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Journal of Organometallic Chemistry 567 (1998) 75–81

Journal of Organometallic Chemistry

New chiral rhenium complexes of unsaturated alcohols: preparation and reactivity

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Received 7 October 1997; received in revised form 8 December 1997

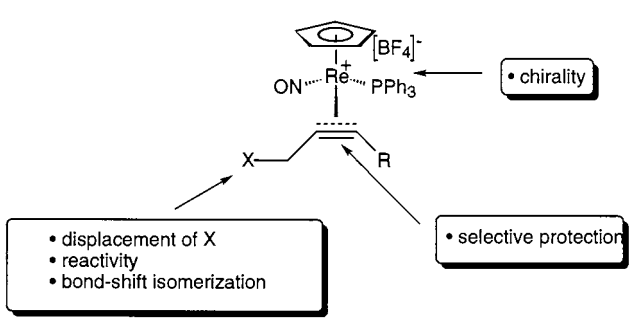
Abstract

New chiral rhenium complexes of allylic, homoallylic and propargylic alcohols have been prepared and their reactivity versus various reagents has been studied. Starting from the allyl alcohol complex, a multistep sequence involving a chemoselective oxidation, a Wittig reaction and a reduction led without bond-shift to conjugated dienone and dienol. The complexed allyl acetate, prepared by reaction of acetic anhydride on the complexed allyl alcohol reacted with sodium dimethylmalonate in a diastereoselective fashion. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Chiral rhenium complexes; Oxidation; Reduction; Wittig reaction; Diastereoselectivity

1. Introduction

The complexation of carbon-carbon double or triple bonds by transition metals has been extensively studied [1]. For instance, complexes of alkynyl compounds are efficiently prepared starting from dicobalt octacarbonyl [2]. Such complexes are very stable and therefore are of much use in organic synthesis. However, they do not have stable chiral centers at the metallic atoms, a limiting factor for their application in asymmetric synthesis. Within the alkenyl complexes family, the iron, osmium and manganese carbonyl derivatives have been studied in more details with regard to their synthetic potentialities. Rosemblum et al. [3] have complexed alkenes with $CpFe(CO)_2$ and obtained good results in reactions with various nucleophiles. Some osmium complexes are able to promote electrophilic addition reactions on η^2-bound arene [4] but questions remain about their potential toxicity. Interesting applications of manganese complexes in stereoselective alkylations have been recently reported [5]; the instability of such derivatives is however a serious limitation to their use in synthetic chemistry. Among all these complexes, none are able to associate a chiral center at the metallic atom along with a good chemical stability, a combination which would be of great versatility in organic and asymmetric synthesis. Gladysz et al. [6] 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 [7]. The corresponding rhenium salt could act as a protecting group for a double or a triple bond, activate a bonded substrate or be useful in enantioselective transformations (Scheme 1).



Scheme 1.

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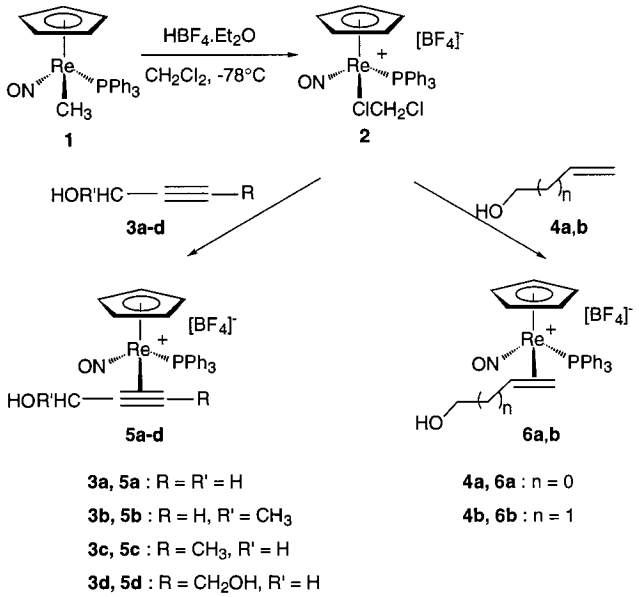


Scheme 2.

We report here the preparation of new chiral rhenium complexes of propargylic, allylic and homoallylic alcohols. We show on several examples the compatibility of such complexes with various organic reactions: a chemoselective oxidation of some of these complexed alcohols, a Wittig reaction on the complexed acrolein and a chemoselective reduction of the formed dienone complex. All these reactions occur without bond-shift. Also described is the preparation of complexed allyl acetate by addition of acetic anhydride on the complexed allyl alcohol and its diastereoselective reaction with sodium dimethylmalonate. A portion of this work has been communicated in a preliminary form [8].

