Condensation of Vicinal Diols with the Oxo Complex {Cp*Re(O)}2(.mu.-O)2 Giving the Corresponding Diolate Complexes

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Notes

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Summary: Reaction of vicinal diols with $\{Cp^*Re(O)\}_2(\mu\text{-}O)_2$, *prepared in situ from* Cp^*ReO_3 *and* PPh_3, *leads to formation of rhenium (V) diolates of the type* $Cp^*Re(O)$(*diolate*) *in moderate to good yields.*

Metal diolate complexes have begun to attract interest as a subclass of metal alkoxides.[1-3] We have explored the cycloreversion chemistry of some rhenium(V) diolates as it relates to its microscopic reverse, alkene oxidation by metal oxides.[1] In the course of this work, we faced some complications with the published synthesis[4] of our target diolates (Scheme 1). Although the individual steps in this sequence gave good yields, the entire procedure was somewhat tedious and gave disappointing overall yields of the diolates.[5] Furthermore, the final step required the addition of an alkali diolate dissolved in diol to a THF solution of Cp^*ReOCl_2, a procedure which was difficult to adapt where the diol in question was not liquid. We therefore chose to explore whether a more direct approach was feasible.

Substantial literature precedent suggested that diols would condense with metal oxo complexes with loss of water.[2,6] Other syntheses have used metathesis between diols and metal alkoxides.[7] Both approaches view the metal oxo unit as being analogous to an organic carbonyl; formation of a diolate is a "ketalization" of sorts. To make the desired Cp*Re(O)(diolate) complexes, we would therefore need a "Cp^*ReO_2" equivalent. Deoxygenation of Cp^*ReO_3 with triphenylphosphine has been shown to form $\{Cp^*Re(O)\}_2(\mu\text{-}O)_2$, the bridged oxo dimer of "Cp^*ReO_2".[8] We report here that generation of this compound in the presence of a vicinal diol leads to facile condensation which forms the desired diolate complex.

Results and Discussion

Addition of vicinal diols to a 1:1 mixture of Cp^*ReO_3 and PPh_3 leads to formation of moderate to good yields of diolates (Scheme 2). The process is facilitated by the presence of 4A molecular sieves to trap the water formed in the reaction. Addition of 1 equiv of *p*-toluenesulfonic acid also accelerates the formation of product. Comparison of two otherwise identical preparations showed that the yield of 1 improved from 28% to 51% on addition of acid. Products can be isolated most easily by column chromatography on silica. Some residual triphenylphosphine oxide typically coelutes with the diolate,[9] but extraction with pentane allows isolation of pure product. Use of polystyrene-supported triphenylphosphine[10] also aids this separation.

The pinacolate **7** required heating to 50 °C to promote condensation, probably for steric reasons. All other condensations proceeded smoothly at room temperature within 15 h.

These compounds are all purple and exist either as an oil (**2**) or as microcrystalline solids. They are modestly air-sensitive in the solid state and more so in solution, although solutions survive exposure to air for periods up to 1 h. Workup and chromatography of reaction mixtures may thus conveniently be carried out on the benchtop rather than in a glovebox. Nevertheless, care was taken to minimize atmospheric exposure.

Their chromatographic behavior is somewhat unusual. These compounds are quite soluble in nonpolar solvents such as pentane; however, even as polar a solvent as

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(1) (a) Gable, K. P.; Phan, T. N. *J. Am. Chem. Soc.* **1993**, *115*, 3036-3037. (b) Gable, K. P.; Phan, T. N. *J. Am. Chem. Soc.* **1994**, *116*, 833-839.

(2) (a) Andrews, M. A.; Gould, G. L. *Organometallics* **1991**, *10*, 387-389. (b) Andrews, M. A.; Voss, E. J.; Gould, G. L.; Klooster, W. T.; Koetzle, T. F. Personal communication.

