ELSEVIER

Journal of Organometallic Chemistry 572 (1999) 213–223

Journal of Organometallic Chemistry

Reactions of the rhenium allyl hydrido complex $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(H)$ with the electrophiles CF_3CO_2H, CF_3SO_3H, $NOBF_4$, $[p\text{-}N_2C_6H_4OMe][BF_4]$ and $[Ph_3C][BF_4]$

Ying-Xia He, Derek Sutton *

Department of Chemistry, Simon Fraser University, Burnaby, BC V5A 1S6, Canada

Received 28 May 1998

Abstract

The rhenium hydrido allyl complex $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(H)$ (**1**) reacted with $NOBF_4$ or $[p\text{-}N_2C_6H_4OMe][BF_4]$ at $-78°C$ to give $[Cp^*Re(\eta^2\text{-}C_3H_6)(CO)(NO)][BF_4]$ (**2**) or $[Cp^*Re(\eta^2\text{-}C_3H_6)(CO)(N_2C_6H_4OMe)][BF_4]$ (**3**), respectively. In these reactions addition of the electrophile is accompanied by transfer of the hydride ligand to the allyl group to form the propene ligand. Complex **1** reacted with $[Ph_3C][BF_4]$ in CH_3CN at $-78°C$ to abstract the hydride ligand and form the allyl acetonitrile complex $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(CH_3CN)][BF_4]$ (**4**). Complex **1** reacted with CF_3CO_2H or CF_3SO_3H to form the hydrido propene complexes $Cp^*Re(\eta^2\text{-}C_3H_6)(H)(CO)(CF_3CO_2)$ **(5)** or $Cp^*Re(\eta^2\text{-}C_3H_6)(H)(CO)(CF_3SO_3)$ (**6**). Studies with CF_3CO_2D demonstrated that both $Cp^*Re(\eta^2\text{-}C_3H_6)(D)(CO)(CF_3CO_2)$ and $Cp^*Re(\eta^2\text{-}C_3H_5D)(H)(CO)(CF_3CO_2)$ are formed. This is consistent with a mechanism in which D^+ attacks the metal followed by transfer of either D or H to the allyl group. Complex **1** was found not to react with C_2H_4, hexene, cyclohexene, MeC≡CMe, PhC≡CMe, CH_3CN or PMe_3.

Keywords: Rhenium allyl hydrido complex; Electrophiles; Ligand

1. Introduction

Previous work from our group has reported the formation of the half-sandwich rhenium η^3-allyl hydrido complex $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(H)$ (**1**), which was obtained by photochemical C–H activation of the coordinated propene ligand in $Cp^*Re(\eta^2\text{-}C_3H_6)(CO)_2$ [1,2]. By comparison with most other transition metal η^3-allyl hydrido complexes reported in the literature [1,3–15], complex **1** is relatively inert, and the *endo* and *exo* isomers interconvert only slowly, which has allowed the X-ray structures of both isomers to be obtained. Complex **1** has recently been made non-photochemically in improved yield from the chloro compound $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Cl$ so that now its chemistry may be better explored [16]. Here, we report some of the reactions with some electrophiles. Some attempted reactions are also described. These include treatment with some alkenes, alkynes and nitriles, with which **1** was found to be unreactive.