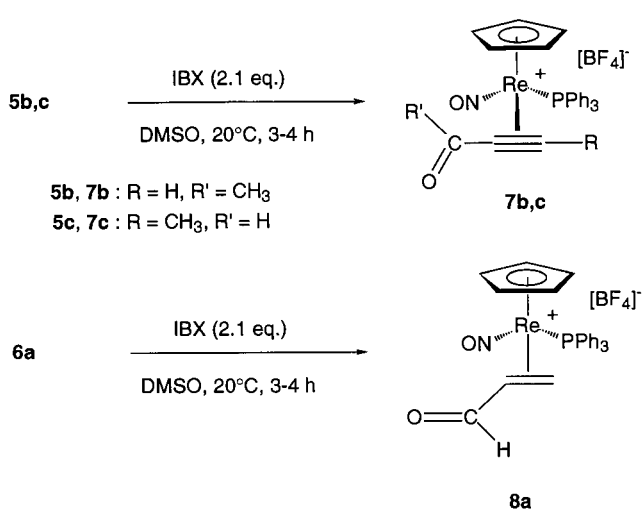
2. Results and discussion

The labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2Cl_2)]^+BF_4^-$ **2**, easily formed at $-78°C$ from the methyl complex **1** [9], reacts with propargylic **3a–d**, allylic **4a** and homoallylic alcohols **4b** to give the corresponding adducts **5a–d** and **6a**,**b** (Scheme 2). Yields range from 54 (**5d**) to 81% (**5c**). Such compounds are easily chromatographed or purified by precipitation.

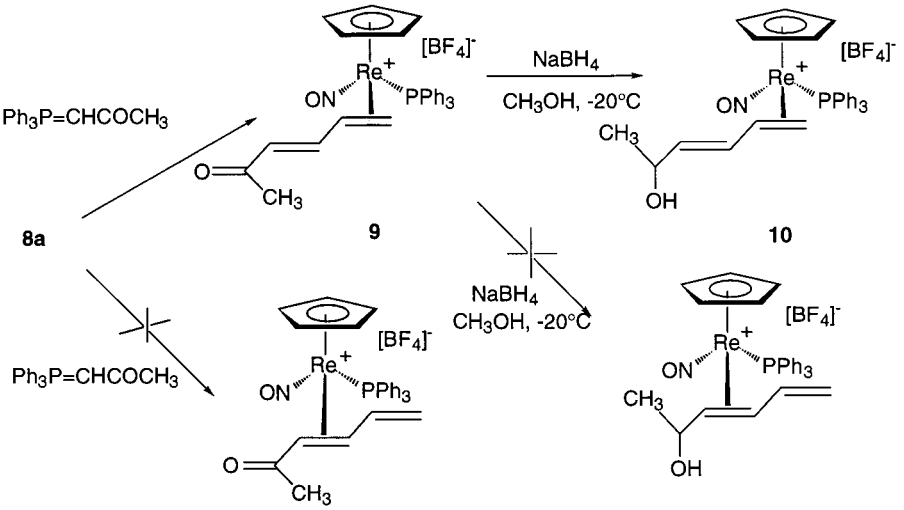
Complexes **5a–d**, **6a**,**b** have been characterized by infrared, ^1H, ^{31}P and ^{13}C-NMR spectroscopy and high resolution mass spectrometry (HRMS). The ^1H and ^{13}C-NMR signals of the complexed C≡C atoms of compounds **5a–d** were shifted down-field to those of the corresponding atoms in the free alcohols while the ^1H and ^{13}C-NMR signals of the complexed C=C atoms of compounds **6a**,**b** were shifted up-field. These chemical shifts are in good agreement with those already reported for other unsaturated derivatives of rhenium complexes [7]. Diastereomers were observed in the ^1H and ^{13}C-NMR spectra of the 3-butyn-2-ol **5b** (ratio: 55:45) and 3-buten-1-ol complexes **6b** (ratio: 84:16). The presence of the two rotamers of 2-butyn-1-ol **5c**, in a 50:50 ratio, has also been clearly evidenced.

The chemoselective oxidation of these complexes was first investigated using compounds **5b**,**c**, **6a**; their reaction with 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 **7b**,**c**, **8a** were obtained in 76, 65 and 61% yields, respectively (Scheme 3). Aldehyde **7c** was obtained as a mixture of two rotamers in a 3:2 ratio. The π-acrolein complex **8a** prepared by the oxidation of **6a** is identical (with a similar 60:1 ratio of diastereomers) to the derivative obtained by direct complexation of acrolein with **2** [11].

The formation of a conjugated dienic compound, selectively complexed at only one carbon-carbon multiple bond has been achieved starting from the acrolein complex **8a**. A Wittig reaction using methyl (triphenylphosphoranylidene)ketone in CH_3CN at 65°C led to the dienone **9**, purified by precipitation (CH_2Cl_2/EtOH) and isolated in a 73% yield (Scheme 4). The chemoselective reduction of the formed compound **9** using $NaBH_4$ in CH_3OH gave the alcohol **10** in a 69% yield. Due to the presence of a newly created stereogenic center, a 55:45 mixture of two diastereoisomers was observed. 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.



Scheme 3.



Scheme 4.

We have recently reported regioselective substitutions of rhenium complexes of allylic alcohols under acidic conditions [12]. It was of interest to study also the possibility of nucleophilic substitution under basic conditions starting from the allylic acetate complex. However since direct additions of nucleophiles on rhenium complexes of alkenes have been reported [11], the competition between the two processes (addition or substitution) had to be studied. The acetate complex **11** was formed in a very low yield by direct complexation. Better results (70% yield) were obtained by reaction of **6a** with acetic anhydride in the presence of pyridine. The reaction of complex **11** with sodium malonate, prepared in situ from NaH and dimethylmalonate, led in a 69% yield to a neutral complex **12** easily identified from the spectral and analytical data (Scheme 5).