(3) (a) Takacs, J.; Kiprof, P.; Riede, J.; Herrmann, W. A. *Organometallics* **1990**, *9*, 782-787. (b) Herrmann, W. A.; Watzlowik, P.; Kiprof, P. *Chem. Ber.* **1991**, *124*, 1101-1106. (c) Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1157-1160. (d) Böhm, G.; Wieghardt, K.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 787-788.

(4) (a) Herrmann, W. A.; Marz, D. W.; Herdtweck, E.; Schäfer, A.; Wagner, W.; Kneuper, H.-J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 462-464. (b) Herrmann, W. A.; Herdtweck, M.; Flöel, M.; Kulpe, J. A.; Küsthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165-1182. (c) Herrmann, W. A.; Flöel, M.; Kulpe, J.; Felixberger, J. F.; Herdtweck, E. *J. Organomet. Chem.* **1988**, *355*, 297-313.

(5) 35-40% from Cp^*ReO_3 in our hands; in each step, we obtained yields similar to those reported by Herrmann.

(6) (a) Criegee, R.; Marchand, B.; Wannowius, H. *Liebigs Ann. Chem.* **1942**, *550*, 99-133. (b) Klänning, U.; Symons, M. C. R. *J. Chem. Soc.* **1961**, 3204-3208. (c) Banerji, K. K. *J. Chem. Soc., Perkin Trans. 2* **1978**, 639-641. (c) Wallis, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 8207-8223. (d) Herrmann, W. A.; Huber, N. W.; Anwander, R.; Priermeier, T. *Chem. Ber.* **1993**, *126*, 1127-1130.

(7) (a) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805-4813. (b) See ref 2.

(8) (a) Herrmann, W. A.; Serrano, R.; Küsthardt, U.; Ziegler, M. L.; Guggolz, E.; Zahn, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 515-517. (b) Herrmann, W. A.; Serrano, R.; Küsthardt, U.; Guggolz, E.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1985**, *287*, 329-344.

(9) The excess diol present after removal of THF requires extensive washing of the residue with hexane. The presence of some diol in this extract causes phosphine oxide to dissolve, necessitating chromatography (to remove diol) and subsequent reextraction.

(10) See ref 4c.

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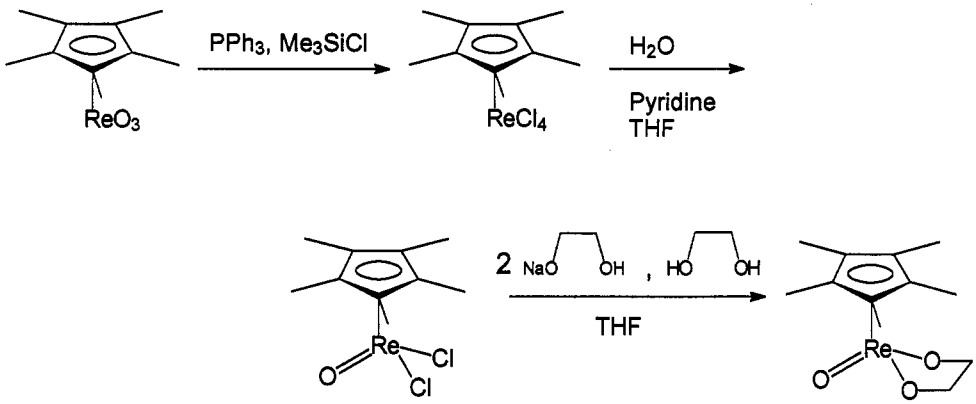
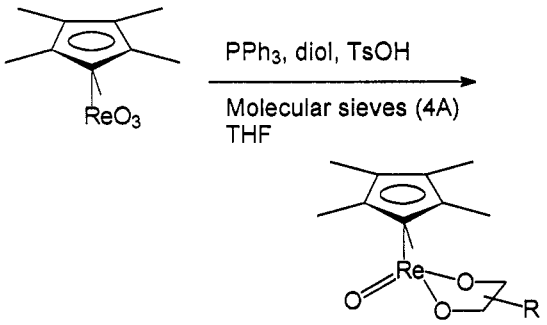
Scheme 1