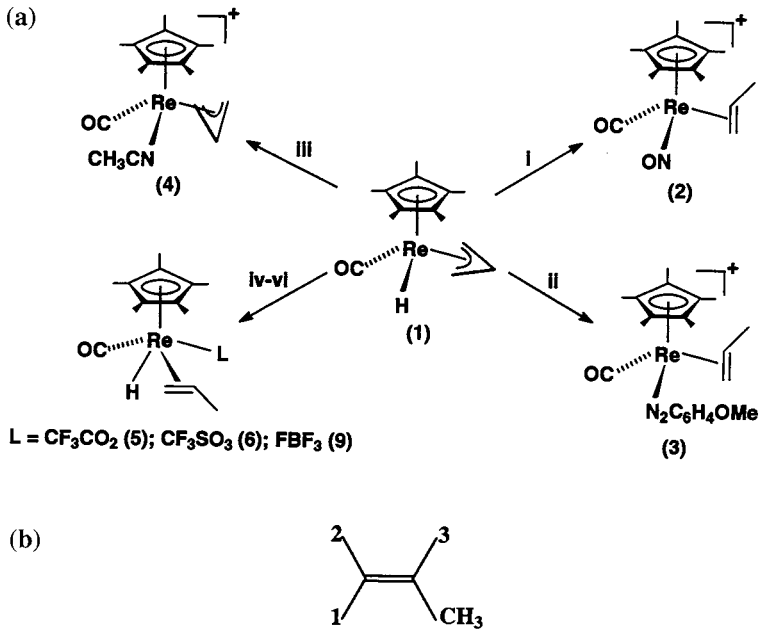
2. Results

2.1. Reactions of 1 with $[NO]^+$, $[N_2C_6H_4OMe]^+$, and $[Ph_3C]^+$

These reactions are shown in Scheme 1(a). Complex **1** reacted with $[NO][BF_4]$ in acetone at $-78°C$ to produce $[Cp^*Re(\eta^2\text{-}C_3H_6)(CO)(NO)][BF_4]$ (**2**). In this reaction the attack of NO^+ at the metal occurs with migration of the hydride ligand to the η^3-allyl group to give a propene ligand. The IR spectrum of **2** exhibited

* Corresponding author. Tel.: +1-604-291-4885; fax: +1-604-291-3765; e-mail: dsutton@sfu.ca.

0022-328X/99/$ - see front matter
PII: S0022-328X(98)00959-0



Scheme 1. (a) Reactions of Cp*Re(η^3-C_3H_5)(CO)(H) **(1)** with electrophiles: (i) $NOBF_4$; (ii) [*p*-$N_2C_6H_4OMe$][BF_4]; (iii) [Ph_3C][BF_4]/MeCN; (iv) CF_3CO_2H; (v) CF_3SO_3H; (vi) HBF_4. (b). Propene position number scheme.

ν(CO) at 2047, and ν(NO) at 1765 cm^{-1}. These are in the typical regions for coordinated CO and NO absorptions in similar cationic rhenium compounds [17–20]. The ^{1}H-NMR spectrum of **2** showed resonances indicative of the presence of two diastereomers **2a** and **2b** in a ratio of 1:1.1 by integration for the propene protons; the two Cp* resonances were overlapped. There was no change in this ratio when the sample in $CDCl_3$ was kept at room temperature (r.t) for 1 week. The two diastereomers may be accounted for by considering the position of attack of NO^+ at the rhenium center as shown in Scheme 2 and discussed below.