Furthermore, the ^{1}H and ^{13}C-NMR spectra clearly show that only one diastereomer has been formed: the signal of the methylene connected to the rhenium atom presents a doublet with a coupling constant $^{2}J_{CP} = 5.3$ Hz while a signal with a smaller coupling constant $^{3}J_{CP} = 4.2$ Hz was observed for the CH group in β-position. By analogy with the reported reaction of cuprates with complexed monosubstituted alkenes [13], the attack of sodium dimethylmalonate is probably performed at the less substituted olefinic carbon and on the C=C face anti to the rhenium. No substitution product has been detected in this reaction.

3. Conclusion

We have shown that propargylic, allylic and homoallylic alcohols can be easily complexed with rhenium complex **2**. Using carefully selected reagents, chemoselective oxidation, reduction or a Wittig reaction can be performed on these complexes. 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) [6] are currently under progress.

4. Experimental section

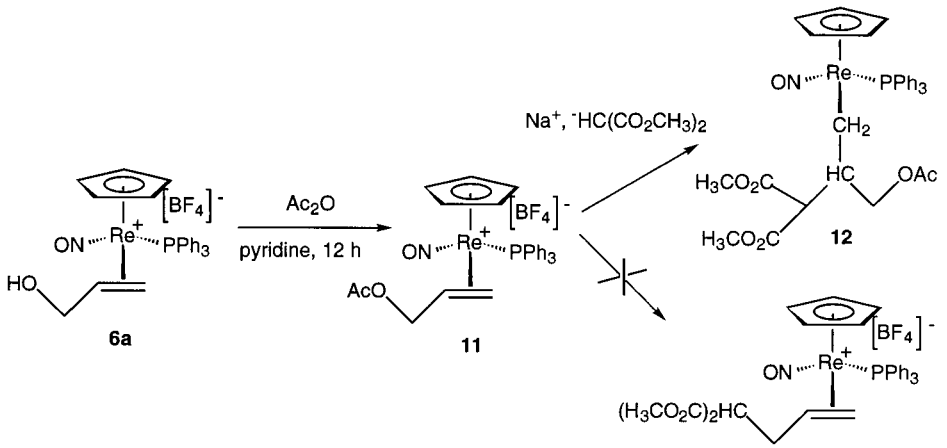
4.1. General

All manipulations were performed under nitrogen atmosphere. Dichloromethane was distilled from P_4O_{10}. $HBF_4 \cdot Et_2O$ was purchased from Aldrich and used as received. All other starting materials were obtained commercially and used as such or purified by standard means.

Proton and carbon magnetic resonance spectra were taken on a Bruker AC 400 spectrometer, and the chemical shifts are reported on the scale δ relative to tetramethylsilane (^{1}H) or to solvent (^{13}C, $\delta = 77.7/CDCl_3$, $\delta = 62.8/CD_3NO_2$). High resolution mass spectra were recorded on an MS/MS ZabSpec TOF VG Analytical spectrometer at a FAB positive ionisation with Cs^+ by the CRMPO (Centre Regional de Mesures Physiques de l'Ouest).

4.1.1. General procedure for preparation of propargylic *5a–d* and homoallylic alcohol complexes *6b*.

A sample of complex (η^5-C_5H_5)Re(NO)(CH_3)(PPh_3) **1** (100 mg, 0.179 mmol) and CH_2Cl_2 (10 ml) were cooled to -78°C and $HBF_4 \cdot OEt_2$ (85%, 32 μl, 0.185 mmol) was added with stirring. After 30 min, a large excess of alcohol (2 ml) was added. The reaction mixture was allowed to warm to room temperature (r.t.) and stirred overnight. Solvent was removed by rotary evaporation. The resulting residue was chromatographed on a silica gel column with use of 4:1



Scheme 5.

dichloromethane/acetone (v/v) to give compound **5a–d** or **6b** as a yellow-brown oil.

4.1.2. [(η^5-C_5H_5)Re(NO)(PPh_3)(HC≡CCH_2OH)]$^+$ [BF_4]$^-$ ***5a***

2-Propynol was used as alcohol. Yield: 72.8 mg, 0.106 mmol, 59%. ^{1}H-NMR (CD_3COCD_3, 400 MHz) δ: 7.60–7.74 (m, 9H, PPh_3); 7.44–7.58 (m, 6H, PPh_3); 6.80 (dt, 1H, $J = 1.5$, $J_{PH} = 19.3$, ≡CH); 6.24 (s, 5H, C_5H_5); 5.25 (m, 1H, CH_2OH); 5.11 (m, 1H, CH_2OH); 5.02 (t, 1H, $J = 5.6$, CH_2OH). ^{13}C-NMR (CD_3COCD_3, 100 MHz) δ: 134.4 ($J_{CP} = 10.3$, *o*–Ph); 133.3 ($J_{CP} = 2.7$, *p*-Ph); 130.6 ($J_{CP} = 11.4$, *m*–Ph); 107.0 (s, –C≡CH); 100.1 (C_5H_5); 79.7 ($J_{CP} = 14.1$, –C≡CH); 61.8 (CH_2OH). ^{31}P {^{1}H} NMR (CD_3COCD_3, 121 MHz) δ: 17.9 (s). IR (cm^{-1}, neat) ν_{NO} 1704 (vs), $\nu_{C\equiv C}$ 1797. HRMS calc. for $C_{26}H_{24}NO_2PRe$: 600.1103, found: 600.1101.

