Regio- and Stereoselective Nucleophilic Substitutions of Chiral Allylic Alcohol Rhenium Complexes

Stéphanie Legoupy, Christophe Crévisy, Jean-Claude Guillemin,* René Grée, and Loic Toupet

Abstract: In the presence of a small amount of a Lewis acid, the nucleophilic substitution by alcohols, thiols, allyltrimethylsilane, or triphenylphosphane of the hydroxy group in allylic alcohols complexed to a chiral rhenium salt affords the corresponding ethers, thioethers, 1,5-dienes, and phosphonium salts in high yield. Similarly, complexed allyl halides are prepared on treatment with thionyl chloride or phosphorus tribromide. The efficiency of the reaction strongly depends on the Lewis acid and the leaving group. The high regioselectivity of this reaction was unambiguously determined by means of a deuterated ligand or with substituted allylic alcohols. The reaction of the separate diastereoisomeric rhenium complexes derived from 3-buten-2-ol established that this substitution is stereospecific with overall retention of configuration.

Keywords: allyl complexes · ligand effects · nucleophilic additions · reaction mechanisms · rhenium

Introduction

The complexes of various transition metals, such as Pd, Pt, Mo, Rh, Ru, Ni, Co, W, and Fe, have been used to perform allylic substitution reactions.[1, 2] For most of these complexes, the regio- and stereoselectivity are strongly dependent upon the nature of the metal, the ligands, and the nucleophiles. Extensive studies have been carried out, particularly with π-allyl complexes of palladium, which are used in organic synthesis both as stoichiometric reagents and as catalysts.[2] Furthermore, complexes with mainly chiral nonracemic ligands have been successfully employed in asymmetric syntheses.[3]

Another possible approach to asymmetric synthesis involves chirality at the metal center. Faller et al. have studied chiral molybdenum complexes in detail: nucleophilic addition gave interesting results in terms of regioselectivity, stereoselectivity, and asymmetric synthesis.[4] Hitherto, very few π-allyl rhenium complexes have been reported. Starting from a *neutral* rhenium complex, Sutton et al. have recently isolated a π-allyl derivative and studied its reactivity with various nucleophiles.[5] Gladysz et al. have prepared the chiral rhenium complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)]$ in which the chirality is centered at the metal atom,[6] and have extensively studied the properties of such complexes.[7] The corresponding rhenium salt, on complexation to an alkene, could act as a protecting group for the double bond, activate a bound substrate, or be useful in enantioselective transformations. Starting from the same intermediate, we have recently prepared several chiral rhenium complexes of unsaturated alcohols and performed a variety of transformations on the appending functionalities (e. g. oxidation of alcohol, Wittig reaction, reduction)[8] which indicates that such a complex can act as an efficient protecting group for the carbon–carbon double bond. Herein we report that these cationic rhenium complexes also activate allylic substitutions on the ligand and therefore promote nucleophilic substitutions *under acidic conditions*. Furthermore, we use simple models to demonstrate that such chiral rhenium complexes offer very interesting new possibilities for regio- and stereocontrolled allylic substitution under mild conditions, and we propose a mechanism for these transformations.[9]

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Results

Synthesis of allylic alcohol rhenium complexes: The allylic complex **1**[8] was prepared as previously reported. A similar experimental procedure was used to synthesize the allyl $[D_2]$alcohol complex **1′** and the 3-buten-2-ol complex **2** with a yield of 79 and 82%, respectively (Scheme 1).[10] The two

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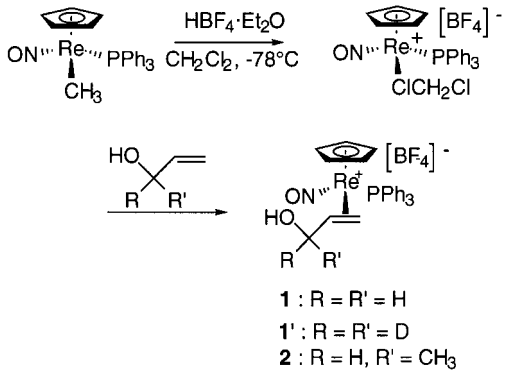


Scheme 1. Synthesis of allylic alcohol rhenium complexes **1**, **1′**, and **2**.

diastereomers of the 3-buten-2-ol complex **2a**,**b** were easily separated by chromatography. The structure of each diastereomer (*RSS*,*SRR*)[11] **2a** and (*RSR*,*SRS*) **2b**, determined by NMR and IR spectroscopy, was unambiguously confirmed by X-ray spectroscopy (Figures 1 and 2).

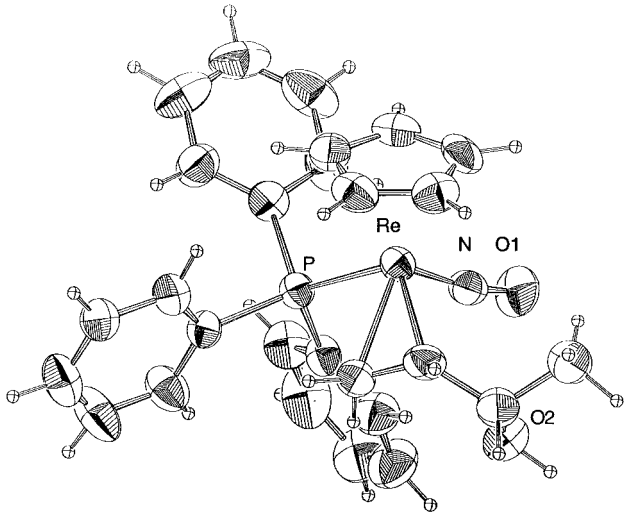


Figure 1. Crystal structure of (*RSS*,*SRR*) diastereomer **2a**.

Abstract in French: *La substitution nucléophile a été étudiée sur des complexes chiraux du rhénium possédant des alcools allyliques comme ligands. En présence d'une petite quantité d'acide de Lewis, l'addition d'alcools, de thiols, d'allyltriméthylsilane ou de triphénylphosphine sur ces complexes conduit aux éthers, thioéthers, 1,5-diène et sel de phosphonium correspondants. Les halogénures d'allyles complexés sont aussi préparés par réaction du chlorure de thionyle ou du tribromure de phosphore. Ces synthèses sont dépendantes de la nature de l'acide de Lewis et du groupe partant qui peut être un hydroxyle, un acétate ou un alkoxy. La grande régiosélectivité de ces substitutions est montrée sur des composés marqués au deutérium ou substitués (alcool crotylique et 3-butèn-2-ol). Cette réaction est aussi stéréospécifique : chaque diastéréoisomère du 3-butène-2-ol complexé conduit en présence d'alcool propargylique à un seul diastéréoisomère de l'éther complexé correspondant avec rétention globale de configuration.*

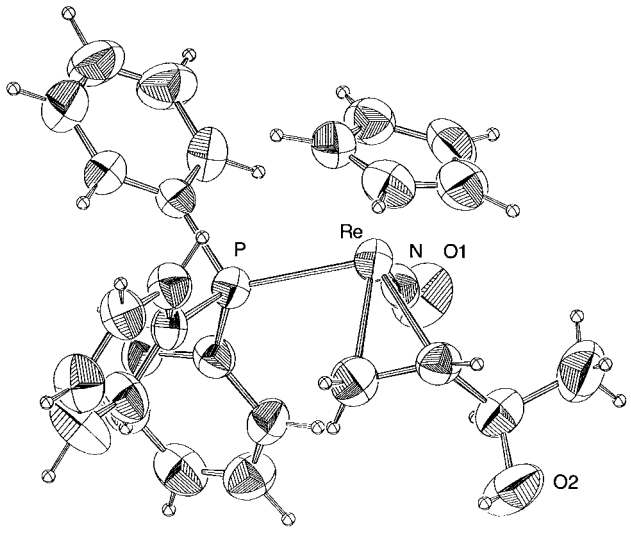
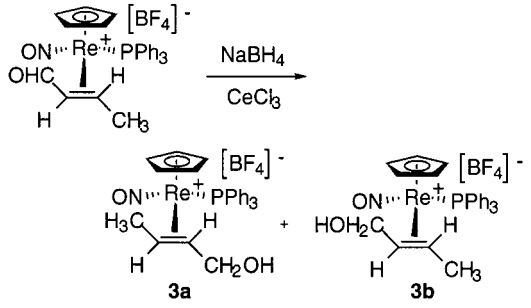


Figure 2. Crystal structure of (*RSR*,*SRS*) diastereomer **2b**.

Attempts to complex the crotyl alcohol by a similar approach only led to traces of the desired product **3a**,**b**. This result can be attributed to the steric hindrance induced by the methyl group on the γ-carbon and is consistent with results obtained with 1,2-disubstituted alkenes[7] or other allylic alcohols, such as the buten-2,3-diol.[8] In order to obtain complexes **3a**,**b**, we chemoselectively reduced the previously reported crotonaldehyde complex.[7b] A low yield (10%) was obtained with diisobutylaluminum hydride (DIBAL-H) as the reducing agent, while the reaction at low temperature with the Luche reagent ($CeCl_3$–$NaBH_4$)[12] led to the crotyl alcohol complex in a 51% yield. The two conformational isomers **3a** and **3b** were observed in a 51/49 ratio (Scheme 2).



Scheme 2. Synthesis of the crotyl alcohol rhenium complexes **3a,b**.

For such rhenium complexes of *trans* disubstituted olefins,[6, 7, 13] it is generally accepted that the two substituents occupy the *a* and *c* positions to minimize the steric hindrance (Figure 3). The conformers **3a** and **3b** were unambiguously identified by their ^{13}C NMR spectra: a singlet at $\delta = 22.9$ for the methyl group is characteristic of the isomer with this substituent *syn* with respect to the NO ligand (**3a**). A J(C,P) coupling constant of 2.7 Hz for the signal at $\delta = 21.4$ is characteristic of the isomer with the methyl group *syn* with respect to the PPh_3 ligand.

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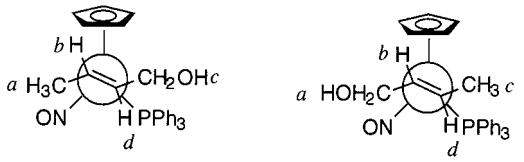
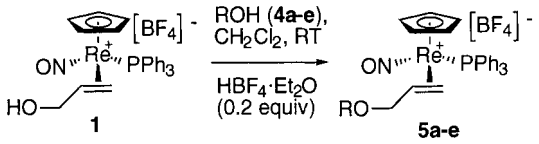


3a **3b**

Figure 3. Rotamers of crotyl complexes **3a** and **3b**.

Nucleophilic substitutions of complexed allylic alcohols: We will now present clear evidence that this complexation activates the allylic function and acts simultaneously as a protection of the carbon–carbon double bond. The addition of a substoichiometric amount (20%) of $HBF_4 \cdot Et_2O$ to a dichloromethane solution of the chiral cationic rhenium complex **1**[6] and a primary or secondary alcohol **4a–e** led to the corresponding complexed unsaturated ether **5a–e** in very good yields (76–87%) (Scheme 3). In the case of



4a, **5a**: R = HC≡C-CH_2 **4d**, **5d**: R = *n*Bu
4b, **5b**: R = MeC≡C-CH_2 **4e**, **5e**: R = CH_2=CH-CH_2
4c, **5c**: R = HC≡C-CH(Me)

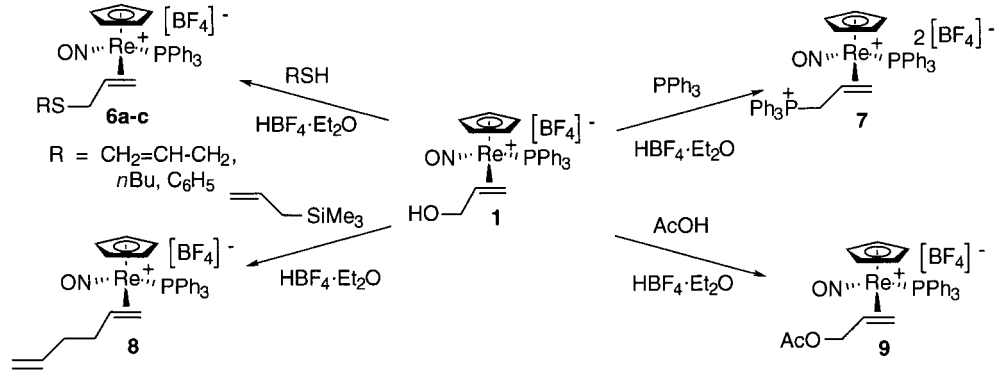
Scheme 3. Nucleophilic substitutions of complexed allylic alcohol **1** with alcohols to give the corresponding complexed unsaturated ethers.

unsaturated nucleophiles, it is noteworthy that the unsymmetrical unsaturated ethers **5a–c** are formed with selective coordination of the carbon–carbon double bond, without any shift of the organometallic unit. Complex **1** reacted with 3-butyn-2-ol **4c** to afford complex **5c** as a mixture of two diastereomers in a 45/55 ratio. It should be noted that the free allylic alcohol did not lead to the corresponding ether in the presence of $HBF_4 \cdot Et_2O$, and our attempts to complex the allylic ethers directly were also unsuccessful. Consequently, our approach is a simple method to synthesize complexed allylic ethers by activation of the allylic position.

