eq 8).[10] Such a [1,2] migration would lead to an intermediate ethoxide complex, which should be similar if not identical to the ethoxy triflate complex **11**. However, independent reactions of **11** (eq 9)[11] show that an ethoxide complex is *not* an intermediate in the oxidation of **5**. Oxidations of **11** by pyO and DMSO form ethanol in addition to the acetaldehyde and **7**, while no ethanol is observed in oxidations of **5**. The oxidation of **11** with DMSO forms an adduct which decays over days at room temperature, while oxidation of **5** by DMSO is complete within minutes. Finally, reaction of a mixture of **5** and ($HBpz_3$)Re(O)(OC_2D_5)(OTf) (**11**-d_5) with pyO gives a mixture of CH_3CHO and CD_3CDO as the aldehyde products but C_2D_5OD as the only alcohol product (by ^1H and ^2H NMR, eq 12). If the ethoxide



5 **11**d_5

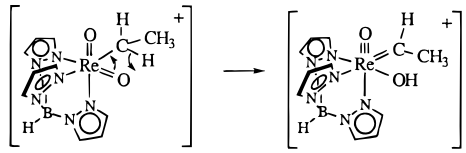


7

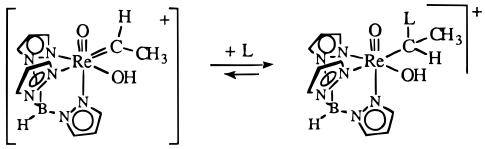
$$+ CH_3CHO + CD_3CDO + CD_3CD_2OD + py + pyD^+OTf \quad (12)$$

were an intermediate along the reaction pathway, some protioethanol should have been produced. The conclusion that alkyl migration to an oxo ligand is not on the pathway for oxidation of **4**−**6** does not imply that this step is unfavorable. Rather the putative dioxo ethyl intermediate **A** has an alternative, more facile reaction pathway.

The nature of the further reaction of **A** is indicated by the trapped carbene complexes **8** and **9**. These species are kinetically competent to be intermediates, as **5** is completely consumed in their formation at low temperature and they progress on to the same products as observed in ambient temperature reactions of **5**. The putative dioxo ethyl intermediate **A** is apparently converted to a carbene species by transfer of an α hydrogen from the ethyl ligand to a neighboring oxo group (eq 13). The resulting cationic carbene complex [($HBpz_3$)ReO(OH)($CHCH_3$)]OTf (**B**) is electrophilic at carbon and is rapidly trapped by pyridine or Me_2S to give **8** or **9** (eq 14). The observed equilibration of bound and free SMe_2 (see above) indicates that this trapping is reversible.



A **B** (13)



B **8,9** (14)

Complex **B** can be thought of as an alkylidene−rhenium(VII) complex, analogous to [($HBpz_3$)ReO_2X]$^+$ species. Alkylidene ligands are not usually electrophilic, but this one should be more electrophilic than oxo ligands in [($HBpz_3$)ReO_2X]$^+$ which have been shown to be quite electrophilic.[10,11] Alternatively, **B** can be thought of as a Fischer carbene−rhenium(V) complex, formed by hydride transfer from the ethyl ligand. Hydride transfer has been suggested as the mechanism for ethoxide oxidation (eq 9).[11] Cationic Fischer carbenes are often strongly electrophilic and trapped species such as **8** or **9** are not uncommon.[26] For example, [$CpFe(CO)_2(CH_2SMe_2)$]BF_4 is similarly in equilibrium with a cationic methylene complex.[26c] Such trapped species display α-proton chemical shifts similar to those of the corresponding alkyl group, with δ (FeCH_2SMe_2) only 0.3 ppm downfield from the corresponding FeCH_3. Consistent with this, the methyne protons for **8** (δ 8.55) and **9a**,**b** (δ 5.8) are not too far from the methylene protons in ($HBpz_3$)ReO(Et)OTf (δ 7.94, 6.61).