4.1.3. [(η^5-C_5H_5)Re(NO)(PPh_3)(HC≡$CCH(CH_3)OH$)]$^+$ [BF_4]$^-$ ***5b***

3-Butyn-2-ol was used as alcohol. Yield: 86.9 mg, 0.124 mmol, 69%. Two diastereomers 45:55 (minor). ^{1}H-NMR (400 MHz, CD_3COCD_3) δ: 7.59–7.75 (m, 9H, PPh_3); 7.43–7.57 (m, 6H, PPh_3); 6.77 (dd, 1H, $J_{PH} = 19.3$, $J = 1.5$, ≡CH); 6.26 (s, 5H, C_5H_5); 5.66–5.77 (m, 1H, CHOH); 5.07–5.16 (m, 1H, CHOH); 1.57 (d, 3H, $J = 6.1$, CH_3). ^{13}C-NMR (100 MHz, CD_3COCD_3) δ: 134.3 ($J_{CP} = 10.7$, *o*–Ph); 133.3 ($J_{CP} = 2.7$, *p*–Ph); 130.6 ($J_{CP} = 10.7$, *m*–Ph); 111.1 (C≡CH); 99.9 (C_5H_5); 78.9 ($J_{CP} = 14.1$, C≡CH); 65.2 (CHOH); 25.0 (CH_3). ^{31}P {^{1}H}-NMR (121 MHz, CD_3COCD_3) δ: 17.6 (s) (major). ^{1}H-NMR (400 MHz, CD_3COCD_3) δ: 7.59–7.75 (m, 9H, PPh_3); 7.43–7.57 (m, 6H, PPh_3); 6.73 (dd, 1H, $J = 1.5$, $J_{PH} = 19.3$, ≡CH); 6.25 (s, 5H, C_5H_5); 5.25–5.35 (m, 1H, CHOH); 5.00 (d, 1H, $J = 5.1$, CHOH); 1.63 (d, 3H, $J = 6.6$, CH_3). ^{13}C-NMR (100 MHz, CD_3COCD_3) δ: 134.3 ($J_{CP} = 10.7$, *o*–Ph); 133.3 ($J_{CP} = 2.7$, *p*–Ph); 130.6 ($J_{CP} = 10.7$, *m*–Ph); 100.2 (C_5H_5); 110.8 (C≡CH); 79.2 ($J_{CP} = 14.1$, C≡CH); 69.5 (CHOH); 24.3 (CH_3). ^{31}P {^{1}H}-NMR (121 MHz, CD_3COCD_3) δ: 17.6 (s). IR (cm^{-1}, neat): ν_{NO} 1703 (vs); $\nu_{C\equiv C}$ 1799 (m). HRMS: calc. for ($C_{27}H_{26}NO_2PRe$)$^+$: 614.1276; found: 614.1267.

4.1.4. [(η^5-C_5H_5)Re(NO)(PPh_3)(H_3CC≡CCH_2OH)]$^+$ [BF_4]$^-$ ***5c***

2-Butyn-1-ol was used as alcohol. Yield: 102 mg, 0.145 mmol, 81%. Two rotamers 50:50. ^{1}H-NMR (400 MHz, DMSO) δ: 7.46–7.85 (m, 24H, PPh_3); 7.14–7.35 (m, 6H, PPh_3); 6.20 (s, 10H, C_5H_5); 5.83 (t, 1H, $J = 6.1$, CH_2OH); 5.54 (t, 1H, $J = 5.1$, CH_2OH); 5.14 (dd, 1H, $J = 16.3$, 5.1, CH_2OH); 4.86 (dd, 1H, $J = 16.3$, 5.1, CH_2OH); 3.74 (dd, 1H, $J = 16.3$, 6.1, CH_2OH); 3.55 (dd, 1H, $J = 16.3$, 6.1, CH_2OH); 3.06 (s, 3H, CH_3); 1.84 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, DMSO) δ: 126.0–135.0 (Ph); 105.5 (C≡C); 99.8 (C_5H_5); 99.1 (C_5H_5); 98.2 (C≡C); 85.8 ($J_{CP} = 12.2$, C≡C); 84.8 ($J_{CP} = 13.3$, C≡C); 61.7 (CH_2OH); 60.8 ($J_{CP} = 6.1$, CH_2OH); 18.2 ($J_{CP} = 1.9$, CH_3); 12.1 ($J_{CP} = 5.7$, CH_3). ^{31}P {^{1}H}-NMR (121 MHz, DMSO) δ: 13.0 (s); 16.9 (s). IR (cm^{-1}, neat): ν_{NO} 1702 (vs); $\nu_{C\equiv C}$ 1880 (m). HRMS: calc. for ($C_{27}H_{26}NO_2PRe$)$^+$: 614.1276; found: 614.1260.

