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Synthesis and Reactivity of New Chiral Rhenium Complexes of Unsaturated Alcohols

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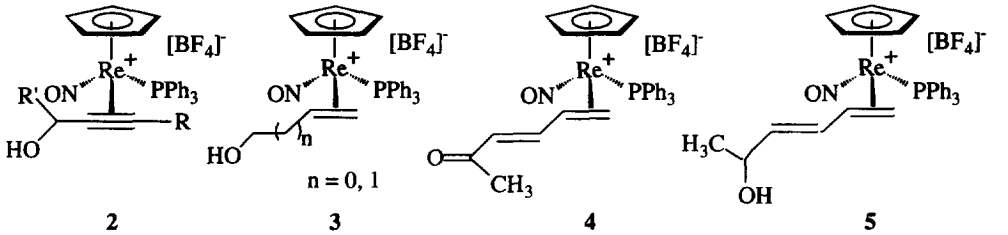
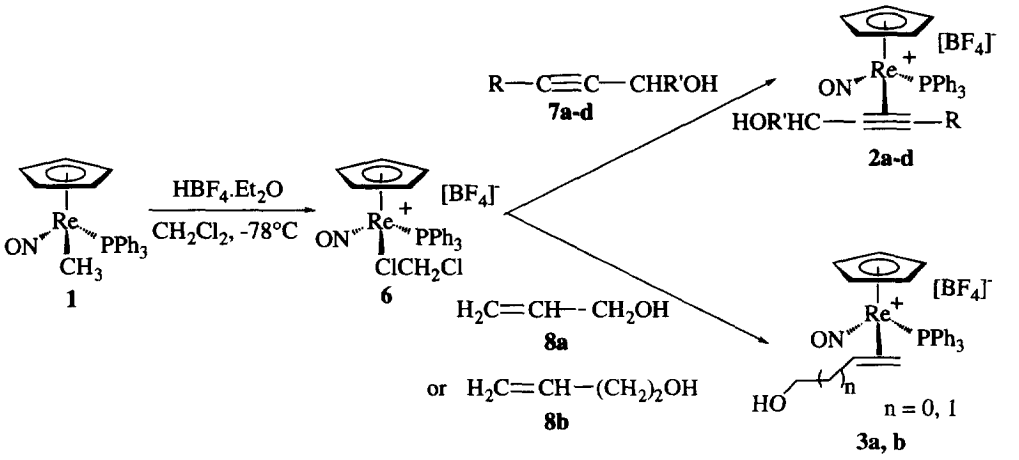
Abstract: *New rhenium complexes of allylic, homoallylic and propargylic alcohols have been prepared. Starting from the allyl alcohol complex, a multistep sequence involving a chemoselective oxidation, a Wittig reaction and a reduction leads to a conjugated dienone and dienol selectively complexed at only one double bond.*

The complexation of carbon-carbon double or triple bonds by transition metals has been extensively studied. For instance, complexes of alkynyl compounds are efficiently prepared starting from dicobalt octacarbonyl while alkenyl derivatives are complexed with iron, osmium or manganese carbonyl compounds.[1] However, none of these complexes have both a chiral metallic atom along with a good chemical stability, a combination which would be of great versatility in organic and asymmetric synthesis. Gladysz *et al.*[2] have prepared chiral rhenium derivatives and the compound $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)]$ **1** has been used to complex alkenes and alkynes.[3] The corresponding rhenium salt can act as a protecting group for a double or a triple bond,[4] activate a bonded substrate or be useful in enantioselective transformations.[5] We report here, in this preliminary communication, the preparation of several complexed unsaturated alcohols (**2** and **3**) and a chemoselective oxidation to the corresponding aldehyde or keto complexes; the formation, *via* a Wittig reaction, of a dienone complex **4**; and the chemoselective reduction of **4** to give a dienol complex **5**.