Scheme 2



1-7

diol	compd no.
ethane-1,2-diol	1
propane-1,2-diol	2
meso-butane-2,3-diol	3
d,l-butane-2,3-diol	4
2-methylpropane-1,2-diol	5
phenylethane-1,2-diol	6
2,3-dimethylbutane-2,3-diol	7

chloroform will not elute them from silica gel. Acetone did successfully elute the products. They are formally 16-electron complexes of Re(V) if one counts the terminal oxo ligand as a 4-electron donor (though it more probably behaves as a 6-electron triply bonded ligand),[11] so the rhenium may exhibit some Lewis acidity toward the chromatographic support. However, they show no tendency to retain coordinating solvents. They apparently exist as monomeric species (consistent with Herrmann's observations),[12] as they all show terminal Re=O IR stretches in the 910–950-cm^{-1} range.

Monosubstituted and *erythro*-1,2-disubstituted diolates exist as an inseparable mixture of diastereomers, for in these compounds the substituent(s) on the diolate ring may be syn or anti to the pentamethylcyclopentadienyl ring. By analogy to our earlier work, we assign the syn stereochemistry to that isomer which exhibits the most downfield carbinol C–H proton;[13] this is consistent with the idea that this isomer will be disfavored (and thus the minor isomer). The observed stereoselectivities, expressed as anti:syn ratios, are 1.0 for **2**, 5.0 for **3**, and 1.25 for **6**. We have not rigorously determined whether these ratios are determined kinetically on closure of the ring or whether they are an equilibrium mixture reflecting ground-state thermodynamics of the two isomers. However, we have seen that diol-for-diolate exchange occurs on a time scale similar to that of the condensation reaction,[14] suggesting that the product ratios are thermodynamic in origin.

Each of these compounds undergoes cycloreversion to Cp^*ReO_3 and alkene at elevated temperature (50–120 °C);[15] further work on the energetics of these reactions is in progress.

Experimental Section

General Procedures. All reactions were performed using standard inert-atmosphere techniques in a nitrogen-filled glovebox (Vacuum Atmospheres Co. HE 493) or on a double-manifold Schlenk line. Solvents were purified by vacuum distillation prior to use; ether, THF, and benzene were distilled from sodium benzophenone ketyl, and hexane was distilled from Na/K alloy. NMR spectra were obtained on either a Bruker AC300 (operating at 300.133 MHz for proton or 75.469 MHz for ^{13}C) or a Bruker AM400 (operating at 400.134 MHz for proton or 100.614 MHz for ^{13}C) spectrometer. All chemical shifts are referenced either to residual protons or to carbons in solvent and are expressed in ppm downfield from tetramethylsilane. Infrared spectra were run on a Nicolet 510P spectrometer.

Cp^*ReO_3 was made by a published synthesis.[16] Diols were used as received from Aldrich, except 2-methylpropane-1,2-diol, which was prepared via a literature procedure.[17] Triphenylphosphine was recrystallized from hexane. Molecular sieves (beads, 4A, Fisher) were crushed in a mortar and pestle and dried in a 100 °C oven for at least 15 h. Elemental analyses were performed by Texas Analytical Laboratories.

General Procedure for Synthesis of Diolates. Cp^*ReO_3 (100 mg, 0.27 mmol), triphenylphosphine (80 mg, 0.30 mmol), *p*-toluenesulfonic acid hydrate (50 mg, 0.27 mmol), and ground molecular sieves (1.0 g) were stirred in 5 mL of THF. Diol (300 μL of liquid or 300 mg of solid) was added, and the mixture was stirred at room temperature for at least 15 h. The THF was removed *in vacuo*, the residue was extracted with 25 mL of hexane, and the filtrate was filtered. Flash chromatography (Baker silica gel, 230–400 mesh) was performed on this filtered extract using a 0.5 × 20 cm column. Initial elution with 100 mL of chloroform was used to remove unreacted diol. Acetone was then used to elute the purple diolate. After removal of solvent, a final extraction with 10 mL of pentane was used to separate product