4.1.5. [(η^5-C_5H_5)Re(NO)(PPh_3)($HOCH_2C$≡CCH_2OH)]$^+$ [BF_4]$^-$ ***5d***

2-Butyn-1,4-diol was used as alcohol. Yield: 69.5 mg, 0.097 mmol, 54%. ^{1}H-NMR (400 MHz, CD_3COCD_3) δ: 7.58–7.83 (m, 11H, PPh_3); 7.27–7.45 (m, 4H, PPh_3); 6.28 (s, 5H, C_5H_5); 5.24 (d, 1H, $J = 16.3$, CH_2); 5.08 (d, 1H, $J = 16.3$, CH_2); 4.98 (s, 1H, CH_2OH); 4.61 (s, 1H, CH_2OH); 3.94 (d, 1H, $J = 16.3$, CH_2); 3.70 (d, 1H, $J = 16.3$, CH_2). ^{13}C-NMR (100 MHz, CD_3COCD_3) δ:

127.5–136.0 (Ph); 105.4 (C≡C); 100.3 (C_5H_5); 90.8 ($J_{CP}=13.7$, C≡C); 62.3 (CH_2OH); 61.5 ($J_{CP}=5.3$, CH_2OH). ^{31}P {^1H}-NMR (121 MHz, CD_3COCD_3) δ: 14.4 (s). IR (cm^{-1}, neat): ν_{NO} 1710 (vs); $\nu_{C\equiv C}$ 1868 (m). HRMS: calc. for $(C_{27}H_{26}NO_3PRe)^+$: 630.1209; found: 630.1219.

4.1.6. [(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=$CHCH_2CH_2OH$)]$^+$[BF_4]$^-$ **6b**

3-Buten-1-ol was used as alcohol. Yield: 83.0 mg, 0.118 mmol, 66%. Two diastereomers in a 84:16 ratio. (major). ^1H-NMR (400 MHz, CD_2Cl_2) δ: 7.45–7.58 (m, 9H, PPh_3); 7.22–7.34 (m, 6H, PPh_3); 5.70 (s, 5H, C_5H_5); 4.42–4.53 (m, 1H, =CH); 3.68–3.78 (m, 1H, CH_2OH); 3.58–3.67 (m, 1H, CH_2OH); 2.43–2.52 (m, 1H, =CH_2); 2.32–2.42 (m, 1H, C$\underline{H}_2$$CH_2OH$); 2.27 (ddd, 1H, $J=10.2$, 4.1, $J_{PH}=6.6$, =CH_2); 1.95–2.08 (m, 1H, C$\underline{H}_2$$CH_2OH$). ^{13}C-NMR (100 MHz, CD_2Cl_2) δ: 133.3 ($J_{CP}=9.9$, *o*–Ph); 132.4 ($J_{CP}=2.7$, *p*–Ph); 130.4 ($J_{CP}=59.5$, *i*–Ph); 129.8 ($J_{CP}=11.1$, *m*–Ph); 97.1 (C_5H_5); 64.2 (CH_2OH); 48.6 (=CH); 40.6 ($\underline{C}H_2CH_2OH$); 38.5 ($J_{CP}=5.7$, CH_2=). ^{31}P {^1H}-NMR (121 MHz, CD_2Cl_2) δ: 10.7 (s) (minor). ^1H-NMR partiel (400 MHz, CD_2Cl_2) δ: 7.45–7.58 (m, 9H, PPh_3); 7.22–7.34 (m, 6H, PPh_3); 5.61 (s, 5H, C_5H_5); 3.68–3.78 (m, 1H, CH_2OH); 3.58–3.67 (m, 1H, CH_2OH); 2.89–2.98 (m, 1H, =CH); 2.63–2.71 (m, 1H, CH_2CH_2OH); 1.95–2.08 (m, 1H, =CH_2); 1.58–1.69 (m, 1H, CH_2CH_2OH). ^{13}C {^1H}-NMR (100 MHz, CD_2Cl_2) δ: 133.4 ($J_{CP}=9.2$, *o*–Ph); 132.5 (*p*–Ph); 129.8 (*m*–Ph); 97.8 (C_5H_5); 66.7 (CH_2OH); 50.6 (=CH); 42.8 ($\underline{C}H_2CH_2OH$); 39.0 ($J_{CP}=4.9$, CH_2=). ^{31}P {^1H}-NMR (121 MHz, CD_2Cl_2) δ: 10.9 (s). IR (cm^{-1}, neat): ν_{NO} 1718 (vs). HRMS: calc. for $(C_{27}H_{28}NO_2PRe)^+$: 616.1416; found: 616.1409.

4.1.7. Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=$CHCH_2OH$)]$^+$[BF_4]$^-$ **6a**