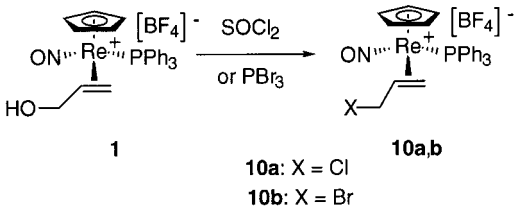
The substitution of the hydroxy group has been extended to several other nucleophiles. The reaction of **1** with allylthiol, butanethiol, and thiophenol led to the corresponding complexed thioethers **6a–c** in 82, 86, and 88% yield, respectively. The formation of thioethers (and not of ethers) is the first indication that the mechanism must involve a nucleophilic attack of the reagent on the ligand of complex **1**. The NMR data provide evidence that there was no shift in the bonding to the sulfur atom: we have thus prepared the first allylic thioethers complexed through a carbon–carbon double bond, since the direct complexation of thioethers leads to compounds complexed at the sulfur atom.[14] The phosphonium salt **7**, which is a potential substrate for Wittig reactions, was formed by the reaction of complex **1** with triphenylphosphine in the presence of one equivalent of $HBF_4 \cdot Et_2O$ (60% yield). A carbon–carbon bond has also been formed by the reaction of compound **1** with allyltrimethylsilane, which yields the 1,5-hexadiene complex **8** in a 74% yield. The allyl acetate complex **9** was similarly prepared in a 63% yield by reaction of complex **1** with acetic acid in the presence of a catalytic amount of $HBF_4 \cdot Et_2O$ (Scheme 4).[15]

We have thus formed C–O, C–C, C–S, and C–P bonds but we failed in our attempts to prepare complexed allylic amines, probably because $HBF_4 \cdot Et_2O$ reacts with the amine and not with the less basic alcohol. The reaction of these complexes with silyl enol ethers was also unsuccessful, as the acid generally decomposed the latter.

Other reactions can be performed on complexed allylic alcohols which lead to compounds that could not be obtained by direct complexation of the corresponding ligands. This is the case with allylic halides: the reaction of complex **1** with thionyl chloride (Scheme 5) in dichloromethane at room temperature gave the allyl chloride complex **10a** in a 79% yield. The reaction with phosphorus tribromide gave the complexed allylic bromide in 80% yield. Complex **10b** was purified by crystallization, as the complex is unstable on silica gel. Thus, compounds **10a** and **10b** are the first examples of allylic halides coordinated to this organometallic unit.



Scheme 4. Further nucleophilic substitutions of complexed allylic alcohol **1**.



Scheme 5. The reaction of complex **1** with thionyl chloride and with phosphorus tribromide.

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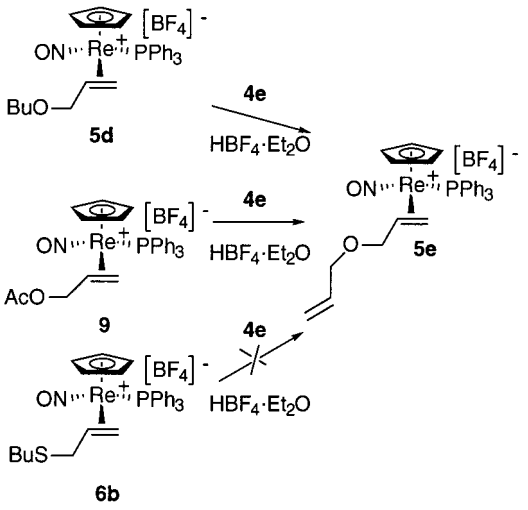
Mechanistic studies: Detailed mechanistic studies were performed to elucidate the effect of the acid and the leaving group and to establish the regio- and stereoselectivity of this reaction. The nucleophilic substitution is dependent on the nature of the acid, and the formation of compounds **5a–e** can be best achieved by the use of substoichiometric amounts of $HBF_4 \cdot Et_2O$; $BF_3 \cdot Et_2O$ proved to be similarly effective, while $SnCl_4$ led to lower yield of the desired product. No reaction was observed with protic acids, such as camphorsulfonic acid or Amberlyst 15. Titanium tetrachloride acted as a chlorination reagent and the complexed allylic chloride **10a** was obtained.

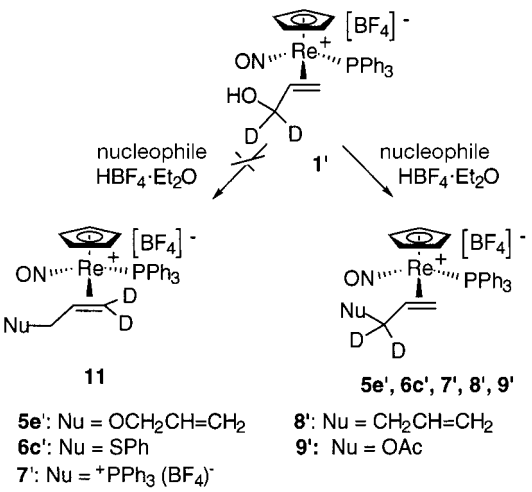
We also found that different leaving groups can be used. For example, the acetate complex **9** reacted with allyl alcohol in the presence of a small amount of $HBF_4 \cdot Et_2O$ to afford complex **5e** in a 86% yield. Similarly, reaction of butyl ether complex **5d** and allyl alcohol gave **5e** in the presence of $HBF_4 \cdot Et_2O$ (95% yield) or $BF_3 \cdot Et_2O$ (87% yield). However, when the sulfide complex **6b** was used, no nucleophilic substitution was observed, either in the presence of allyl alcohol or allyl thiol (Scheme 6). This result can be correlated with the poor leaving group properties of thiols.



Scheme 6. The effect of different leaving groups on the reaction with **4e**.

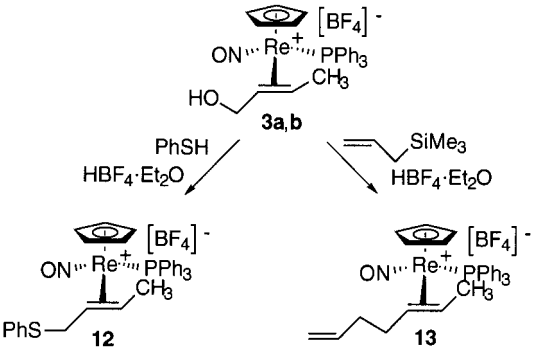
The regioselectivity of these substitution reactions was clearly established by the use of isotopically labeled allyl alcohol (complex **1′**) as well as with the crotyl alcohol **3** or 3-buten-2-ol complex **2**. Complex **1′** participated in nucleophilic substitution reactions with allyl alcohol, thiophenol, triphenylphosphane, allyltrimethylsilane, and acetic acid. In each case, only the products **5e′**, **6c′**, **7′**, **8′,** and **9′**, respectively, were formed which bear the two deuterium atoms on the sp^3 carbon; no allylic rearrangement product was detected by NMR spectroscopy (Scheme 7). The 1,1-dideutero-allyl chloride complex **10a′** was similarly obtained with $SOCl_2$. Since none of the corresponding isomeric complexes **11** was detected at high field in the NMR spectra, these results demonstrate the very high regioselectivity ($\geq$96%) of these reactions.

The nucleophilic substitution is also highly regioselective with the crotyl alcohol complexes **3a**,**b**. In the presence of thiophenol and small amounts of $HBF_4 \cdot Et_2O$, compounds



Scheme 7. The regioselectivity of the substitution reaction was established by the use of isotopically labeled allyl alcohol **1′**.

3a,**b** gave three isomers of the crotyl thioether complex **12**, which could not be separated. They were obtained in a 54/38/8 ratio and in 88% yield (Scheme 8). Under similar conditions, the reaction of **3a**,**b** with the nucleophile allyltrimethylsilane gave three isomers of the 1,5-heptadiene complex **13** in a 40/35/25 ratio. On the basis of the *J*(P,H) and *J*(P,C) coupling

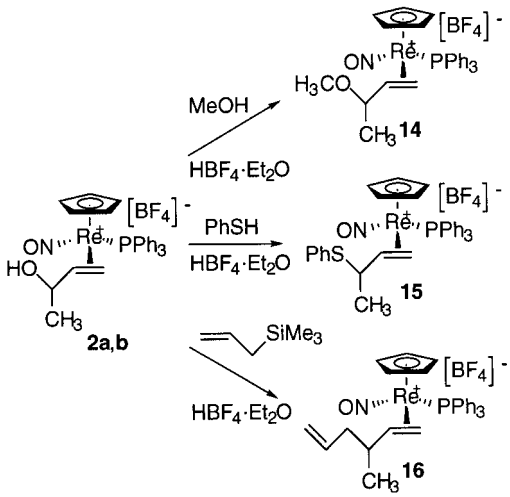


Scheme 8. Regioselective reaction of the crotyl alcohol complexes **3a**,**b** with thiophenol and with allyltrimethylsilane.

constants observed in the ^1H and ^{13}C NMR spectra, we tentatively assign the structure to two compounds with the methyl group *syn* with respect to NO ligand and only one with the methyl group *syn* with respect to the PPh_3 ligand. Although the stereochemistry of the three isomers has not been unambiguously assigned for both reactions, only crotyl derivatives have been identified: all attempts to detect the NMR signals characteristic of the vinylic hydrogens of complexes which could have been formed by an allylic transposition were unsuccessful.

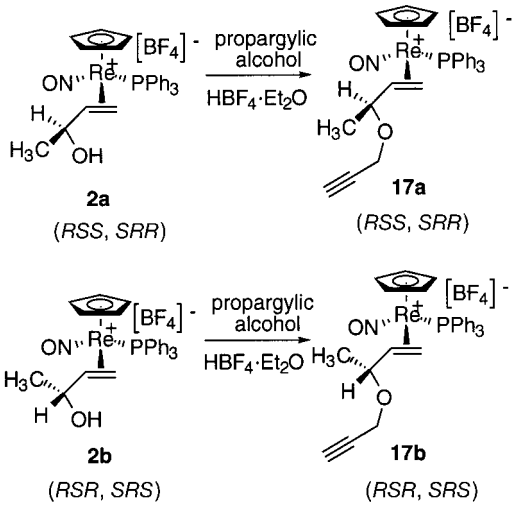
The high regioselectivity of the substitution was also confirmed starting from the 3-buten-2-ol complexes **2a** and **2b** as a mixture of the two diastereomers. Reaction with methanol, thiophenol, or allyltrimethylsilane as nucleophile gave the corresponding complexed ether **14**, thioether **15**, or diene **16** in 74, 80, or 85% yield, respectively. Thus, starting from the complexed secondary alcohols **2a**,**b**, all the nucle-

ophiles added to the most substituted carbon atom and no products from an allylic rearrangement were observed. Furthermore, in each case, the two diastereomeric products were formed in a 45:55 ratio, identical to the diastereomer ratios of the starting complexes **2a**,**b** (Scheme 9). The stereospecificity of the substitution was confirmed by the reaction of



Scheme 9. Regioselective substitution reactions of the 3-buten-2-ol complexes **2a** and **2b**.

2a with thiophenol or allyltrimethylsilane which gave **15a** and **16a**, respectively, as single diastereomers, and, by the reaction of complex **2b** with thiophenol which afforded only the diastereomer **15b**. The stereospecificity was finally unambiguously established by the exclusive formation of complexes **17a** or **17b** in the reaction of the separate diastereomers **2a** and **2b** with propargylic alcohol (Scheme 10). The absolute



Scheme 10. Stereospecific reaction of the separate diastereomers **2a** and **2b** with propargylic alcohol.

structures of both derivatives **17a** and **17b** were established by X-ray analysis, which proved that this reaction occurred with an overall retention of configuration (Figures 4 and 5). Therefore, substitution reactions with these chiral rhenium complexes are highly regioselective and stereospecific.