The formation of **7** and acetaldehyde from **9** to appears to involve the free carbene ligand, as the decay of **9** is inhibited by added Me_2S indicating pre-equilibrium loss of Me_2S. There are two reasonable pathways for C−O bond formation from an oxo−carbene complex such as **B**. Coupling of carbene and oxygen ligands could form an η^2-bound acetaldehyde complex. The reverse of this process, cleavage of a bound ketone into oxo and alkylidene ligands, has been reported in a tungsten system.[27] An alternative mechanism, which we favor, involves attack of DMSO or pyO on the carbene ligand. The observed exchange of carbene-bound and free Me_2S suggests that Me_2S could also exchange with DMSO, which should give an acetaldehyde complex. Similar transformations have been proposed for the conversions of rhenium methylene complexes to η^2-formaldehyde compounds: [CpRe(NO)(PPh_3)(=CH_2)]$^+$ plus iodosylbenzene gives [CpRe(NO)(PPh_3)(η^2-CH_2=O)]$^+$ [28] and [Cp_2Re=CH_2]$^+$ plus pyO gives [Cp_2Re(η^2-CH_2=O)]$^+$.[29] Loss of acetaldehyde and oxidation of the rhenium center by additional pyO or DMSO would generate the observed products. The proposed pathway for oxidation of **5** by DMSO is summarized in Scheme 1.

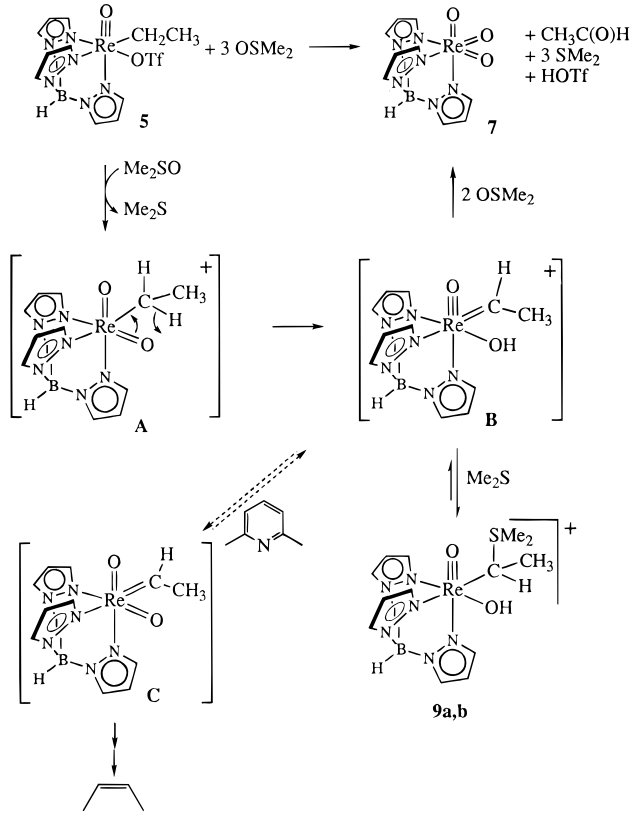
(26) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Valley, CA, 1987; pp 133−135. (b) Rhenium examples: Nakazawa, H.; Johnson, D. L; Gladysz, J. A. *Organometallics* **1983**, *2*, 1846−1851. McCormick, F. B.; Gleason, W. B.; Zhao, X.; Heah, O. C.; Gladysz J. A. *Organometallics* **1986**, *5*, 1778−1785. O'Connor, E. J.; Helquist, P.; Brandt, S. *J. Am. Chem. Soc.* **1987**, *109*, 3739−3747. (c) Helquist, P.; Brandt, S. *J. Am. Chem. Soc.* **1979**, *101*, 6473.

(27) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298.