Complex (η^5-C_5H_5)Re(NO)(CH_3)(PPh_3) **1** (100 mg, 0.179 mmol) and CH_2Cl_2 (10 ml) were cooled to −78°C and $HBF_4\cdot OEt_2$ (85%, 32 μl, 0.18 mmol) was added with stirring. After 30 min, a large excess of allyl alcohol (2 ml) was added. The reaction mixture was stirred for 1 h at −78°C, was then allowed to warm to −23°C over the course of 1 h and was stirred overnight at r.t. Solvent was removed by rotary evaporation. The resulting residue was chromatographed on a silica gel column with use of 4:1 dichloromethane/acetone (v/v) to give compound **6a** as a white–yellow oil. Yield: 97.4 mg, 0.141 mmol, 79%. Only one diastereomer was observed. ^1H-NMR (400 MHz, CD_3COCD_3) δ: 7.62–7.71 (m, 9H, PPh_3); 7.53–7.61 (m, 6H, PPh_3); 6.10 (s, 5H, C_5H_5); 4.67–4.77 (m, 1H, =CH); 4.28–4.37 (m, 1H, $CH_2O\underline{H}$); 4.32–4.37 (m, 1H, $J=5.6$, C$\underline{H}_2$OH); 4.00–4.09 (m, 1H, $J=5.6$, C$\underline{H}_2$OH); 2.67 (ddd, 1H, $J=11.2$, 3.6, $J_{PH}=11.2$, =CH_2); 2.24 (ddd, 1H, $J=9.7$, 3.6, $J_{PH}=6.6$, =CH_2). ^{13}C-NMR (100 MHz, CD_3COCD_3) δ: 134.3 ($J_{CP}=9.9$, *o*–Ph); 132.9 ($J_{CP}=2.7$, *p*–Ph); 131.5 ($J_{CP}=58.7$, *i*-Ph); 130.4 ($J_{CP}=11.1$, *m*–Ph); 98.4 (C_5H_5); 66.9 (CH_2OH); 51.6 (=CH); 36.4 ($J_{CP}=5.7$, CH_2=). ^{31}P {^1H}-NMR (121 MHz, CD_3COCD_3) δ: 12.6 (s). IR (cm^{-1}, neat): ν_{NO} 1731 (vs); 1614 (m). HRMS: calc. for $(C_{26}H_{26}NO_2PRe)^+$: 602.1259; found: 602.1253.

4.1.8. Preparation of α,β-unsaturated aldehyde and ketone complexes

To complex **5c**, **6a**,**b** (50 mg) in DMSO (1.5 ml) IBX (2.1 equivalents) was added by portions under nitrogen. The mixture was stirred for 4 h at r.t. Water (2 ml) and dichloromethane (10 ml) were added and the organic phase was separated, washed twice with water, dried over $MgSO_4$. Solvents were removed by rotary evaporation. The resulting yellow syrup was rapidly chromatographed on a short silica gel column (l:1.5 cm) with use of 4:1 dichloromethane/acetone (v/v).

4.1.9. [(η^5-C_5H_5)Re(NO)(PPh_3)(HC≡$CC(CH_3)O$)]$^+$[BF_4]$^-$ **7b**

The reaction was performed starting from complex **5b**. Yield: 37.9 mg, 0.054 mmol, 76%. ^1H-NMR (400 MHz, CD_3COCD_3) δ: 8.20 (d, 1H, $J_{PH}=18.4$, CH); 7.58–7.77 (m, 9H, PPh_3); 7.42–7.55 (m, 6H, PPh_3); 6.28 (s, 5H, C_5H_5); 2.77 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, CD_3COCD_3) δ: 192.3 ($J_{CP}=2.3$, CO); 135.0 ($J_{CP}=10.7$, *o*–Ph); 134.2 ($J_{CP}=2.7$, *p*–Ph); 131.4 ($J_{CP}=11.4$, *m*–Ph); 109.9 ($J_{CP}=14.5$, –C≡$\underline{C}$H); 101.3 ($\underline{C}$≡CH); 101.1 (C_5H_5); 34.2 (CH_3). ^{31}P {^1H}-NMR (121 MHz, CD_3COCD_3) δ: 17.1 (s). IR (cm^{-1}, neat): ν_{NO} 1718 (vs); ν_{CO} 1680 (vs).

4.1.10. [(η^5-C_5H_5)Re(NO)(PPh_3)(H_3CC≡$CCHO$)]$^+$[BF_4]$^-$ **7c**

The reaction was performed starting from complex **5c**. Yield: 65.0 mg, 0.093 mmol, 65%. Two rotamers 42:58 (minor). ^1H-NMR (400 MHz, CD_3COCD_3) δ: 11.04 (s, 1H, CHO); 7.86–7.52 (m, 9H, PPh_3); 7.24–7.47 (m, 6H, PPh_3); 6.30 (s, 5H, C_5H_5); 2.31 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, CD_3COCD_3) δ: 183.9 ($J_{CP}=2.3$, CHO); 135.9–129.8 (Ph); 119.4 ($J_{CP}=12.5$, C≡C); 100.1 (C_5H_5); 93.1 (C≡C); 14.5 ($J_{CP}=4.9$, CH_3). ^{31}P {^1H}-NMR (121 MHz, CD_3COCD_3) δ: 17.6. IR (cm^{-1}, neat): ν_{NO} 1719 (vs); ν_{CO} 1667 (vs) (major). ^1H-NMR (400 MHz, CD_3COCD_3) δ: 10.05 (s, 1H, CHO); 7.86–7.52 (m, 9H, PPh_3); 7.24–7.47 (m, 6H, PPh_3); 6.29 (s, 5H, C_5H_5); 3.34 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, CD_3COCD_3) δ: 185.5 ($J_{CP}=5.7$, CHO); 135.9–129.8 (Ph); 126.8 (C≡C); 101.5 ($J_{CP}=0.8$, C_5H_5); 86.6 ($J_{CP}=13.8$, C≡C); 19.3 ($J_{CP}=1.9$, CH_3). ^{31}P {^1H}-NMR (121 MHz, CD_3COCD_3) δ: 17.6. IR (cm^{-1}, neat): ν_{NO} 1719 (vs); ν_{CO} 1667 (vs).

*4.1.11. $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCHO)]^+ [BF_4]^-$ **8a***

The reaction was performed starting from complex **6a**. Yield: 60.8 mg, 0.089 mmol, 61%. The spectroscopic data are consistent with those previously reported by Gladysz et al. [11].