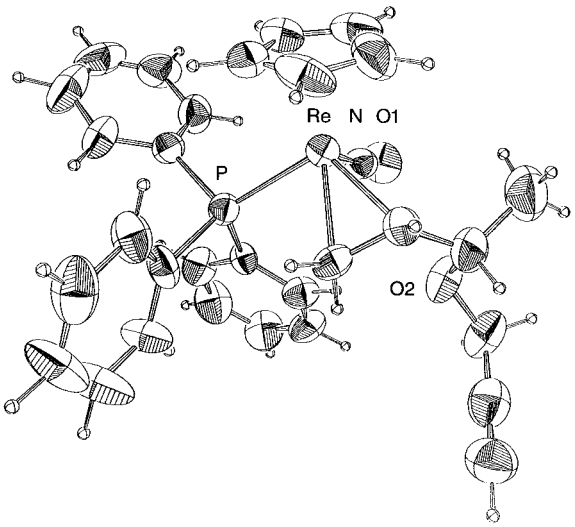


Figure 4. Crystal structure of (*RSS*,*SRR*) diastereomer **17a**.

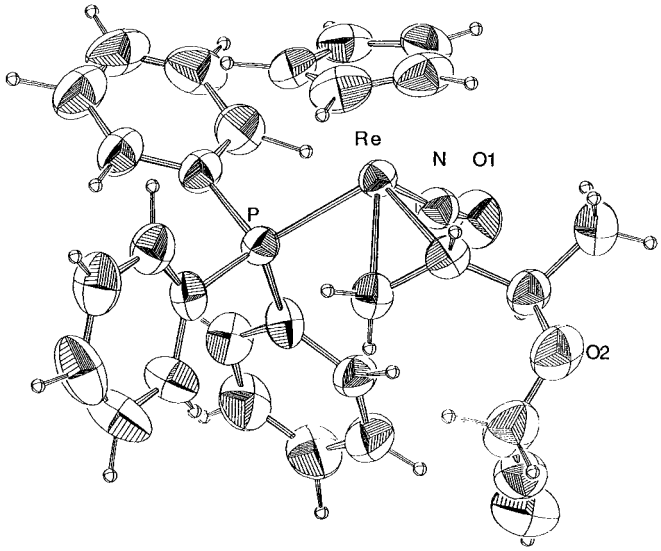


Figure 5. Crystal structure of (*RSR*,*SRS*) diastereomer **17b**.

Discussions

It is generally accepted that allylic substitution on transition metal complexes usually occurs via π-allyl complex intermediates.[2–4] In most cases, the major product is the one which is produced by nucleophilic attack on the less substituted carbon atom, but nucleophilic substitutions can also occur at the more substituted carbon atom.[3] The high regioselectivity observed with the complexed deutero allylic alcohol **1′** or crotyl alcohols **3a**,**b** together with the regio- and stereospecifity of the nucleophilic substitution with complexed 3-buten-2-ol **2a**,**b** provide important evidence concerning the mechanism of the reaction.

In a preliminary communication,[9] we envisaged for these rhenium complexes a reaction occurring by a S_N2-type mechanism rather than by a π-allylic complex, since that pathway could directly explain the lack of allylic rearrangement. However, this hypothesis can now be excluded since the substitu-

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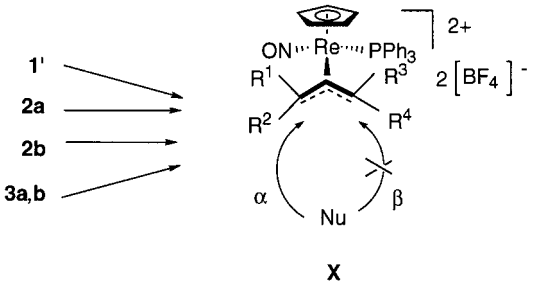
tion with the complexes **2a**,**b** occurs with overall retention of configuration. Thus, type **X** π-allyl intermediates, with chirality at the metal center, have to be considered (Scheme 11).[16]



X

1': $R^1 = R^2 = D$; $R^3 = R^4 = H$
2a: $R^1 = Me$; $R_2 = R^3 = R^4 = H$
2b: $R^2 = Me$; $R^1 = R^3 = R^4 = H$
3a,b: $R^1 = R^2 = H$; R^3, $R^4 = Me$, H

Scheme 11. Possible π-allyl intermediates in the nucleophilic substitution reactions.

The regioselectivity observed in these reactions excludes any control by the substituents of the corresponding π-allyl systems:

1) In the case of the intermediate derived from **1′**, the terminal atoms have either a CH_2 or a CD_2 system and reactions only occur at the CD_2 center.
2) For the derivatives of the butenol complexes **2a**,**b**, addition only occurred at the more substituted carbon atom , while for the products from the closely related crotyl derivatives **3a**,**b**, these additions occurred at the less substituted carbon atom.

This clearly indicates that, as already observed in similar molybdenum complexes,[4] the process is controlled by the chirality at the metal center and by the steric and electronic effects of PPh_3 and NO ligands. The conformational properties of the starting complexes and the π-allyl intermediates must also be considered.

Gladysz et al. have demonstrated conformational preferences of the π ligands in alkenyl complexes: the unsubstituted part of the double bond is on the same side as the bulky triphenylphosphane ligand.[7b, c] The ^1H NMR spectrum of complex **1** is in good agreement with this structure: for instance the coupling constants with the phosphorus atom ($J(P,H) = 11.2$ and 6.6 Hz and $J(C,P) = 5.7$ Hz) were only observed with the methylene group. Similar data were obtained for the two diastereomers **2a** and **2b**. The aforementioned regioselectivity could then be explained for **1′**, **2a**, and **2b** by the *bicationic* π-allyl-type intermediate **X** provided that: i) there is no rotation of the ligand during the protonation step and the departure of the leaving group, ii) there is no isomerization of the π-allyl ligand in this intermediate, and iii) the regioselectivity is controlled by the differences in the steric and electronic effects between the PPh_3 and NO ligands (Scheme 11, path α and not β). After protonation of the hydroxyl group, the departure of H_2O probably occurs *anti* from the rhenium center to produce the intermediates **X**. The nucleophile would then add to this allylic cation on the same, less encumbered side and also from the face opposite to the rhenium center and *syn* from the NO ligand. Such a reaction pathway could also explain the stereoselectivity with the overall retention of configuration observed in the substitution starting from complexes **2a** and **2b**. It is important to point out that previous studies on closely related molybdenum complexes give good support for such a mechanism and indicates that the NO ligand plays a key role in this process.[4] Although the very high regioselectivity of the nucleophilic substitution with crotyl complexes has been proved, the determination of the reaction pathway for these compounds is complicated by the presence of rotamers for both the starting complexes (**3a** and **3b**) and the final products (**12** and **13**). Further studies are still necessary in order to establish the scope and limitations of these substitutions in the case of such 1,2-disubstituted alkenes and to obtain a complete analysis of the reaction pathway.

Conclusion

To conclude, the allylic function of these rhenium complexes is strongly activated towards nucleophilic substitution under acidic conditions. A very high regioselectivity has been observed with labeled allylic and crotylic alcohol complexes. The reaction of the 3-buten-2-ol complexes has provided evidence of the regio- and stereospecifity of this nucleophilic substitution. A mechanism involving a π-allyl bicationic complex has been proposed. Extension of these reactions and further applications in synthesis are under investigation.

Experimental Section

General: All manipulations were performed under an atmosphere of dry nitrogen. 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 were purified by standard methods.

^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer, and the chemical shifts are reported relative to tetramethylsilane (^1H) or to the solvent (^{13}C, $\delta = 77.7$ in $CDCl_3$, $\delta = 62.8$ in CD_3NO_2). High-resolution mass spectra were recorded on a MS/MS ZabSpec TOF VG analytical spectrometer with a FAB positive ionization with Cs^+ by the CRMPO (Centre Regional de Mesures Physiques de l'Ouest).

Preparation of complexed allylic alcohols: General procedure: [(η^5-C_5H_5)Re(NO)(CH_3)(PPh_3)][6] (100 mg, 0.179 mmol) and anhydrous CH_2Cl_2 (10 mL) were cooled to −78 °C and $HBF_4 \cdot OEt_2$ (85 %, 32 μL, 0.179 mmol) was added with stirring. After 30 min, a large excess of the appropriate alcohol (2 mL) was added. The reaction mixture was kept for 1 h at −78 °C and was then allowed to warm to room temperature slowly. The mixture was stirred overnight and the solvent was then removed by rotary evaporation. The resulting residue was chromatographed on a silica gel column (dichloromethane/acetone 4:1(v/v)) to give compound **1′** or **2a**,**b** as yellow-brown oils.

[(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=CHCD_2OH)]$^+$[BF_4]$^-$ (**1′**): 2-[D_2]propen-1-ol was used as the alcohol. Yield: 79 %; ^1H NMR (400 MHz, CD_3CN): $\delta = 7.56-7.68$ (m, 9H; PPh_3), 7.41–7.50 (m, 6H; PPh_3), 5.80 (d, $J(P,H) = 0.8$ Hz, 1H; C_5H_5), 4.48 (ddd, $J = 11.8$, 10.0 Hz, $J(P,H) = 2.1$ Hz, 1H; =CH), 2.57 (ddd, $J = 11.4$, 3.9 Hz, $J(P,H) = 10.4$ Hz, 1H; H_2C=), 2.13 (ddd, J = 10.7, 3.9 Hz, $J(P,H) = 6.7$ Hz, 1H; H_2C=); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): $\delta = 134.2$ (d, $J(C,P) = 9.9$ Hz; *o*-Ph), 133.0 (d, $J(C,P) = 2.7$ Hz; *p*-Ph), 131.4 (d, $J(C,P) = 59.1$ Hz; *i*-Ph), 130.4 (d, $J(C,P) = 11.1$ Hz; *m*-Ph), 98.3 (d, $J(C,P) = 0.8$ Hz; C_5H_5), 50.5 (d, $J(C,P) = 1.0$ Hz; =CH), 36.5 (d, $J(C,P) = 5.7$ Hz; $=CH_2$); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 11.1$; IR (neat):

$\tilde{\nu}_{NO} = 1725$ (vs) cm^{-1}; HRMS calcd for $(C_{26}H_{24}D_2NO_2PRe)^+$: 602.1353, found: 602.1351.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH(CH_3)OH)]^+[BF_4]^-$ (2a,b): 3-Buten-2-ol was used as the alcohol. Yield: 82%. Two diastereomers were observed in a 54:46 ratio. Separation was effected by chromatography (silica gel (13 g) for 150 mg of the two diastereomers, dichloromethane/acetone 4:1 (v/v)).

Minor diastereomer (RSS,SRR) **2a**: ^1H NMR (400 MHz, CD_3COCD_3): $\delta =$ 7.61 – 7.78 (m, 15H; PPh_3), 6.18 (s, 5H; C_5H_5), 4.66 – 4.74 (m, 1H; =CH), 4.42 – 4.47 (m, 1H; CH), 4.36 (d, $J = 4.6$ Hz, 1H; OH), 2.77 (ddd, $J = 10.2$, 4.1 Hz, $J(P,H) = 10.2$ Hz, 1H; $=CH_2$), 2.11 (ddd, $J = 11.2$, 4.1 Hz, $J(P,H) =$ 7.6 Hz, 1H; $=CH_2$), 1.54 (d, $J = 6.1$ Hz, 3H; CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3COCD_3): $\delta = 133.2$ (d, $J(C,P) = 9.9$ Hz; *o*-Ph), 131.8 (d, $J(C,P) =$ 2.7 Hz; *p*-Ph), 130.3 (d, $J(C,P) = 59.5$ Hz; *i*-Ph), 129.2 (d, $J(C,P) =$ 11.1 Hz; *m*-Ph), 97.2 (d, $J(C,P) = 0.8$ Hz; C_5H_5), 70.2 (s; CH), 57.5 (d, $J(C,P) = 1.5$ Hz; =CH), 32.7 (d, $J(C,P) = 6.1$ Hz; CH_2=), 26.6 (s; CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 11.3$ (s); IR (neat): $\tilde{\nu}_{NO} = 1727$ (vs) cm^{-1}; elemental analysis calcd for $C_{27}H_{28}BF_4NO_2PRe \cdot CH_2Cl_2$: C 45.01, H 4.20; found: C 44.79, H 4.23.