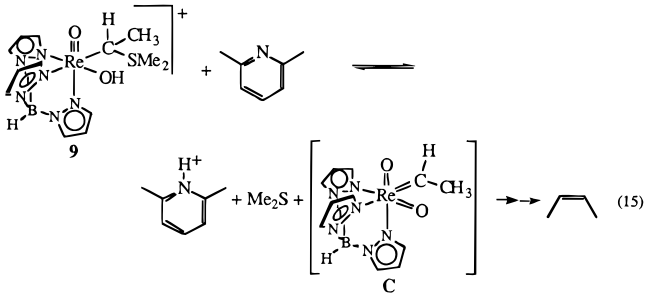
(28) Gladysz, J. A.; Buhro, W. E.; Georgiou, S.; Fernandez, J. M.; Patton, A. T.; Strouse, C. E. *Organometallics* **1986**, *5*, 956.

(29) Radzewich, C.; Heinekey, D. M. Personal communication, 1996.

Scheme 1. Proposed Mechanism for the Oxidation of $(HBpz_3)Re(O)Et(OTf)$ by Me_2SO



In the presence of the noncoordinating base 2,6-lutidine, the reaction of **5** and DMSO at low temperatures gives *cis*-2-butene instead of acetaldehyde. Similarly, **6** gives *cis*-4-octene. This formation of alkenes supports the intermediacy of carbene species. The *cis*-2-butene does not arise from a Wittig-like reaction of a rhenium alkylidene with acetaldehyde, as no deuterium is incorporated in the alkene when the reaction is run in the presence of added acetaldehyde-d_4. Most likely the *cis*-2-butene arises from the coupling of two methylcarbene (ethylidene) species. Formation of ethylene on coupling of methylene ligands is a common reaction, although ethylidene ligands more often rearrange intramolecularly to ethylene complexes by a [1,2] hydrogen shift.[30] The effect of 2,6-lutidine can be explained by shifts in an equilibrium between the hydroxy-trapped carbene complex **9** and the dioxo alkylidene compound **C** (eq 15). **C** would be analogous to the stable trioxo compound **7**, and could couple with itself to give *cis*-2-butene. In oxidations by DMSO, 2,6-lutidine acts as a base to deprotonate **9** with loss of the weakly binding Me_2S. Because 2,6-lutidine is too bulky to bind to the carbene, the equilibrium is shifted toward **C**, leading to 2-butene. In oxidations by pyridine *N*-oxide, pyridine likely binds more strongly to the carbene intermediate, inhibiting the formation of **C**. This explains why the addition of 2,6-lutidine to this reaction mixture dose not promote formation of *cis*-2-butene.



Conclusions

Reported here is a rare example of the oxidation of an alkyl ligand in a transition metal complex. The rhenium(V) oxo alkyl triflate complexes $(HBpz_3)ReO(R)OTf$ are oxidized by oxygen atom donors pyridine *N*-oxide and Me_2SO to give $(HBpz_3)ReO_3$ (**7**) and the corresponding aldehyde. For R = Et and *n*-Bu (**5** and **6**) these oxidations are essentially quantitative. Surprisingly, these reactions do not proceed through alkoxide intermediates. The data suggest that oxidation involves initial displacement of the triflate ligand with the oxygen atom donor, which generates a Re(VII) dioxo alkyl cation (Scheme 1). Transfer of an α-hydrogen from the alkyl group to an oxo ligand forms a carbene complex, which is trapped by pyridine or SMe_2 to form the ylide complexes $[(HBpz_3)ReO(OH)\{CH(L)CH_3\}]OTf$ (L = py, **8**; SMe_2, **9**). These ylide compounds are observed by NMR at low temperatures. Conversion to **7** and acetaldehyde could proceed by carbene−oxo coupling on the rhenium center or by attack of the oxygen atom donor on the carbene. The low-temperature oxidation of **5** by DMSO in the presence of 2,6-lutidine gives *cis*-2-butene rather than acetaldehyde, apparently by the coupling of two ethylidene ligands.

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Supporting Information Available: Tables of atom positional and thermal parameters and bond distances and angles for $(HBpz_3)ReO(n\text{-}Bu)Cl$ (**3**) (5 pages). See any current masthead page for ordering and Internet access instructions.

JA962426C

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