*4.1.12. Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH{-}CH{=}CH{-}C(CH_3)O)]^+[BF_4]^-$ **9***

To complex **8a** (520 mg, 0.76 mmol) and anhydrous CH_3CN (50 ml) methyl(triphenylphosphoranylidene)ketone (506 mg, 1.59 mmol) was added. The reaction mixture was stirred for 5 h at 65°C. The solvent was removed by rotary evaporation. The resulting residue was added to a CH_2Cl_2/EtOH solution. The resulting tan powder was collected by filtration, washed with Et_2O and dried under oil-pump vacuum to give complex **9** as a white-yellow solid. Yield: 402 mg, 0.55 mmol, 73%. Only one diastereomer was observed. ^{1}H-NMR (CD_3CN, 400 MHz) δ: 7.55–7.68 (m, 9H, PPh_3); 7.39–7.48 (m, 6H, PPh_3); 6.47 (dd, 1H, $J = 9.7$, 15.8, $\underline{H}C{=}CH{-}CO$); 6.29 (d, 1H, $J = 15.8$, $HC{=}C\underline{H}{-}CO$); 5.83 (s, 5H, C_5H_5); 4.94 (m, 1H, $J =$ 9.2, 9.7, 10.7, $J_{PH} = 2.0$, $H_2C{=}C\underline{H}{-}$); 2.73 (ddd, 1H, $J = 9.2$, 4.6, $J_{PH} = 10.7$, $\underline{H}_2C{=}CH{-}$); 2.48 (ddd, 1H, $J = 10.7$, 4.6, $J_{PH} = 6.1$, $\underline{H}_2C{=}CH$); 2.18 (s, 3H, CH_3). ^{13}C {^{1}H}-NMR (CD_3CN, 100 MHz) δ: 197.9 (CO); 149.2 (CH=CH); 134.1 ($J_{CP} = 9.9$, *o*–Ph), 133.1 ($J_{CP} = 3.0$, *p*–Ph); 130.9 (CH=CH); 130.4 ($J_{CP} =$ 11.6, *m*–Ph), 99.1 (C_5H_5), 45.6 ($H_2C{=}\underline{C}H$), 38.7 ($J_{CP} =$ 6.1, $H_2\underline{C}{=}CH$); 27.1 (CH_3). ^{31}P {^{1}H}-NMR (CD_3CN, 121 MHz) δ: 11.1. IR (cm^{-1}, neat): ν_{NO} 1726 (vs). HRMS calc. for $C_{29}H_{28}NO_2PRe$: 640.1417, found: 640.1415.

*4.1.13. Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH{-}CH{=}CH{-}CH(CH_3)OH)]^+[BF_4]^-$ **10***

Complex **9** (110 mg, 0.15 mmol) and anhydrous methanol (17 ml) were cooled to −20°C and $NaBH_4$ (8.5 mg, 0.225 mmol) was added with stirring. The reaction mixture was stirred for 20 min at this temperature then hydrolysed. The organic compounds were extracted three times with CH_2Cl_2. The organic phases were dried and solvents were removed in vacuo. The resulting residue was chromatographed on a silica gel column with use of 1:1 dichloromethane/diethyl ether/hexane solution. Complex **10** was isolated as a grey solid. Two diastereomers in a 55:45 ratio. Yield: 75.0 mg, 0.103 mmol, 68%. ^{1}H-NMR (CD_3CN, 400 MHz) δ: 7.32–7.66 (m, 15H, PPh_3); 5.93 and 5.89 (2dd, 2H, $J = 5.7$, 12.8, $C\underline{H}CHOH$); 5.75 and 5.74 (2s, 10H, C_5H_5); 5.53 and 5.49 (2dd, 2H, $J = 9.6$, 12.8, $\underline{H}C{=}CH{-}$ CHOH); 5.09 and 5.06 (2m, 2H, $H_2C{=}C\underline{H}{-}$); 4.36 and 4.32 (2m, 2H, $C\underline{H}{-}OH$); 2.68 (dt, 2H, $J = 4.3$, 10.9, $J_{PH} = 10.9$, $\underline{H}_2C{=}CH{-}$); 2.27 (m, 2H, $J = 4.3$, 9.8, $J_{PH} = 5.8$, $\underline{H}_2C{=}CH$); 1.18 and 1.20 (2d, 6H, $J = 6.3$, CH_3). ^{13}C {^{1}H}-NMR (CD_3CN, 100 MHz) δ: 139.7 ($-\underline{C}H{=}CH{-}CHOH$ or $-CH{=}\underline{C}H{-}CHOH$); 134.0 ($J_{CP} = 9.9$, *o*–Ph), 132.9 ($J_{CP} = 2.7$, *p*–Ph); 131.3 ($J_{CP} = 58.7$, *i*–Ph); 131.1 and 131.0 ($-\underline{C}H{=}CH{-}CHOH$ or $-CH{=}\underline{C}H{-}CHOH$); 130.3 ($J_{CP} = 11.1$, *m*–Ph), 98.3 ($C_5H_5$), 67.4 (CHOH); 50.7 and 50.6 ($H_2C{=}\underline{C}H$), 36.3 and 36.2 ($J_{CP} = 5.7$, $H_2\underline{C}{=}CH$); 24.7 and 24.5 (CH_3). ^{31}P {^{1}H}-NMR (CD_2Cl_2, 121 MHz) δ: 11.0 (s). IR (cm^{-1}, neat): ν_{NO} 1720 (vs). HRMS calc. for $C_{29}H_{30}NO_2PRe$: 642.1573, found: 642.1571.