Major diastereomer (RSR,SRS) **2b**: ^1H NMR (400 MHz, CD_3COCD_3): $\delta =$ 7.51 – 7.71 (m, 15H; PPh_3), 6.11 (s, 5H; C_5H_5), 4.56 – 4.67 (m, 1H; =CH), 4.37 (d, $J = 4.1$ Hz, 1H; OH), 3.87 – 4.87 (m, 1H; CH), 2.82 (ddd, $J = 10.7$, 4.1 Hz, $J(P,H) = 10.7$ Hz, 1H; $=CH_2$), 2.01 (ddd, $J = 10.7$, 4.1 Hz, $J(P,H) =$ 6.6 Hz, 1H; $=CH_2$), 1.49 (d, $J = 6.1$ Hz, 3H; CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3COCD_3): $\delta = 133.2$ (d, $J(C,P) = 10.3$ Hz; *o*-Ph), 131.8 (d, $J(C,P) =$ 2.7 Hz; *p*-Ph), 130.3 (d, $J(C,P) = 58.7$ Hz; *i*-Ph), 129.3 (d, $J(C,P) =$ 11.1 Hz; *m*-Ph), 97.4 (d, $J(C,P) = 0.8$ Hz; C_5H_5), 71.0 (s; CH), 54.9 (d, $J(C,P) = 1.5$ Hz; =CH), 33.4 (d, $J(C,P) = 6.1$ Hz; CH_2=), 24.9 (s; CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 10.9$ (s); IR (neat): $\tilde{\nu}_{NO} = 1722$ (vs) cm^{-1}; HRMS calcd for $(C_{27}H_{28}NO_2P^{187}Re)^+$ (mixture of the two diastereomers): 616.1415, found: 616.1418; analysis calcd for $C_{27}H_{28}BF_4NO_2PRe \cdot H_2O$: C 42.71, H 3.84; found: C 42.79, H 3.91.

Preparation of the crotylic alcohol complex 3a,b: The crotonaldehyde complex (100 mg, 0.143 mmol), CH_2Cl_2 (2 mL), and methanol (4 mL) were cooled to $-50\,^\circ C$ and cerium(III) chloride (53 mg, 1.5 equiv) was added with stirring. After 5 min, $NaBH_4$ (8 mg, 1.5 equiv) was added. The reaction mixture was stirred for 20 min, allowed to warm to room temperature, and then hydrolyzed. 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 (silica gel, dichloromethane/acetone 4:1 (v/v)) to afford compound **3** as an oil.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3CH{=}CHCH_2OH)]^+[BF_4]^-$ (3): Yield: 51%, two rotamers **3a** and **3b** in a 51:49 ratio; ^1H NMR (400 MHz, CD_3COCD_3): $\delta =$ 7.57 – 7.67 (m, 18H; PPh_3), 7.42 – 7.53 (m, 12H; PPh_3), 6.16 (s, 5H; C_5H_5), 6.13 (s, 5H; C_5H_5), 4.57 – 4.64 (m, 1H; =CH), 4.48 – 4.57 (m, 1H; =CH), 4.29 – 4.37 (m, 1H; OH), 4.43 – 4.34 (m, 2H; CH_2), 3.81 – 3.89 (m, 2H; one of CH_2 and OH), 3.08 – 3.24 (m, 2H; =CH and one of CH_2), 2.18 (m, 1H; =CH), 2.11 (d, $J = 6.1$ Hz, 3H; CH_3), 1.33 (d, $J = 6.1$ Hz, 3H; CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3COCD_3): $\delta = 133.2$ (d, $J(C,P) = 10.3$ Hz; *o*-Ph), 133.1 (d, $J(C,P) = 10.3$ Hz; *o*-Ph), 131.8 (d, $J(C,P) = 2.7$ Hz; *p*-Ph), 131.75 (d, $J(C,P) = 2.7$ Hz; *p*-Ph), 129.9 (d, $J(C,P) = 55.3$ Hz; *i*-Ph), 129.2 (d, $J(C,P) = 10.7$ Hz; *m*-Ph), 129.1 (d, $J(C,P) = 11.1$ Hz; *m*-Ph), 97.6 (d, $J(C,P) = 0.7$ Hz; C_5H_5), 96.9 (d, $J(C,P) = 0.8$ Hz; C_5H_5), 66.9 (s; CH), 63.0 (d, $J(C,P) = 3.1$ Hz; =CH), 61.5 (d, $J(C,P) = 5.7$ Hz; =CH), 53.5 (s; =CH), 51.9 (d, $J(C,P) = 5.3$ Hz; =CH), 45.3 (s; CH), 21.4 (d, $J(C,P) = 2.7$ Hz; CH_3), 22.9 (s; CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, CD_3COCD_3): $\delta = 8.7$ (s), 8.6 (s); IR (neat): $\tilde{\nu}_{NO}$ 1722 (vs) cm^{-1}; HRMS calcd for $(C_{27}H_{28}NO_2P^{187}Re)^+$: 616.1416, found: 616.1427.

General procedure for nucleophilic substitutions: $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2OH)]^+[BF_4]^-$ (**1**, 60 mg, 0.087 mmol) was diluted in anhydrous CH_2Cl_2 (4 mL) at room temperature. The nucleophile (2 equiv) and then $HBF_4 \cdot Et_2O$ (2.5 μL, 0.017 mmol) were added. After 30 min, the reaction mixture was hydrolyzed and the organic phase was separated and dried over $MgSO_4$. Solvents were removed by rotary evaporation. The resulting residue was chromatographed on a 3 cm silica gel column (dichloromethane/acetone 4:1 (v/v)) to afford compounds **5a – e**, **6a – c**, **7**, **8**, and **9** as oils.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2OCH_2C{\equiv}CCH_3)]^+[BF_4]^-$ (5a): 2-Butyn-1-ol was used as the nucleophile. Yield: 80%; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.52 – 7.61$ (m, 9H; PPh_3), 7.33 – 7.52 (m, 6H; PPh_3), 5.82 (s, 5H; C_5H_5), 4.55 – 4.65 (m, 1H; =CH), 4.36 (dd, $J = 11.2$, 4.1 Hz, 1H; one of CH_2C=), 4.08 – 4.19 (m, 2H; $CH_2C{\equiv}$), 3.90 (dd, $J = 11.2$, 6.6 Hz, 1H; one of CH_2C=), 2.50 (ddd, $J = 11.2$, 4.1 Hz, $J(P,H) = 11.2$ Hz, 1H; one of H_2C=), 2.39 (ddd, $J = 10.2$, 4.1 Hz, $J(P,H) = 6.6$ Hz, 1H; one of H_2C=), 1.84 (t, $J =$ 2.2 Hz, 3H; CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta = 133.2$ (d, $J(C,P) =$ 10.3 Hz; *o*-Ph), 132.2 (d, $J(C,P) = 2.7$ Hz; *p*-Ph), 129.9 (d, $J(C,P) = 61.4$ Hz; *i*-Ph), 129.6 (d, $J(C,P) = 11.1$ Hz; *m*-Ph), 97.2 (s; C_5H_5), 82.9 (s; C≡C), 74.9 (s; C≡C), 73.4 (s; CH_2O), 58.5 (s; CH_2O), 47.6 (s; =CH), 36.2 (d, $J(C,P) =$ 5.7 Hz; $=CH_2$), 3.6 (s; CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): $\delta = 10.8$; IR (neat): $\tilde{\nu}_{NO} = 1725$ (vs) cm^{-1}; elemental analyis calcd for $C_{30}H_{30}BF_4NO_2PRe$: C 48.66, H 4.08; found: C 48.64, H 4.18.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2OCH_2C{\equiv}CH)]^+[BF_4]^-$ (5b): Propargylic alcohol was used as the nucleophile. Yield: 87%; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.52 – 7.61$ (m, 9H; PPh_3), 7.33 – 7.42 (m, 6H; PPh_3), 5.82 (s, 5H; C_5H_5), 4.52 – 4.63 (m, 1H; =CH), 4.30 (dd, $J = 11.2$, 4.1 Hz, 1H; one of CH_2C=), 4.14 – 4.24 (m, 2H; $CH_2C{\equiv}$), 3.97 (dd, $J = 11.2$, 6.1 Hz, 1H; one of CH_2C=), 2.49 (ddd, $J = 10.7$, 3.6 Hz, $J(P,H) = 10.7$ Hz, 1H; H_2C=), 2.44 (t, $J = 2.0$ Hz, 1H; CH≡C), 2.39 (ddd, $J = 10.2$, 3.6 Hz, $J(P,H) = 6.6$ Hz, 1H; H_2C=); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 133.9$ (d, $J(C,P) =$ 9.9 Hz; *o*-Ph), 132.9 (d, $J(C,P) = 2.3$ Hz; *p*-Ph), 130.6 (d, $J(C,P) =$ 56.1 Hz; *i*-Ph), 130.3 (d, $J(C,P) = 11.1$ Hz; *m*-Ph), 97.8 (s; C_5H_5), 80.1 (s; *C*≡CH), 75.6 (s; ≡CH), 74.3 (s; CH_2O), 58.5 (s; CH_2O), 47.6 (s; =CH), 36.9 (d, $J(C,P) = 6.1$ Hz; $=CH_2$); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 10.8$; IR (neat): $\tilde{\nu}_{NO} = 1738$ (vs) cm^{-1}; elemental analysis calcd for $C_{29}H_{28}BF_4NO_2PRe$: C 47.94, H 3.88; found: C 48.01, H 3.91.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2OCH(CH_3)C{\equiv}CH)]^+[BF_4]^-$ (5c): 3-Butyn-2-ol was used as the nucleophile. Yield: 82%; Two isomers in a 55:45 ratio. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.52 – 7.61$ (m, 18H; PPh_3), 7.32 – 7.42 (m, 12H; PPh_3), 5.82 (s, 5H; C_5H_5), 5.81 (s, 5H; C_5H_5), 4.48 – 4.68 (m, 3H; =CH and CH_2O), 4.38 (dd, $J = 11.2$, 5.3 Hz, 1H; one of CH_2O), 4.26 (qd, $J = 6.6$, 2.0 Hz, 1H; OCH), 4.16 (m, 2H; one of CH_2O and OCH), 3.62 (dd, $J = 10.7$, 6.6 Hz, 1H; one of CH_2O), 2.53 – 2.61 (m, 1H; one of CH_2=), 2.46 (d, $J = 2.0$ Hz, 1H; ≡CH), 2.41 – 2.49 (m, 2H; CH_2=), 2.38 (d, $J = 2.0$ Hz, 1H; ≡CH), 2.31 – 2.37 (m, 1H; CH_2=), 1.44 (d, $J = 6.6$ Hz, 3H; CH_3), 1.43 (d, $J = 6.6$ Hz, 3H; CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta =$ 133.9 (d, $J(C,P) = 10.3$ Hz; *o*-Ph), 133.8 (d, $J(C,P) = 10.3$ Hz; *o*-Ph), 132.9 (d, $J(C,P) = 2.6$ Hz; *p*-Ph), 132.8 (d, $J(C,P) = 2.6$ Hz; *p*-Ph), 130.6 (d, $J(C,P) = 59.1$ Hz; *i*-Ph), 130.3 (d, $J(C,P) = 11.1$ Hz; *m*-Ph), 130.2 (d, $J(C,P) = 11.1$ Hz; *m*-Ph), 97.9 (s; C_5H_5), 97.8 (s; C_5H_5), 84.1 (s; *C*≡CH), 83.9 (s; *C*≡CH), 74.3 (s; C≡*C*H), 74.2 (s; C≡CH), 73.4 (s; CH_2O), 72.7 (s; CH_2O), 66.1 (s; CH), 65.4 (s; CH), 48.4 (s; =CH), 48.2 (s; =CH), 37.3 (d, $J(C,P) = 6.1$ Hz; $=CH_2$), 36.6 (d, $J(C,P) = 6.1$ Hz; $=CH_2$), 22.8 (s; CH_3), 22.7 (s; CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 11.0$, 10.9; IR (neat): $\tilde{\nu}_{NO} =$ 1725 (vs) cm^{-1}; elemental analysis calcd for $C_{30}H_{30}BF_4NO_2PRe$: C 48.66, H 4.08; found: C 48.69, H 4.21.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2OBu)]^+[BF_4]^-$ (5d): *n*-Butanol was used as the nucleophile. Yield: 81%; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.53 – 7.60$ (m, 9H; PPh_3), 7.32 – 7.42 (m, 6H; PPh_3), 5.80 (s, 5H; C_5H_5), 4.53 – 4.64 (m, 1H; =CH), 4.29 (dd, $J = 11.4$, 3.7 Hz, 1H; one of CH_2O), 3.89 (dd, $J = 11.4$, 6.3 Hz, 1H; one of CH_2O), 3.46 – 3.53 (m, 1H; one of CH_2O), 3.34 – 3.42 (m, 1H; one of CH_2O), 2.51 (ddd, $J = 11.4$, 3.9 Hz, $J(P,H) =$ 11.4 Hz, 1H; one of H_2C=), 2.36 (ddd, $J = 10.4$, 3.9 Hz, $J(P,H) = 7.4$ Hz, 1H; one of H_2C=), 1.47 – 1.63 (m, 2H; CH_2), 1.30 – 1.41 (m, 2H; CH_2), 0.92 (t, $J = 7.3$ Hz, 3H; CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 133.9$ (d, $J(C,P) = 10.3$ Hz; *o*-Ph), 132.8 (d, $J(C,P) = 2.7$ Hz; *p*-Ph), 130.7 (d, $J(C,P) = 58.8$ Hz; *i*-Ph), 130.3 (d, $J(C,P) = 11.5$ Hz; *m*-Ph), 97.7 (s; C_5H_5), 74.9 (s; CH_2O), 71.4 (s; CH_2O), 49.6 (s; =CH), 36.8 (d, $J(C,P) = 5.7$ Hz; $=CH_2$), 32.6 (s; CH_2), 20.0 (s; CH_2), 14.6 (s; CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 11.1$; IR (neat): $\tilde{\nu}_{NO} = 1725$ (vs) cm^{-1}; elemental analysis calcd for $C_{30}H_{34}BF_4NO_2PRe$: C 48.39, H 4.61; found: C 48.34, H 4.56.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2OCH_2CH{=}CH_2)]^+[BF_4]^-$ (5e): Allyl alcohol was used as the nucleophile. Yield: 76%; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.53 – 7.60$ (m, 9H; PPh_3), 7.32 – 7.41 (m, 6H; PPh_3), 5.84 – 5.94 (m, 1H; =CH), 5.81 (d, $J(P,H) = 0.6$ Hz, 5H; C_5H_5), 5.25 (ddt, $J = 17.2$, 1.6, 1.6 Hz, 1H; $=CH_2$), 5.19 (m, $J = 10.3$ Hz, 1H; $=CH_2$), 4.60 – 4.69 (m, 1H; =CH), 4.33 (dd, $J = 11.6$, 3.5 Hz, 1H; CH_2O), 4.05 (ddt, $J = 12.4$, 5.6, 1.3 Hz, 1H; one of CH_2O), 3.96 (ddt, $J = 12.4$, 5.9, 1.3 Hz, 1H; one of CH_2O), 3.93 (dd, $J = 11.6$, 6.3 Hz, 1H; one of CH_2O), 2.53 (ddd, $J =$ 11.6, 3.9 Hz, $J(P,H) = 10.3$ Hz, 1H; one of H_2C=), 2.38 (ddd, $J = 10.6$, 3.9 Hz, $J(P,H) = 6.6$ Hz, 1H; one of H_2C=); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 135.3$ (s; =CH), 133.9 (d, $J(C,P) = 9.8$ Hz; *o*-Ph), 132.8 (d,