(11) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds;* Wiley-Interscience: New York, 1988; pp 23, 175–177.
(12) Herrmann, W. A.; Marz, D. W.; Herdtweck, E. *J. Organomet. Chem.* **1990**, *394*, 285–303.
(13) A reviewer has suggested this is due to the ring current of the Cp* ring; we gratefully acknowledge this suggestion, but since the downfield proton (in the syn isomer) is actually anti to the Cp* ring, we feel the anisotropies in this molecule are more complex. Of course, it is possible that our assignments are reversed in some or all of these.
(14) We thank a reviewer for suggesting this experiment.
(15) The phenyl-substituted **6** fragments most rapidly ($t_{1/2}$ of several hours at 50 °C), while all of the methyl-substituted compounds require heating to at least 80 °C for the rate of cycloreversion to be appreciable.
(16) Gable, K. P.; Phan, T. N. *J. Organomet. Chem.* **1994**, *466*, C5–C6. See references therein for alternative methods.
(17) Milas, N. A.; Sussman, S. *J. Am. Chem. Soc.* **1936**, *58*, 1302–1304.

from residual triphenylphosphine oxide. Removal of the pentane gave the diolate as a purple solid or oil in analytical purity. Yields and characterization are listed below.

(Pentamethylcyclopentadienyl)oxorhenium Ethane-1,2-diolate. Yield from 100 mg of Cp^*ReO_3: 55 mg (0.14 mmol, 51%) of purple solid. ^1H and ^{13}C NMR matched those of material made by the method of Herrmann et al.[4]

(Pentamethylcyclopentadienyl)oxorhenium Propane-1,2-diolate. Yield from 100 mg of Cp^*ReO_3: 50 mg (0.12 mmol, 45%) of purple oil. ^1H NMR (C_6D_6) for two inseparable isomers (1:1 mixture): 1.46 d, J = 6.0 Hz (3H); 1.51 d, J = 6.0 Hz (3H); 1.73 s (15H); 1.74 s (15H); 3.06 dd, J = 9.9, 9.9 Hz (1H); 3.78 m (3H); 4.08 dd, J = 9.9, 5.5 Hz (1H); 4.42 ddq, J = 9.9, 5.5, 6.0 Hz (1H). ^{13}C NMR (C_6D_6): 11.06, 11.17, 18.88, 19.26, 85.98, 86.14, 86.26, 86.77, 107.55 (both isomers accidentally equivalent). IR (CH_2Cl_2): 2969, 2919, 2849, 1457, 1378, 1061, 991, 938, 846, 660 cm^{-1}. Anal. Found (calcd for $C_{13}H_{21}O_3Re$): C, 37.84 (37.94); H, 5.28 (5.14).

(Pentamethylcyclopentadienyl)oxorhenium *erythro*-Butane-2,3-diolate. Yield from 100 mg of Cp^*ReO_3: 78 mg (0.18 mmol, 68%) of purple solid. ^1H NMR (C_6D_6) for two inseparable isomers (5:1 mixture) follows. Major isomer: 1.42 dd, J = 4.6, 1.4 Hz (6H); 1.76 s (15H); 3.74 m, (2H). Minor isomer: 1.18 dd, J = 4.5, 1.6 Hz (6H); 1.80 s (15H); 4.50 m (2H). ^{13}C NMR (C_6D_6): major isomer 11.09, 16.29, 86.35, 107.41; minor isomer 11.49, 17.55, 88.25, 107.82. IR (CH_2Cl_2): 2972, 2926, 2855, 1454, 1375, 1061, 1008, 936, 907, 790, 642 cm^{-1}. Anal. Found (calcd for $C_{14}H_{23}O_3Re$): C, 39.46 (39.52); H, 5.57 (5.45).