2 **3** **4** **5**

The labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2Cl_2)]^+BF_4^-$ **6**, easily formed[6] at -78° C from the methyl complex **1**, reacts with propargylic **7a-d**, allylic **8a** and homoallylic alcohols **8b** to give, in satisfactory yields, the corresponding adducts **2a-d** and **3a,b** (Scheme 1, Table 1).[7]



Scheme 1

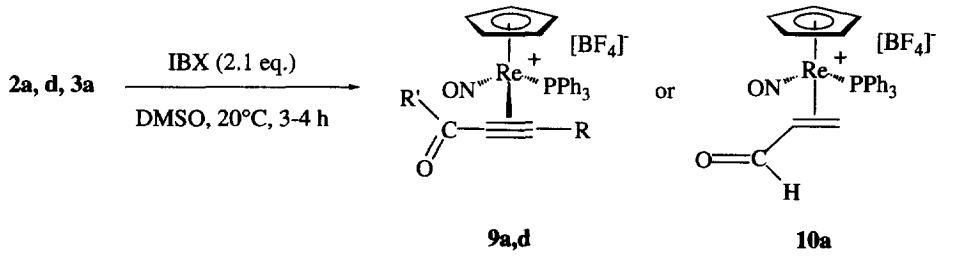
Table 1

Alcohol	Product	Yield (%)
H-C≡C-CH(CH_3)OH **7a**	**2a**	69 [a]
H-C≡C-CH_2OH **7b**	**2b**	59
HO-CH_2-C≡C-CH_2OH **7c**	**2c**	54
CH_3-C≡C-CH_2OH **7d**	**2d**	81 [b]
H_2C=CH-CH_2OH **8a**	**3a**	79
H_2C=CH-CH_2CH_2OH **8b**	**3b**	66 [c]

[a] mixture of 2 diastereomers (55/45). [b] mixture of two rotamers (50/50).
[c] mixture of two (RS, SR)/(RR,SS) [8] diastereomers (84/16).

Complexes **2a-d, 3a,b** have been characterized by infrared, ^1H, ^{31}P and ^{13}C NMR spectroscopy and High Resolution Mass Spectrometry (HRMS). The ^1H and ^{13}C NMR signals of the complexed C=C and C≡C atoms are observed at up-field and down-field respectively from the signals of the corresponding atoms in the free alcohols. These observations are in good agreement with those already reported for other unsaturated derivatives of rhenium complexes.[3, 9]

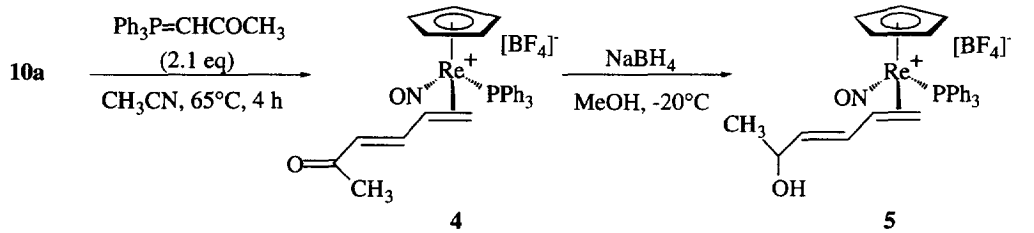
Our aim was to perform selective reactions on the alcohol function without affecting the rhenium salt. So conversion of compounds **2a, d** and **3a** into the corresponding aldehyde or keto complexes was investigated. The use of manganese dioxide or pyridinium chlorochromate (PCC) was not successful while only partial reaction was observed using TEMPO (2, 2, 6, 6-tetramethyl-1-piperidinyloxy). Iodoxybenzoic acid (IBX)[10] was found to be a very efficient and mild reagent in these transformations. Compounds **9a,d, 10a** were obtained in 76, 92 and 61% yields respectively. Aldehyde **9d** is obtained as a mixture of two rotamers in a 3:2 ratio. The π-acrolein complex **10a** prepared by the oxidation of **3a** or by direct complexation of acrolein with **2**[9] led to a similar ratio of the two diastereoisomers in a 60:1 ratio (Scheme 2).



9a,d **10a**

Scheme 2

The formation of dienic compounds, ***selectively complexed at only one carbon-carbon multiple bond*** has been achieved starting from the acrolein complex **10a**. A Wittig reaction using methyl(triphenylphosphoranylidene)ketone in CH_3CN at 65 °C led to the dienone **4**, purified by precipitation (CH_2Cl_2/ EtOH) and isolated in a 73 % yield (Scheme 3).[11] Moreover, the chemoselective reduction of compound **4** using $NaBH_4$ in MeOH gave a 55:45 mixture of the two diastereomers of the alcohol **5** in a 53 % yield (Scheme 3).[12] In both reactions no bond-shift was observed, and this is an important result with regard to the possible use of such complexes as selective chiral protecting groups for one double bond in a conjugated polyenic system.