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J(C,P) = 2.7 Hz; *p*-Ph), 130.7 (d, J(C,P) = 59.1 Hz; *i*-Ph), 130.3 (d, J(C,P) = 11.1 Hz; *m*-Ph), 118.1 (s; H_2C=), 97.7 (s; C_5H_5), 74.3 (s; CH_2O), 72.5 (s; CH_2O), 49.0 (s; =CH), 36.6 (d, J(C,P) = 6.1 Hz; =CH_2); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 10.9$; IR (neat): $\tilde{\nu}_{NO} = 1725$ (vs) cm^{-1}; HRMS calcd for $(C_{29}H_{30}NO_2PRe)^+$: 642.1573, found: 642.1598; elemental analysis calcd for $C_{29}H_{30}BF_4NO_2PRe$: C 47.81, H 4.15; found: C 47.41, H 4.13.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H_2C=CHCH$_2$SCH$_2$CH=CH$_2$)]$^+$[BF_4]$^-$ (6a): Allyl thiol was used as the nucleophile. Yield: 82%; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.53-7.63$ (m, 9H; PPh_3), 7.31–7.40 (m, 6H; PPh_3), 5.83 (s, 5H; C_5H_5), 5.68–5.82 (m, 1H; =CH), 5.02–5.12 (m, 2H; =CH_2), 4.48–4.61 (m, 1H; =CH), 3.25 (d, $J = 6.6$ Hz, 2H; CH_2S), 3.07 (dd, $J = 13.2$, 5.5 Hz, 1H; one of CH_2S), 2.90 (dd, $J = 13.2$, 8.6 Hz, 1H; CH_2S), 2.60–2.69 (m, 1H; H_2C=), 2.35 (ddd, $J = 11.2$, 4.1 Hz, J(P,H) = 11.2 Hz, 1H; one of H_2C=); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 134.9$ (s; CH=), 133.9 (d, J(C,P) = 9.9 Hz; *o*-Ph), 133.0 (d, J(C,P) = 2.7 Hz; *p*-Ph), 130.5 (d, J(C,P) = 59.1 Hz; *i*-Ph), 130.4 (d, J(C,P) = 11.1 Hz; *m*-Ph), 118.4 (s; H_2C=), 97.9 (s; C_5H_5), 48.5 (s; =CH), 39.4 (d, J(C,P) = 5.7 Hz; =CH_2), 39.0 (s; CH_2S), 35.3 (s; CH_2S); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 10.2$; IR (neat): $\tilde{\nu}_{NO} = 1719$ (vs) cm^{-1}; HRMS calcd for $(C_{29}H_{30}NOSPRe)^+$: 658.1343, found: 658.1358.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H_2C=CHCH$_2$SBu)]$^+$[BF_4]$^-$ (6b): *n*-Butanethiol was used as the nucleophile. Yield: 86%; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.53-7.62$ (m, 9H; PPh_3), 7.32–7.42 (m, 6H; PPh_3), 5.83 (s, 5H; C_5H_5), 4.48–4.63 (m, 1H; =CH), 3.12 (dd, $J = 13.2$, 5.1 Hz, 1H; one of CH_2S), 2.96 (dd, J = 13.2, 8.1 Hz, 1H; one of CH_2S), 2.64 (ddd, $J = 10.2$, 4.1 Hz, J(P,H) = 6.1 Hz, 1H; one of H_2C=), 2.59 (t, $J = 7.6$ Hz, 2H; CH_2S), 2.33 (ddd, $J = 10.7$, 4.1 Hz, J(P,H) = 10.7 Hz, 1H; one of H_2C=), 1.45–1.55 (m, 2H; CH_2), 1.31–1.43 (m, 2H; CH_2), 0.88 (t, $J = 7.6$ Hz, 3H; CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 133.9$ (d, J(C,P) = 9.9 Hz; *o*-Ph), 132.9 (d, J(C,P) = 2.7 Hz; *p*-Ph), 130.5 (d, J(C,P) = 58.7 Hz; *i*-Ph), 130.4 (d, J(C,P) = 11.1 Hz; *m*-Ph), 97.9 (s; C_5H_5), 48.7 (s; =CH), 40.5 (s; CH_2S), 39.2 (d, J(C,P) = 6.1 Hz; =CH_2), 32.5 (s; CH_2), 32.2 (s; CH_2), 22.5 (s; CH_2S), 14.4 (s; CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 10.2$; IR (neat): $\tilde{\nu}_{NO} = 1738$ (vs) cm^{-1}; HRMS calcd for $(C_{30}H_{34}NOSPRe)^+$: 674.1656, found: 674.1654.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H_2C=CHCH$_2$SPh)]$^+$[BF_4]$^-$ (6c): Thiophenol was used as the nucleophile. Yield: 88%; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.15-7.60$ (m, 20H; PPh_3 and SPh), 5.79 (s, 5H; C_5H_5), 4.47–4.60 (m, 1H; =CH), 3.44 (dd, $J = 13.7$, 6.1 Hz, 1H; CH_2S), 3.34 (dd, $J = 13.7$, 8.1 Hz, 1H; CH_2S), 2.46 (ddd, $J = 10.2$, 4.6 Hz, J(P,H) = 6.1 Hz, 1H; H_2C=), 2.11 (ddd, $J = 10.7$, 4.6 Hz, J(P,H) = 10.7 Hz, 1H; H_2C=); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 135.6$ (s; SPh), 133.8 (d, J(C,P) = 10.3 Hz; *o*-Ph), 133.0 (d, J(C,P) = 2.7 Hz; *p*-Ph), 131.9 (s; SPh), 130.4 (d, J(C,P) = 59.1 Hz; *i*-Ph), 130.3 (d, J(C,P) = 11.4 Hz; *m*-Ph), 129.9 (s; SPh), 127.8 (s; SPh), 97.9 (s; C_5H_5), 47.2 (s; =CH), 43.8 (s; CH_2S), 38.8 (d, J(C,P) = 5.7 Hz; =CH_2); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 10.2$; IR (neat): $\tilde{\nu}_{NO} = 1719$ (vs) cm^{-1}; HRMS calcd for $(C_{34}H_{30}NOSPRe)^+$: 694.1343, found: 694.1329.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H_2C=CHCH$_2$CH$_2$CH=CH$_2$)]$^+$[BF_4]$^-$ (7): Allyltrimethylsilane was used as the nucleophile. Yield: 76%; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.53-7.62$ (m, 9H; PPh_3), 7.31–7.40 (m, 6H; PPh_3), 5.77–5.88 (m, 1H; =CH), 5.78 (s, 5H; C_5H_5), 5.07 (br d, $J = 15.8$ Hz, 1H; one of =CH_2), 5.02 (br d, $J = 10.2$ Hz, 1H; one of =CH_2), 4.43–4.55 (m, 1H; =CH), 2.46–2.54 (m, 1H; one of H_2C=), 2.42 (ddd, $J = 12.9$, 4.7 Hz, J(P,H) = 12.9 Hz, 1H; one of H_2C=), 2.20–2.37 (m, 2H; CH_2), 1.99–2.18 (m, 2H; CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 138.1$ (s; =CH), 133.8 (d, J(C,P) = 9.9 Hz; *o*-Ph), 132.9 (d, J(C,P) = 2.3 Hz; *p*-Ph), 130.7 (d, J(C,P) = 59.1 Hz; *i*-Ph), 130.3 (d, J(C,P) = 11.1 Hz; *m*-Ph), 116.5 (s; H_2C=), 97.5 (s; C_5H_5), 51.9 (s; =CH), 39.4 (d, J(C,P) = 5.3 Hz; =CH_2), 38.3 (s; CH_2), 37.6 (s; CH_2); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 10.7$; IR (neat): $\tilde{\nu}_{NO} =$ 1718 (vs) cm^{-1}; elemental analysis calcd for $C_{29}H_{30}BF_4NOPRe$: C 48.88, H 4.24; found: C 48.91, H 4.29.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H_2C=CHCH$_2$PPh$_3$)]$^{2+}$2[BF_4]$^-$ (8): Triphenylphosphane was used as the nucleophile and 13 μL de $HBF_4 \cdot Et_2O$ (1 equiv) was added Yield: 60%; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.52-7.78$ (m, 24H; PPh_3), 7.25–7.36 (m, 6H; PPh_3), 5.87 (s, 5H; C_5H_5), 4.89 (m, $J =$ 12 Hz, J(P,H) = 12 Hz, 1H; one of CH_2P), 4.15–4.28 (m, 1H; =CH), 2.81–2.93 (m, 1H; one of =CH_2), 2.53 (ddd, $J = 12.2$, 12.2, 2.5 Hz, J(P,H) = 14.7 Hz, 1H; one of CH_2P), 1.43 (ddd, $J = 10.2$, 4.1 Hz, J(P,H) = 10.2 Hz, 1H; one of H_2C=); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3NO_2): $\delta = 136.8$ (d, J(C,P) = 3.1 Hz; PPh_3), 135.4 (d, J(C,P) = 9.9 Hz; PPh_3), 134.6 (d, J(C,P) = 9.9 Hz; PPh_3), 133.8 (d, J(C,P) = 2.7 Hz; PPh_3), 131.8 (d, J(C,P) = 12.9 Hz; PPh_3), 131.2 (d, J(C,P) = 59.9 Hz; PPh_3), 131.0 (d, J(C,P) = 11.4 Hz; PPh_3), 118.7 (dd, J(C,P) = 85.1, 1.5 Hz; PPh_3), 99.7 (s; C_5H_5), 40.2 (d, J(C,P) = 4.6 Hz; =CH_2), 34.2 (s; =CH), 33.9 (d, J(C,P) = 42.3 Hz; CH_2P).$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 25.6$, 9.0; HRMS calcd for $[M - PPh_3]^+$ ($(C_{26}H_{25}NOPRe)^+$): 585.1232, found: 585.1232.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H_2C=CHCH$_2$OCOCH$_3$)]$^+$[BF_4]$^-$ (9): Acetic acid was used as the nucleophile. Yield: 63%. The NMR, IR, and mass spectra have already been reported.[8b]