(Pentamethylcyclopentadienyl)oxorhenium *threo*-Butane-2,3-diolate. Yield from 100 mg of Cp^*ReO_3: 94 mg (0.22 mmol, 82%) of purple solid. ^1H and ^{13}C NMR matched those of material made by the method of Herrmann et al.[4] ^1H NMR (C_6D_6): 1.40 d, J = 6.0 Hz (3H); 1.46 d, J = 6.1 Hz (3H); 1.68 s (15H); 3.04 dq, J = 8.9, 6.1 Hz(1H); 3.92 dq, J = 8.9, 6.0 Hz (1H). ^{13}C NMR (C_6D_6): 11.18, 19.36, 20.02, 91.18, 91.90, 107.46.

(Pentamethylcyclopentadienyl)oxorhenium 2-Methylpropane-1,2-diolate. Yield from 100 mg of Cp^*ReO_3: 86 mg (0.20 mmol, 75%) of purple oil. ^1H NMR (C_6D_6): 1.41 s (3H); 1.48 s (3H); 1.77 s (15H); 3.30 d, J = 9.8 Hz (1H); 3.90 d, J = 9.8 Hz (1H). ^{13}C NMR (C_6D_6): 11.12, 26.34, 26.91, 87.83, 90.32, 107.56. IR (CH_2Cl_2): 2967, 2924, 2848, 1458, 1377, 1363, 1190, 1145, 1003, 964, 937, 883, 792, 675, 603 cm^{-1}. Anal. Found (calcd for $C_{14}H_{23}O_3Re$): C, 39.41 (39.52); H, 5.56 (5.45).

(Pentamethylcyclopentadienyl)oxorhenium Phenylethane-1,2-diolate. Yield from 200 mg of Cp^*ReO_3: 178 mg (0.38 mmol, 70%) of purple solid. ^1H NMR (C_6D_6) for two inseparable isomers (5:4 mixture) follows. Major isomer: 1.69 s (15H); 3.39 dd, J = 10.8, 10.1 Hz (1H); 4.29 dd, J = 10.1, 5.6 Hz (1H); 5.30 dd, J = 10.8, 5.6 Hz (1H); 6.9–7.1 m (3H); 7.15–7.25 m (2H). Minor isomer: 1.69 s (15H); 4.12 second-order multiplet (2H); 4.50 dd, J = 8.8, 6.6 Hz (1H); 7.37 m (2H); 7.46 m (2H); 7.74 m (1H). ^{13}C NMR (C_6D_6): 11.10, 11.11, 87.39, 87.40, 92.94, 93.27, 107.94, 108.01, 141.46, 142.27; other aromatic peaks obscured by solvent. IR (CH_2Cl_2): 2925, 2850, 1453, 1379, 1028, 991, 923, 914, 773, 675 cm^{-1}.

(Pentamethylcyclopentadienyl)oxorhenium 2,3-Dimethylbutane-2,3-diolate. The preparation was as above, but the reaction mixture was heated to 50 °C for 15 h. Yield from 100 mg of Cp^*ReO_3: 84 mg (0.185 mmol, 67%) of purple solid. ^1H NMR (C_6D_6): 1.19 s (6H); 1.42 s (6H); 1.72 s (15H). ^{13}C NMR (C_6D_6): 11.55, 22.81, 26.36, 91.02, 107.69. IR (CH_2Cl_2): 2966, 2922, 1456, 1383, 1364, 1192, 1128, 934, 868, 665, 619, 542 cm^{-1}. Anal. Found (calcd for $C_{16}H_{27}O_3Re$): C, 42.12 (42.28); H, 6.16 (5.99).

Diol/diolate Exchange. Ethanediolate **1** (5 mg) was dissolved in 0.5 of mL THF-d_8 with an 11-fold excess of *meso*-butane-2,3-diol. After the solution was allowed to stand for 24 h at room temperature, the ^1H NMR spectrum showed complete conversion to a 5:1 mixture of *anti*- and *syn*-**3**.

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