*4.1.14. Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2OCOCH_3)]^+[BF_4]^-$ **11***

Pyridine (2 ml, 25 mmol) and acetic anhydride (1 ml, 11 mmol) were added to complex **6a** (200 mg, 0.29 mmole) with stirring. After 24 h of stirring at r.t., CH_2Cl_2 (10 ml) was added to the reaction mixture. The solution was washed with aqueous KH_2PO_4, brine and water. The organic phase was dried on $MgSO_4$ and the volatile part was removed in vacuo. To the resulting residue was added a 1:1 dichloromethane/diethyl ether solution. The resulting tan powder was collected by filtration, washed with diethyl ether and dried under oil-pump vacuum to give complex **11** as a brown solid. Yield: 148 mg, 0.203 mmol, 70%. Only one diastereomer was observed. ^{1}H-NMR (400 MHz, CD_3NO_2) δ: 7.60–7.72 (m, 9H, PPh_3); 7.52–7.58 (m, 6H, PPh_3); 5.98 (s, 5H, C_5H_5); 4.43–4.60 (m, 3H, CH_2O and =CH); 2.69 (ddd, 1H, $J = 10.7$, 4.6, $J_{PH} = 10.7$, $H_2C{=}$); 2.36 (ddd, 1H, $J = 9.7$, 4.6, $J_{PH} = 6.6$, $H_2C{=}$); 2.06 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, CD_3NO_2) δ: 172.3 (CO); 134.8 ($J_{CP} = 9.9$, *o*–Ph); 133.7 ($J_{CP} = 2.7$, *p*–Ph); 131.5 ($J_{CP} = 59.9$, *i*–Ph); 130.9 ($J_{CP} = 11.1$, *m*–Ph); 99.2 (C_5H_5); 69.7 (CH_2O); 44.4 (=CH); 37.6 ($J_{CP} =$ 6.1, $=CH_2$); 21.0 (CH_3). ^{31}P {^{1}H}-NMR (121 MHz, $CDCl_3$) δ: 10.3. HRMS: calc. for $(C_{28}H_{28}NO_3PRe)^+$: 644.1366; found: 644.1376.

*4.1.15. Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH(CH_2OC(O)CH_3))-(CH(CO_2CH_3)_2)$ **12***

In a flask sodium hydride (3 mg, 0.125 mmol), THF (4 ml) and dimethylmalonate (18 μl, 0.157 mmol) were added. After 15 min of stirring, a solution of the complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2OAc)]^+ BF_4^-$ **11** (100 mg, 0.137 mmol) in THF (2 ml) was added and the reaction mixture was stirred for 4 h. Dichloromethane (20 ml) was then added, the solution was washed with a 10% aqueous KOH, brine and water. The organic phase was dried on $MgSO_4$ and the solvents were removed in vacuum. The resulting residue was chromatographed on a 3 cm silica gel column with use of 4:1 dichloromethane/acetone (v/v). The complex **12** was isolated as a yellow oil. Yield: 81.5 mg, 0.095 mmol, 69%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.31–7.43

(m, 15H, PPh_3); 5.02 (s, 5H, C_5H_5); 4.61 (dd, 1H, $J = 11.2$, 3.6, CH_2OAc); 3.98 (dd, 1H, $J = 11.2$, 7.6, CH_2OAc); 3.69 (s, 3H, CO_2CH_3); 3.52 (s, 3H, CO_2CH_3); 3.43 (d, 1H, $J = 7.1$, $C\underline{H}(CO_2CH_3)_2$); 2.53–2.63 (m, 1H, $C\underline{H}CH_2Re$); 2.02 (s, 3H, $C(O)CH_3$); 1.62–1.79 (m, 2H, CH_2Re). ^{13}C-NMR 100 MHz, CD_3NO_2) δ: 171.7 (CO); 170.4 (CO); 170.3 (CO); 136.8 ($J_{CP} =$ 51.5, *i*–Ph); 134.2 ($J_{CP} = 10.3$, *o*–Ph); 130.6 ($J_{CP} = 2.3$, *p*–Ph); 129.0 ($J_{CP} = 9.9$, *m*–Ph); 90.6 ($J_{CP} = 1.5$, C_5H_5); 68.1 (CH_2O); 58.1 ($\underline{C}H(CO_2CH_3)_2$); 52.8 ($CO_2\underline{C}H_3$); 52.6 ($CO_2\underline{C}H_3$); 49.4 ($J_{CP} = 4.2$, $\underline{C}HCH_2Re$); 21.8 ($OC(O)\underline{C}H_3$); 0.5 ($J_{CP} = 5.3$, $\underline{C}H_2Re$). ^{31}P {^{1}H}-NMR (121 MHz, $CDCl_3$) δ: 24.1. IR (cm^{-1}, neat): ν_{NO} 1732 (vs); ν_{CO} 1629 (vs). HRMS: calc. for $(C_{33}H_{35}NO_7PRe)^+$: 775.1710; found: 775.1732.

Acknowledgements

We thank Dr P. Guenot for performing the mass spectral experiments.

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