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H_2C=CHCD$_2$OCH$_2$CH=CH$_2$)]$^+$[BF_4]$^-$ (5e′): Allyl alcohol was used as the nucleophile. Yield: 78%; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.52-7.60$ (m, 9H; PPh_3), 7.32–7.42 (m, 6H; PPh_3), 5.83–5.94 (m, $J = 17.2$, 10.4 Hz, 1H; =CH), 5.81 (5H; C_5H_5), 5.24 (ddt, $J = 17.2$, 1.6, 1.6 Hz, 1H; one of =CH_2), 5.18 (m, $J = 10.4$ Hz, 1H; one of =CH_2), 4.61 (ddd, $J = 11.8$, 10.2 Hz, J(P,H) = 2.0 Hz, 1H; =CH), 4.05 (ddt, J = 12.5, 5.6, 1.4 Hz, 1H; one of CH_2O), 3.97 (ddt, J = 12.5, 6.0, 1.3 Hz, 1H; one of CH_2O), 2.53 (ddd, $J = 11.7$, 3.9 Hz, J(P,H) = 10.2 Hz, 1H; one of H_2C=), 2.35 (ddd, $J = 11.1$, 3.9 Hz, J(P,H) = 7.1 Hz, 1H; one of H_2C=); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 134.6$ (s; =CH), 133.2 (d, J(C,P) = 10.3 Hz; *o*-Ph), 132.2 (d, J(C,P) = 2.7 Hz; *p*-Ph), 129.9 (d, J(C,P) = 59.1 Hz; *i*-Ph), 129.6 (d, J(C,P) = 11.1 Hz; *m*-Ph), 117.4 (s; H_2C=), 97.1 (s; C_5H_5), 71.7 (s; CH_2O), 48.1 (s; =CH), 36.0 (d, J(C,P) = 6.1 Hz; =CH_2); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 10.9$; IR (neat): $\tilde{\nu}_{NO} = 1725$ (vs) cm^{-1}; HRMS calcd for $(C_{29}H_{28}D_2NO_2PRe)^+$: 642.1666, found: 642.1643.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H_2C=CHCD$_2$SPh)]$^+$[BF_4]$^-$ (6c′): Thiophenol was used as the nucleophile. Yield: 63%; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.51-7.59$ (m, 9H; PPh_3), 7.15–7.38 (m, 11H; PPh_3 and SPh), 5.78 (s, 5H; C_5H_5), 4.52 (m, $J = 10$ Hz, J(P,H) = 2.0 Hz, 1H; =CH), 2.44 (ddd, $J =$ 10.7, 4.6 Hz, J(P,H) = 6.6 Hz, 1H; one of H_2C=), 2.09 (ddd, $J = 11.2$, 4.6 Hz, J(P,H) = 11.2 Hz, 1H; one of H_2C=); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta =$ 135.6 (s; SPh), 133.8 (d, J(C,P) = 9.9 Hz; *o*-Ph), 132.9 (d, J(C,P) = 2.7 Hz; *p*-Ph), 131.9 (s; SPh), 130.4 (d, J(C,P) = 59.1 Hz; *i*-Ph), 130.3 (d, J(C,P) = 11.4 Hz; *m*-Ph), 129.9 (s; SPh), 127.8 (s; SPh), 97.9 (s; C_5H_5), 46.9 (s; =CH), 38.7 (d, J(C,P) = 5.7 Hz; =CH_2); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 10.1$.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H_2C=CHCD$_2$PPh$_3$)]$^{2+}$2[BF_4]$^-$ (7′): Triphenylphosphane was used as the nucleophile and $HBF_4 \cdot Et_2O$ (13 μL (1 equiv)) was added. Yield: 58%; ^1H NMR (400 MHz, CD_3NO_2): $\delta = 7.57-7.97$ (m, 24H; PPh_3), 7.42–7.52 (m, 6H; PPh_3), 5.98 (s, 5H; C_5H_5), 4.30–4.38 (m, 1H; =CH), 2.46–2.55 (m, 1H; one of =CH_2), 1.96–2.06 (m, 1H; one of =CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3NO_2): $\delta = 136.9$ (d, J(C,P) = 3.1 Hz; PPh_3), 135.4 (d, J(C,P) = 9.9 Hz; PPh_3), 134.6 (d, J(C,P) = 9.9 Hz; PPh_3), 133.9 (d, J(C,P) = 2.7 Hz; PPh_3), 131.9 (d, J(C,P) = 12.6 Hz; PPh_3), 131.2 (d, J(C,P) = 59.9 Hz; PPh_3), 131.0 (d, J(C,P) = 11.1 Hz; PPh_3), 118.6 (d, J(C,P) = 85.1 Hz; PPh_3), 99.8 (s; C_5H_5), 40.3 (d, J(C,P) = 6.5 Hz; =CH_2), 34.1 (s; =CH); $^{31}P\{^1H\}$ NMR (121 MHz, CD_3NO_2): $\delta = 25.2$, 9.5; IR (neat): $\tilde{\nu}_{NO} = 1730$ (vs).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H_2C=CHCD$_2$CH$_2$CH=CH$_2$)]$^+$[BF_4]$^-$ (8′): Allyltrimethylsilane was used as the nucleophile. Yield: 81%; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.52-7.62$ (m, 9H; PPh_3), 7.30–7.40 (m, 6H; PPh_3), 5.77–5.88 (m, 1H; =CH), 5.78 (s, 5H; C_5H_5), 5.06 (dd, $J = 16.8$, 1.5 Hz, 1H; one of =CH_2), 5.00 (dd, $J = 10.2$, 1.5 Hz, 1H; one of =CH_2), 4.47 (m, $J =$ 10 Hz, J(P,H) = 1.5 Hz, 1H; =CH), 2.48 (ddd, $J = 9.7$, 4.1 Hz, J(P,H) = 6.1 Hz, 1H; one of H_2C=), 2.42 (ddd, $J = 11.2$, 4.1 Hz, J(P,H) = 11.2 Hz, 1H; one of H_2C=), 2.20–2.34 (m, 2H; CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 138.1$ (s; =CH), 133.8 (d, J(C,P) = 9.9 Hz; *o*-Ph), 132.9 (d, J(C,P) = 2.7 Hz; *p*-Ph), 130.7 (d, J(C,P) = 58.7 Hz; *i*-Ph), 130.3 (d, J(C,P) = 11.1 Hz; *m*-Ph), 116.4 (s; H_2C=), 97.5 (s; C_5H_5), 51.6 (s; =CH), 39.4 (d, J(C,P) = 5.7 Hz; =CH_2), 37.4 (s; CH_2); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 10.7$.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H_2C=CHCD$_2$OCOCH$_3$)]$^+$[BF_4]$^-$ (9′): Acetic acid was used as the nucleophile. Yield: 61%; ^1H NMR (400 MHz, CD_3NO_2): $\delta = 7.60-7.72$ (m, 9H; PPh_3), 7.52–7.58 (m, 6H; PPh_3), 5.98 (s, 5H; C_5H_5), 4.49 (m, J Å 11 Hz, J(P,H) = 2.0 Hz, 1H; =CH), 2.69 (ddd, $J =$ 11.2, 4.6 Hz, J(P,H) = 10.2 Hz, 1H; one of H_2C=), 2.36 (ddd, $J = 11.2$, 4.6 Hz, J(P,H) = 7.1 Hz, 1H; one of H_2C=), 2.06 (s, 3H; CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3NO_2): $\delta = 172.3$ (s; CO), 134.8 (d, J(C,P) = 10.3 Hz; *o*-Ph), 133.7 (d, J(C,P) = 2.7 Hz; *p*-Ph), 131.5 (d, J(C,P) = 59.9 Hz; *i*-Ph), 130.9 (d, J(C,P) = 11.1 Hz; *m*-Ph), 99.2 (s; C_5H_5), 44.1 (s; =CH), 37.7 (d, J(C,P) = 6.1 Hz; =CH_2), 21.1 (s; CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 10.3$; IR (neat): $\tilde{\nu} = 1735$ (NO, vs), 1730 (CO, vs) cm^{-1}.

Nucleophilic substitutions starting from the crotylic alcohol complex (3a,b): The experimental procedure was similar to that reported above for

the allylic alcohol complex **1** and used $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3HC{=}CHCH_2OH)]^+[BF_4]^-$ (**3a,b**, 25 mg, 3.56×10^{-2} mmol).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3HC{=}CHCH_2SPh)]^+[BF_4]^-$ (12): Thiophenol was used as the nucleophile. Yield: 88%; three isomers in a 54:38:8 ratio were obtained. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.11–7.72 (m; 3 PPh_3 and 3 SPh), 5.87 (s, 5H; C_5H_5), 5.86 (s, 5H; C_5H_5), 5.74 (s, 5H; C_5H_5), 4.27–4.36 (m, 1H; =CH), 3.96–4.04 (m, 1H; =CH), 3.48 (dd, J = 13.7, 4.6 Hz, 1H; one of CH_2S), 3.19–3.27 (m, 2H; CH_2S), 2.55–2.72 (m, 1H; one of CH_2S), 2.38 (dd, J = 12.7 Hz, J(P,H) = 2.6 Hz, 1H; HC=), 2.24 (d, J = 11.7 Hz, 1H; HC=), 1.80 (d, J = 6.1 Hz, 3H; CH_3), 1.62 (d, J = 6.6 Hz, 3H; CH_3), 1.24 (d, J = 6.1 Hz, 3H; CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 134.7–127.2 (SPH and PPh_3), 97.6 (s; C_5H_5), 97.1 (s; C_5H_5), 97.10 (s; C_5H_5), 56.0 (d, J(C,P) = 5.7 Hz; =CH), 54.3 (d, J(C,P) = 5.3 Hz; =CH), 50.0 (s; CH_2S), 47.5 (s; CH_2S), 44.1 (s; =CH), 42.1 (d, J(C,P) = 1.8 Hz; =CH), 23.5 (s; CH_3), 22.3 (s, J(C,P) = 2.6 Hz; CH_3), 22.2 (s; CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 12.4, 6.9, 6.7; HRMS calcd for $(C_{33}H_{33}NOSPRe)^+$: 708.1500, found: 708.1499.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3H_2C{=}CHCH_2CH_2CH{=}CH_2)]^+[BF_4]^-$ (13): Allyltrimethylsilane was used as the nucleophile. Yield: 77%; three isomers in a 39:37:24 ratio were obtained. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.20–7.72 (m, 45H; PPh_3), 5.86 (s, 5H; C_5H_5), 5.84 (s, 5H; C_5H_5), 5.73 (s, 5H; C_5H_5), 5.74–5.87 (m, 2H; =CH), 5.30–5.43 (m, 1H; =CH), 4.99–5.11 (m, 4H; $=CH_2$), 4.74–4.85 (m, 2H; $=CH_2$), 4.36–4.44 (m, 1H; HC=), 4.26–4.35 (m, 1H; HC=), 2.89–3.12 (m, 4H; HC= and CH_2), 2.02–2.47 (m, 8H; HC= and CH_2), 1.81–2.02 (m, 4H; CH_2), 2.10 (d, J = 6.1 Hz, 3H; CH_3), 1.35 (d, J = 6.6 Hz, 3H; CH_3), 1.28 (d, J = 6.6 Hz, 3H; CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 137.4 (s; =CH), 136.9 (s; =CH), 136.1 (s; =CH), 128.4–133.4 (PPh_3), 117.2 (s; H_2C=), 116.0 (s; H_2C=), 115.8 (s; H_2C=), 97.4 (s; C_5H_5), 97.3 (s; C_5H_5), 97.1 (s; C_5H_5), 66.4 (s; =CH), 61.1 (d, J(C,P) = 5.3 Hz; =CH), 54.6 (d, J(C,P) = 4.9 Hz; =CH), 54.2 (s; =CH), 49.8 (s; =CH), 48.2 (s; CH_2), 41.4 (s; =CH), 40.1 (s; CH_2), 38.3 (s; CH_2), 37.2 (s; CH_2), 37.1 (s; CH_2), 34.7 (s; CH_2), 24.1 (s; CH_3), 22.5 (d, J(C,P) = 2.3 Hz; CH_3), 20.8 (s; CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 12.4, 7.6, 7.5; HRMS calcd for $(C_{30}H_{32}NOPRe)^+$: 640.1779, found: 640.1779.

Nucleophilic substitutions starting from the 3-buten-2-ol complex (2a,b): The experimental procedure was similar to that reported above for the allylic alcohol complex **1** and used $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH(CH_3)OH)]^+[BF_4]^-$ (**2a,b**, 60 mg, 0.854 mmol).