4 **5**

Scheme 3

To conclude, we have shown that propargylic, allylic and homoallylic alcohols can be easily complexed with rhenium complex **6**. Using carefully selected reagents, chemoselective oxidation, reduction or a Wittig reaction can be performed on these complexes. Thus, a dienone and a dienol selectively complexed on one double bond, have been prepared. Studies of the reactivity of these complexes in such reactions as nucleophilic or electrophilic additions and cycloadditions as well as extension to asymmetric synthesis (the complex **1** has been resolved)[2] are currently under progress.

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References and Notes.

1. Hegedus, L. S. "Transition Metals in the Synthesis of Complexes Organic Molecules" University Science Books, Mill Valley, Calif. 1994.
2. Agbossou, F.; O'Connor, E. J.; Garner, C. M.; Quiros Mendez, N.; Fernandez, J. M.; Patton, A.T.; Ramsden, J. A.; Gladysz, J. A. *Inorg. Synth.* **1992**, *29*, 211-225.

3. See for example : Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, *124*, 729-742 *Organometallics* **1991**, *10*, 1079-1088. Pu, J.; Peng, T.-S.; Mayne, C. L.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2686-2698. Peng, T.-S.; Winter, C. H.; Gladysz, J. A. *Inorg. Chem.* **1994**, *33*, 2534-2542. Peng, T.-S.; Pu, J.; Gladysz, J. A. *Organometallics* **1994**, *13*, 929-940.

4. Peng, T.-S.; Wang, Y.; Arif, A. M.; Gladysz, J.A. *Organometallics* **1993**, *12*, 4535-4544.

5. Wang, Y.; Gladysz, J. A. *J. Org. Chem.* **1995**, *60*, 903-909.

6. Fernandez, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207-219.

7. A typical procedure is described for the synthesis of **2b** : a solution of **1** (100 mg, 0.179 mmol) in CH_2Cl_2 (10 mL) was cooled to -78°C and $HBF_4.OEt_2$ (28 µL, 0.162 mmol) was added. After 30 min., a large excess of propargyl alcohol (2 mL) was added. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was then removed in vacuo and the oily residue was chromatographed with 4:1 CH_2Cl_2/acetone (v/v). Compound **2b** was isolated as a solid (73 mg, 0.106 mmol, 59 % yield) IR (cm^{-1}, neat)ν_{NO} 1704 (vs), $\nu_{C\equiv C}$ 1797. HRMS calcd for $C_{26}H_{24}NO_2PRe$: 600.1103, found : 600.1101. ^1H NMR (CD_3COCD_3, 400 MHz) δ : 7.44-7.75 (m, 15H, PPh_3); 6.80 (dt, 1H, J_{HH} = 1.5, J_{HP} = 19.3, ≡C<u>H</u>); 6.24 (s, 5H, C_5H_5); 5.25 (m, 1H, C<u>H</u>$_2$OH); 5.11 (m, 1H, C<u>H</u>$_2$OH); 5.02 (t, 1H, J_{HH} = 5.6, CH_2O<u>H</u>). ^{13}C {^1H} NMR (CD_3COCD_3, 100 MHz) δ : 134.4 (d, J_{CP} = 10.3, *o*-Ph), 133.3 (d, J_{CP} = 2.7, *p*-Ph), 130.6 (d, J_{CP} = 11.4, *m*-Ph), 107.0 (s, -<u>C</u>≡CH), 100.1 (d, J_{CP} = 0.8, C_5H_5), 79.7 (d, J_{CP} = 14.1, -C≡<u>C</u>H), 61.8 (s, <u>C</u>H_2OH). ^{31}P {^1H} NMR (CD_3COCD_3, 121 MHz) δ : 17.9 (s).

8. Peng, T.S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 4174-4181.

9. Wang, Y.; Agbossou, F.; Dalton, D. M.; Liu, Y.; Arif, A. M.; Gladysz, J.A. *Organometallics* **1993**, *12*, 2699-2713.