Nucleophilic substitutions starting from the racemate 2a,b:

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH(CH_3)OMe)]^+[BF_4]^-$ (14): Methanol was used as the nucleophile. Yield: 74%; two diastereomers in a 60:40 ratio were obtained. *Major diastereomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.59 (m, 9H; PPh_3), 7.33–7.42 (m, 6H; PPh_3), 5.79 (s, 5H; C_5H_5), 4.39–4.54 (m, 1H; =CH), 3.57–3.68 (m, 1H; CH), 3.27 (s, 3H; CH_3O), 2.73 (ddd, J = 10.7, 4.1 Hz, J(P,H) = 10.7 Hz, 1H; one of H_2C=), 1.94 (ddd, J = 10.7, 4.1 Hz, J(P,H) = 7.1 Hz, 1H; one of H_2C=), 1.45 (d, J = 6.1 Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 133.3 (d, J(C,P) = 9.9 Hz; *o*-Ph), 132.1 (d, J(C,P) = 3.0 Hz; *p*-Ph), 130.0 (d, J(C,P) = 58.4 Hz; *i*-Ph), 129.5 (d, J(C,P) = 11.1 Hz; *m*-Ph), 96.9 (s; C_5H_5), 79.2 (s; CH), 55.3 (s; OCH_3), 54.1 (s; =CH), 33.3 (d, J(C,P) = 6.1 Hz; $=CH_2$), 22.8 (s; CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 11.4. *Minor diastereomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.59 (m, 9H; PPh_3), 7.33–7.42 (m, 6H; PPh_3), 5.80 (s, 5H; C_5H_5), 4.39–4.54 (m, 1H; =CH), 3.57–3.68 (m, 1H; CH), 3.31 (s, 3H; CH_3O), 2.44 (ddd, J = 10.7, 4.1 Hz, J(P,H) = 10.7 Hz, 1H; one of H_2C=), 2.21 (ddd, J = 10.7, 4.1 Hz, J(P,H) = 7.6 Hz, 1H; one of H_2C=), 1.39 (d, J = 6.1 Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 133.3 (d, J(C,P) = 9.9 Hz; *o*-Ph), 132.2 (d, J(C,P) = 2.7 Hz; *p*-Ph), 130.0 (d, J(C,P) = 58.4 Hz; *i*-Ph), 129.6 (d, J(C,P) = 11.1 Hz; *m*-Ph), 97.0 (s; C_5H_5), 79.8 (s; CH), 56.3 (s; OCH_3), 55.7 (s; =CH), 34.1 (d, J(C,P) = 5.7 Hz; $=CH_2$), 22.4 (s, CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 11.1; IR (neat): $\tilde{\nu}_{NO}$ = 1729 (vs) cm^{-1}; HRMS calcd for $(C_{28}H_{30}NO_2P^{187}Re)^+$: 630.1572, found: 630.1573.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH(CH_3)SPh)]^+[BF_4]^-$ (15): Thiophenol was used as the nucleophile. Yield: 80%; two diastereomers in a 55:45 ratio were obtained. See below for the ^{1}H, ^{13}C, and ^{31}P NMR data of each diastereomer; IR (neat): $\tilde{\nu}_{NO}$ = 1720 (vs) cm^{-1}; HRMS calcd for $(C_{33}H_{32}NOSP^{187}Re)^+$: 708.1500, found: 708.1504.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH(CH_3)CH_2CH{=}CH_2)]^+[BF_4]^-$ (16): Allyltrimethylsilane was used as the nucleophile. Yield: 85%; two diastereomers in a 56:44 ratio were obtained. *Major diastereomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.62 (m, 9H; PPh_3), 7.30–7.40 (m, 6H; PPh_3), 5.78 (s, 5H; C_5H_5), 5.66–5.88 (m, 1H; =CH), 5.00 (br d, J = 17.0 Hz, 1H; one of $=CH_2$), 4.98 (br d, J = 9.7 Hz, 1H; one of $=CH_2$), 4.22–4.32 (m, 1H; =CH), 2.33–2.48 (m, 2H; H_2C=), 2.27 (br d, J = 6.6 Hz, 1H; one of CH_2), 2.25 (br d, J = 6.6 Hz, 1H; one of CH_2), 1.32–1.42 (m, 1H; CH), 1.20 (d, J = 6.5 Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 136.1 (s, =CH), 133.2 (d, J(C,P) = 10.9 Hz; *o*-Ph), 132.3 (d, J(C,P) = 2.3 Hz; *p*-Ph), 129.9 (d, J(C,P) = 58.4; *i*-Ph), 129.6 (d, J(C,P) = 11.1 Hz; *m*-Ph), 117.0 (s; $=CH_2$), 96.9 (s; C_5H_5), 58.1 (s; =CH), 46.2 (s; CH_2), 42.1 (s; CH_2), 37.2 (d, J(C,P) = 5.7 Hz; $=CH_2$), 21.4 (s; CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 10.6. *Minor diastereomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.62 (m, 9H; PPh_3), 7.30–7.40 (m, 6H; PPh_3), 5.79 (s, 5H; C_5H_5), 5.66–5.88 (m, 1H; =CH), 5.12 (br d, J = 16.3 Hz, 1H; one of $=CH_2$), 5.08 (br d, J = 9.5 Hz, 1H; one of $=CH_2$), 4.33–4.42 (m, 1H; =CH), 2.33–2.48 (m, 4H; H_2C= and CH_2), 1.42–1.50 (m, 1H; CH), 1.17 (d, J = 6.6 Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 136.2 (s; =CH), 133.2 (d, J(C,P) = 10.9 Hz; *o*-Ph), 132.3 (d, J(C,P) = 2.3 Hz; *p*-Ph), 129.8 (d, J(C,P) = 58.4 Hz; *i*-Ph), 129.7 (d, J(C,P) = 11.1 Hz; *m*-Ph), 117.10 (s; $=CH_2$), 96.9 (s; C_5H_5), 57.7 (s; =CH), 42.7 (s; CH_2), 41.9 (s; CH_2), 36.2 (d, J(C,P) = 5.7 Hz; $=CH_2$), 24.8 (s; CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 10.9; IR (neat): $\tilde{\nu}_{NO}$ = 1718 (vs) cm^{-1}; HRMS calcd for $(C_{30}H_{32}NOP^{187}Re)^+$: 640.1779, found: 640.1772.

Nucleophilic substitutions starting from the (*RSS*,*SRR*) 3-buten-2-ol complex diastereomer 2a:

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH(CH_3)SPh)]^+[BF_4]^-$ (15a): Thiophenol was used as the nucleophile. Yield: 83%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.63 (m, 9H; Ph), 7.34–7.43 (m, 8H; Ph), 7.25–7.32 (m, 4H; Ph), 5.88 (s, 5H; C_5H_5), 4.36–4.45 (m, J = 9.6 Hz, 1H; =CH), 2.97 (dq, J = 9.6, 6.6 Hz, 1H; CH), 2.70 (ddd, J = 9.7, 4.6 Hz, J(P,H) = 7.1 Hz, 1H; one of H_2C=), 2.27 (ddd, J = 11.2, 4.6 Hz, J(P,H) = 11.2 Hz, 1H; one of H_2C=), 1.43 (d, J = 6.6 Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 134.6 (s; SPh), 134.0 (s; SPh), 133.9 (d, J(C,P) = 9.9 Hz; *o*-Ph), 133.0 (d, J(C,P) = 2.7 Hz, *p*-Ph); 130.4 (d, J(C,P) = 11.1 Hz, *m*-Ph), 130.2 (d, J(C,P) = 58.7 Hz; *i*-Ph), 129.7 (s; SPh), 128.5 (s; SPh), 98.3 (s; C_5H_5), 53.8 (s; CH), 53.2 (s; CH), 37.8 (d, J(C,P) = 6.1 Hz; $=CH_2$), 27.6 (s; CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 9.7; HRMS calcd for $(C_{33}H_{32}NOSP^{187}Re)^+$: 708.1500, found: 708.1500.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH(CH_3)CH_2CH{=}CH_2)]^+[BF_4]^-$ (16a): Allyltrimethylsilane was used as the nucleophile. Yield: 73%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.62 (m, 9H; PPh_3), 7.32–7.49 (m, 6H; PPh_3), 5.80–5.91 (m, 1H; =CH), 5.80 (s; 5H, C_5H_5), 5.13 (d, J = 15.8 Hz, 1H; one of $=CH_2$), 5.10 (d, J = 8.1 Hz, 1H; one of $=CH_2$), 4.34–4.44 (m, 1H; =CH), 2.35–2.47 (m, 3H; one of H_2C= and CH_2), 2.14–2.23 (m, 1H; one of H_2C=), 1.42–1.52 (m, 1H; CH), 1.18 (d, J = 6.7 Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 136.9 (s; =CH), 133.9 (d, J(C,P) = 9.9 Hz; *o*-Ph), 132.9 (d, J(C,P) = 2.7 Hz; *p*-Ph), 130.5 (d, J(C,P) = 59.1 Hz; *i*-Ph), 130.3 (d, J(C,P) = 11.1 Hz; *m*-Ph), 117.9 (s; H_2C=), 97.6 (s; C_5H_5), 58.6 (s; =CH), 42.8 (s; CH_2), 42.7 (s; CH), 37.1 (d, J(C,P) = 5.7 Hz; $=CH_2$), 25.5 (s; CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 10.5; HRMS calcd for $(C_{30}H_{32}NOP^{187}Re)^+$: 640.1780, found: 640.1775.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH(CH_3)OCH_2C{\equiv}CH)]^+[BF_4]^-$ (*RSS*,*SRR*) (17a): Propargylic alcohol was used as the nucleophile. Yield: 81%; ^{1}H NMR (400 MHz, CD_3COCD_3): δ = 7.62–7.68 (m, 9H; PPh_3), 7.53–7.59 (m, 6H; PPh_3), 6.11 (s, 5H; C_5H_5), 4.55–4.64 (m, 1H; =CH), 4.41–4.49 (m, J = 6.1 Hz, 1H; CH), 4.33 (dd, J = 15.8, 2.5 Hz, 1H; one of CH_2O), 4.21 (dd, J = 15.8, 2.5 Hz, 1H; one of CH_2O), 2.70 (ddd, J = 14.2, 4.1 Hz, J(P,H) = 11.7 Hz, 1H; one of H_2C=), 2.05 (t, J = 2.5 Hz, 1H; HC≡), 1.99 (ddd, J = 10.7, 4.1 Hz, J(P,H) = 7.6 Hz, 1H; one of H_2C=), 1.47 (d, J = 6.1 Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (100 MHz, CD_3NO_2): δ = 134.7 (d, J(C,P) = 9.9 Hz; *o*-Ph), 133.4 (d, J(C,P) = 2.7 Hz; *p*-Ph), 131.8 (d, J(C,P) = 58.8 Hz; *i*-Ph), 130.5 (d, J(C,P) = 11.1 Hz; *m*-Ph), 98.7 (s; C_5H_5), 81.7 (s; C≡C), 79.0 (s; C≡C), 75.4 (s; CH_2O), 57.0 (s; CH), 55.7 (s; =CH), 33.9 (d, J(C,P) = 6.5 Hz; $=CH_2$), 23.1 (s; CH_3); ^{31}P{^{1}H} NMR (121 MHz, CD_3COCD_3): δ = 12.8; elemental analysis calcd for $C_{30}H_{30}BF_4NO_2PRe$: C 48.66, H 4.08; found: C 48.46, H 4.09.

Nucleophilic substitutions starting from the (*RSR*,*SRS*) 3-buten-2-ol complex diastereomer 2b:

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH(CH_3)SPh)]^+[BF_4]^-$ (15b): Thiophenol was used as the nucleophile. Yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.62 (m, 10H; Ph), 7.38–7.44 (m, 3H; Ph), 7.17–7.27 (m, 7H; Ph), 5.78 (s, 5H; C_5H_5), 4.33–4.53 (m, J = 10.2 Hz, 1H; =CH), 2.78

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(dq, $J = 10.2$, 6.6 Hz, 1H; CH), 2.02–2.08 (m, $J = 4.6$ Hz, 1H; one of H_2C=), 1.70 (ddd, $J = 11.7$, 4.6 Hz, $J(P,H) = 11.7$ Hz, 1H; one of H_2C=), 1.56 (d, $J = 6.6$ Hz, 3H; CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 136.2$ (s; SPh), 134.2 (s; SPh), 133.7 (d, $J(C,P) = 9.9$ Hz; *o*-Ph), 132.9 (d, $J(C,P) = 2.7$ Hz; *p*-Ph), 130.3 (d, $J(C,P) = 11.5$ Hz; *m*-Ph), 130.2 (d, $J(C,P) = 59.5$ Hz; *i*-Ph), 129.8 (s; SPh), 129.1 (s; SPh), 97.8 (s; C_5H_5), 54.9 (s; CH), 53.9 (s; CH), 36.4 (d, $J(C,P) = 5.3$ Hz; $=CH_2$), 22.8 (s; CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 10.1$.

[(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=CHCH(CH_3)OCH_2C≡CH)]$^+$[BF_4]$^-$ (*RSR*,-*SRS*) (17b): Propargylic alcohol was used as the nucleophile. Yield: 81%; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.53-7.60$ (m, 9H; PPh_3), 7.33–7.42 (m, 6H; PPh_3), 5.81 (s, 5H; C_5H_5), 4.23–4.32 (m, 1H; =CH), 4.20 (d, $J = 2.6$ Hz, 1H; one of CH_2O), 4.19 (d, $J = 2.6$ Hz, 1H; one of CH_2O), 3.72 (dq, $J = 6.6$, 6.1 Hz, 1H; CH), 2.69 (ddd, $J = 11.2$, 4.6 Hz, $J(P,H) = 11.2$ Hz, 1H; one of H_2C=), 2.35 (t, $J = 2.6$ Hz, 1H; HC≡), 2.17 (ddd, $J = 10.7$, 4.6 Hz, $J(P,H) = 7.1$ Hz, 1H; one of H_2C=), 1.50 (d, $J = 6.6$ Hz, 3H; CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 133.9$ (d, $J(C,P) = 10.3$ Hz; *o*-Ph), 132.9 (d, $J(C,P) = 2.7$ Hz; *p*-Ph), 130.3 (d, $J(C,P) = 11.1$ Hz; *m*-Ph), 97.9 (s; C_5H_5), 80.6 (s; C≡C), 78.4 (s; C≡C), 75.2 (s; CH_2O), 55.7 (s; CH), 52.2 (s; =CH), 35.4 (d, $J(C,P) = 6.1$ Hz; $=CH_2$), 23.4 (s; CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 11.0$; elemental analysis calcd for $C_{30}H_{30}BF_4NO_2PRe$: C 48.66, H 4.08; found: C 48.51, H 4.06.

Preparation of allyl halides complexes (10a,b): General procedure: [(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=$CHCH_2OH$)]$^+$[BF_4]$^-$ (**1,** 60 mg, 0.087 mmol) was diluted in CH_2Cl_2 (3 mL) and the halogenation reagent (3 equiv) was added at room temperature. The reaction mixture was stirred for 4 h and then hydrolyzed. The organic compounds were extracted three times with CH_2Cl_2. The combined organic phases were dried and solvents were removed in vacuo. The resulting residue was chromatographed on a silica gel column or precipitated. The halogenated complex was isolated as a yellow powder.

[(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=$CHCH_2Cl$)]$^+$[BF_4]$^-$ (10a): Thionyl chloride was used as the halogenation reagent. The resulting residue was chromatographed on a 3 cm silica gel column (dichloromethane/acetone 4:1 (v/v)). Yield: 79%; ^1H NMR (400 MHz, CD_3CN): $\delta = 7.52-7.69$ (m, 9H; PPh_3), 7.36–7.48 (m, 6H; PPh_3), 5.85 (s; C_5H_5), 4.39–4.52 (m, 1H; =CH), 4.27 (dd, $J = 10.7$, 4.6 Hz, 1H; one of CH_2Cl), 3.66 (dd, $J = 10.7$, 9.7 Hz, 1H; one of CH_2Cl), 2.45 (ddd, J = 9.7, 4.6 Hz, $J(P,H) = 6.6$ Hz, 1H; one of H_2C=), 2.24 (ddd, $J = 10.7$, 4.6 Hz, $J(P,H) = 10.7$ Hz, 1H; one of H_2C=); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): $\delta = 134.9$ (d, $J(C,P) = 9.9$ Hz; *o*-Ph), 133.9 (d, $J(C,P) = 3.0$ Hz; *p*-Ph), 131.5 (d, $J(C,P) = 59.1$ Hz; *i*-Ph), 131.2 (d, $J(C,P) = 11.1$ Hz; *m*-Ph), 99.6 (s: C_5H_5), 52.1 (s; CH_2Cl), 45.9 (d, $J(C,P) = 1.1$ Hz; =CH), 38.4 (d, $J(C,P) = 6.5$ Hz; $=CH_2$); $^{31}P\{^1H\}$ NMR (121 MHz, CD_3CN): $\delta = 11.3$; IR (neat): $\tilde{\nu}_{NO} = 1724$ (vs) cm^{-1}; elemental analysis calcd for $C_{26}H_{25}BF_4ClNOPRe$: C 44.18, H 3.56; found: C 44.26, H 3.72.

[(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=$CHCD_2Cl$)]$^+$[BF_4]$^-$ (10a′): Thionyl chloride was used as the halogenation reagent. The resulting residue was chromatographed on a 3 cm silica gel column (dichloromethane/acetone 4:1 (v/v)). Yield: 69%; ^1H NMR (400 MHz, CD_3CN): $\delta = 7.52-7.67$ (m, 9H; PPh_3), 7.38–7.46 (m, 6H; PPh_3), 5.84 (s; C_5H_5), 4.44 (t, $J = 9.6$ Hz, 1H; =CH), 2.45 (ddd, $J = 10.7$, 4.6 Hz, $J(P,H) = 10.7$ Hz, 1H; one of H_2C=), 2.24 (ddd, $J = 9.7$, 4.6 Hz, $J(P,H) = 6.6$ Hz, 1H; one of H_2C=); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): $\delta = 134.2$ (d, $J(C,P) = 10.3$ Hz; *o*-Ph), 133.2 (d, $J(C,P) = 2.7$ Hz; *p*-Ph), 130.9 (d, $J(C,P) = 59.9$ Hz; *i*-Ph), 130.6 (d, $J(C,P) = 11.1$ Hz; *m*-Ph), 99.0 (s; C_5H_5), 45.2 (s; =CH), 37.8 (d, $J(C,P) = 6.5$ Hz; $=CH_2$); $^{31}P\{^1H\}$ NMR (121 MHz, CD_3CN): $\delta = 11.3$; IR (neat): $\tilde{\nu}_{NO} = 1724$ (vs) cm^{-1}; HRMS calcd for ($C_{26}H_{23}D_2ClNOPRe$)$^+$: 622.1041, found: 622.1033.

[(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=$CHCH_2Br$)]$^+$[BF_4]$^-$ (10b): Phosphorus tribromide was used as the halogenation reagent. The resulting residue was precipitated in a dichloromethane/hexane mixture. Yield: 80%; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.54-7.64$ (m, 9H; PPh_3), 7.33–7.44 (m, 6H; PPh_3), 6.02 (s; C_5H_5), 4.65–4.81 (m, 1H; =CH), 3.92–4.03 (m, 1H; one of CH_2Br), 3.68–3.79 (m, 1H; one of CH_2Br), 2.70–2.80 (m, 1H; one of H_2C=), 2.28–2.40 (m, 1H; one of H_2C=); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 133.9$ (d, $J(C,P) = 9.9$ Hz; *o*-Ph), 133.1 (d, $J(C,P) = 2.7$ Hz; *p*-Ph), 130.5 (d, $J(C,P) = 11.1$ Hz; *m*-Ph), 130.0 (d, $J(C,P) = 59.5$ Hz; *i*-Ph), 99.6 (s; C_5H_5), 47.2 (s; CH_2Br), 39.9 (s; =CH), 39.8 (d, $J(C,P) = 5.1$ Hz; $=CH_2$); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 10.0$; IR (neat): $\tilde{\nu}_{NO} = 1722$ (vs) cm^{-1}; HRMS calcd for ($C_{26}H_{25}BrNOPRe$)$^+$: 664.0398, found: 664.0390.

X-ray structure determinations of 2a, 2b, 17a, and 17b: All X-ray structural analyses were recorded on an Enraf–Nonius CAD4 diffractometer with $Mo_{K\alpha}$ radiation at $T = 294$ K. The structures were solved by direct methods with the SIR-92 program. All the calculations were performed on a Silicon Graphics Indy computer with the MOLEN package (Enraf–Nonius, **1990**). Atomic scattering factors were taken from the International Tables for X-ray Crystallography (**1974**).[17]

Crystal structure analysis of **2a**: $RePC_{27}H_{30}O_2NBF_4 \cdot H_2O$: Crystal dimensions: $0.15 \times 0.26 \times 0.29$ mm, $M_r = 720.52$, monoclinic, $P2_1/n$, $a = 17.148(7)$, $b = 10.367(9)$, $c = 16.394(10)$ Å, $\beta = 110.04(5)^\circ$, $V = 2738(3)$ Å^{-3}, $Z = 4$, $\rho_{calcd} = 1.748$ Mg m^{-3}, $2\theta_{max} = 50^\circ$, $\lambda(Mo_{K\alpha}) = 0.70926$ Å, $\mu = 46.10$ cm^{-1}, $F(000) = 1416$, 3635 reflections were independent ($R_{int} = 0.012$) with $I > 3\sigma(I)$. The whole structure was refined by full-matrix least-square techniques (use of F magnitude; x, y, z, β_{ij} for Re, P, C, B, O, and N atoms, x, y, z, B for F atoms, and x, y, z fixed for H atoms; 319 variables and 3635 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04\,F_o^2)^2]^{-1/2}$) with the resulting $R = 0.045$, $R_w = 0.038$, and $S_w = 3.22$ (residual $\Delta\rho \le 1.20$ e Å^{-3}).

Crystal structure analysis of **2b:** $RePC_{27}H_{30}O_2NBF_4 \cdot CH_2Cl_2$: Crystal dimensions: $0.22 \times 0.24 \times 0.27$ mm, $M_r = 786.43$, monoclinic, $P2_1/n$, $a = 12.131(6)$, $b = 22.599(4)$, $c = 11.375(3)$ Å, $\beta = 103.76(3)^\circ$, $V = 3029(2)$ Å^{-3}, $Z = 4$, $\rho_{calcd} = 1.725$ Mg m^{-3}, $2\theta_{max} = 50^\circ$, $\lambda(Mo_{K\alpha}) = 0.70926$ Å, $\mu = 43.46$ cm^{-1}, $F(000) = 1540$, 3377 reflections were refined by full-matrix least-square techniques (use of F magnitude; x, y, z, β_{ij} for Re, P, C, B, O, and N atoms, x, y, z, B for F and Cl atoms, and x, y, z fixed for H atoms; 327 variables and 3377 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04\,F_o^2)^2]^{-1/2}$) with the resulting $R = 0.063$, $R_w = 0.055$, and $S_w = 3.45$ (residual $\Delta\rho \le 1.40$ e Å^{-3}).

Crystal structure analysis of **17a**: $RePC_{30}H_{30}O_2NBF_4$: Crystal dimensions: $0.15 \times 0.24 \times 0.33$ mm, $M_r = 740.56$, monoclinic, $P2_1/n$, $a = 17.467(3)$, $b = 10.580(8)$, $c = 17.335(3)$ Å, $\beta = 113.76(1)^\circ$, V = 2934(2) Å^{-3}, $Z = 4$, $\rho_{calcd} = 1.677$ Mg m^{-3}, $2\theta_{max} = 50^\circ$, $\lambda(Mo_{K\alpha}) = 0.70926$ Å, $\mu = 43.03$ cm^{-1}, $F(000) = 1456$, 3132 reflections were independent ($R_{int} = 0.014$) with $I > 4\sigma(I)$. The whole structure was refined by full-matrix least-square techniques (use of F magnitude; x, y, z, β_{ij} for Re, P, C, B, O, and N atoms, x, y, z, B for F atoms, and x, y, z fixed for H atoms; 353 variables and 3132 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04\,F_o^2)^2]^{-1/2}$) with the resulting $R = 0.043$, $R_w = 0.036$, and $S_w = 1.45$ (residual $\Delta\rho \le 0.85$ e Å^{-3}).

Crystal structure analysis of **17b**: $RePC_{30}H_{30}O_2NBF_4$: Crystal dimensions: $0.24 \times 0.32 \times 0.35$ mm, $M_r = 740.56$, monoclinic, $P2_1/n$, $a = 17.515(7)$, $b = 10.496(4)$, $c = 17.211(3)$ Å, $\beta = 112.91(3)^\circ$, $V = 2914(2)$ Å^{-3}, $Z = 4$, $\rho_{calcd} = 1.688$ Mg m^{-3}, $2\theta_{max} = 50^\circ$, $\lambda(Mo_{K\alpha}) = 0.70926$ Å, $\mu = 43.32$ cm^{-1}, $F(000) = 1456$, 3952 reflections were independent ($R_{int} = 0.011$) with $I > 3\sigma(I)$. The whole structure was refined by full-matrix least-square techniques (use of F magnitude; x, y, z, β_{ij} for Re, P, C, B, O, and N atoms, x, y, z, B for F atoms, and x, y, z fixed for H atoms; 353 variables and 3952 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04\,F_o^2)^2]^{-1/2}$) with the resulting $R = 0.039$, $R_w = 0.035$, and $S_w = 0.67$ (residual $\Delta\rho \le 0.96$ e Å^{-3}).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101 334. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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