10. Frigerio, M.; Santagostino, M. *Tetrahedron Lett.* **1994**, *35*, 8019-8022, Frigerio, M.; Santagostino, M., Sputore, S., Palmisano, G. *J. Org. Chem.* **1995**, *60*, 7272-7276.

11. Compound **4** : Yield 73%. IR (cm^{-1}, neat) : ν_{NO} 1726 (vs). HRMS calcd for $C_{29}H_{28}NO_2PRe$: 640.1417, found : 640.1415. ^1H NMR (CD_3CN, 400 MHz) δ : 7.39-7.68 (m, PPh_3); 6.47 (dd, 1H, J_{HH} = 9.7, 15.8, <u>H</u>C=CH-CO); 6.29 (d, 1H, J_{HH} = 15.8, HC=C<u>H</u>-CO); 5.83 (s, 5H, C_5H_5); 4.94 (m, 1H, J_{HH} = 9.2, 9.7, 10.7, J_{HP} = 2.0, H_2C=C<u>H</u>-); 2.73 (dt, 1H, J_{HH} = 4.6, 9.2, J_{HP} = 10.7, <u>H</u>$_2$C=CH-); 2.48 (m, 1H, J_{HH} = 4.6, 10.7, J_{HP} = 6.1, <u>H</u>$_2$C=CH); 2.18 (s, 3H, CH_3). ^{13}C {^1H} NMR (CD_3CN, 100 MHz) δ : 197.9 (s, CO); 149.2 (s, CH=CH); 134.1 (d, J_{CP} = 9.9, *o*-Ph), 133.1 (d, J_{CP} = 3.0, *p*-Ph); 130.9 (s, CH=CH); 130.4 (d, J_{CP} = 11.6, *m*-Ph), 99.1 (s, C_5H_5), 45.6 (s, H_2C=<u>C</u>H), 38.7 (d, J_{CP} = 6.1, H_2<u>C</u>=CH); 27.1 (s, CH_3). ^{31}P {^1H} NMR (CD_3CN, 121 MHz) δ : 11.15 (s).

12. Compound **5** : Yield 53%. IR (cm^{-1}, neat) : ν_{NO} 1720 (vs). HRMS calcd for $C_{29}H_{30}NO_2PRe$: 642.1573, found : 642.1571. ^1H NMR (CD_3CN, 400 MHz) δ : 7.32-7.66 (m, PPh_3); 5.93 and 5.89 (2dd, 2H, J_{HH} = 5.7, 12.8, C<u>H</u>CHOH); 5.75 and 5.74 (s, 10H, C_5H_5); 5.53 and 5.49 (2dd, 2H, J_{HH} = 9.6, 12.8, <u>H</u>C=CH-CHOH); 5.09 and 5.06 (2m, 2H, H_2C=C<u>H</u>-); 4.36 and 4.32 (2m, 2H, C<u>H</u>-OH); 2.68 (dt, 2H, J_{HH} = 4.3, 10.9, J_{HP} = 10.9, <u>H</u>$_2$C=CH-); 2.27 (m, 2H, J_{HH} = 4.5, 9.8, J_{HP} = 5.8, <u>H</u>$_2$C=CH); 1.18 and 1.20 (2d, 6H, J_{HH} = 6.3, CH_3). ^{13}C {^1H} NMR (CD_3CN, 100 MHz) δ : 139.7 (2s, -<u>C</u>H=CH-CHOH or -CH=<u>C</u>H-CHOH); 134.0 (d, J_{CP} = 9.9, *o*-Ph), 132.9 (d, J_{CP} = 2.7, *p*-Ph); 131.3 (d, J_{CP} = 58.7, *i*-Ph); 131.1 and 131.0 (2s, -<u>C</u>H=CH-CHOH or -CH=<u>C</u>H-CHOH); 130.3 (d, J_{CP} = 11.1, *m*-Ph), 98.3 (s, C_5H_5), 67.4 (s, CHOH); 50.7 and 50.6 (2s, H_2C=<u>C</u>H), 36.3 and 36.2 (2d, J_{CP} = 5.7, H_2<u>C</u>=CH); 24.7 and 24.5 (2s, CH_3). ^{31}P {^1H} NMR (CD_2Cl_2, 121 MHz) δ : 11.0 (s).

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