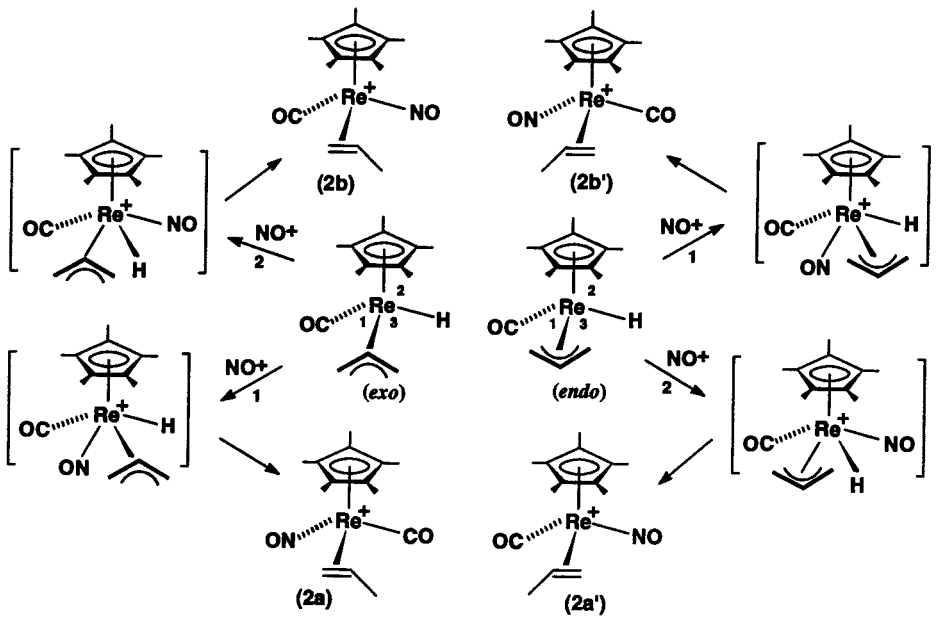
When complex **1** was treated with [$N_2C_6H_4OMe$][BF_4] in acetone at -78°C, the $[N_2C_6H_4OMe]^+$ ion attacked the rhenium instead of inserting into the Re–H bond [21], and the hydride transferred to the η^3-allyl group to produce the propene complex [Cp*Re(η^2-C_3H_6)(CO)($N_2C_6H_4OMe$)][BF_4] (**3**). The IR of **3** showed ν(CO) at 1982, and ν(NN) at 1711 cm^{-1}, indicative of a singly-bent aryldiazenide ligand [22]. The ^{1}H-NMR spectrum of **3** showed a multiplet at δ 7.04 (integration 4H) for the C_6H_4 protons and a singlet at δ 3.87 for OCH_3. The coordinated propene proton resonances were assigned as multiplets at 4.10, 3.47, and δ 3.10 for H_3, H_1 and H_2, respectively, and a doublet at δ 2.16 for the methyl group (see Scheme 1(b)). The Cp* resonance was a singlet at δ 2.17.

Complex **1** reacted with [Ph_3C][BF_4] in CH_3CN at -78°C to remove the hydride ligand and form the acetonitrile complex **4**, which was first synthesized previously from [Cp*Re(η^3-C_3H_5)$(CO)_2$][BF_4] by using PhIO in CH_3CN to oxidatively remove one of the CO ligands [23].

2.2. Protonation of Cp*Re(η^3-C_3H_5)(CO)(H) (1)

When complex **1** was reacted with CF_3CO_2H at -78°C in acetone-d_6, the IR spectrum of the reaction solution after 5 min showed a new ν(CO) band at 1962 cm^{-1}. The reaction was completed at about -60°C and the product was isolated, purified, and identified by spectroscopy as the new hydrido propene complex Cp*Re(η^2-C_3H_6)(H)(CO)(CF_3CO_2) (**5**) (Scheme 1). The CI-MS of **5** gave a peak for the parent ion at m/z 506, but a stronger peak at m/z 505 for [M^+–H], and a base peak at m/z 391 which is consistent with loss of CF_3CO_2H and one H atom from the parent ion. The ^{1}H-NMR spectrum of isolated **5** in C_6D_6 showed all the expected resonances for the propene protons, which were assigned as a multiplet at δ 3.22 for H_3, two at δ 2.60 and δ 2.20 for the terminal methylene protons, and a doublet at δ 2.36 integrating for three methyl protons. The hydride ligand gave a singlet at δ -9.28, which was in the expected region for a neutral rhenium hydride complex by comparison with **1**.

The protonation of **1** was conducted again by using CF_3SO_3H in either acetone-d_6 at -78°C, or C_6D_6 at r.t., and the hydrido propene complex Cp*Re(η^2-C_3H_6)(H)(CO)(CF_3SO_3) (**6**) was obtained (Scheme 1).



Scheme 2. Scheme to show the formation of diastereomers **2a** and **2b** from the reaction of *exo* and *endo* **1** with NO^+.

The IR spectrum of **6** in C_6D_6 showed ν(CO) at 1975 cm^{-1}. The CI-MS of **6** gave a parent peak at m/z 542. The ^{1}H-NMR spectrum of **6** in C_6D_6 gave almost the same propene resonances as did **5**. The Cp* signal was a singlet at δ 1.58, and the major Re–H resonance was at δ −9.68. In addition, there were two minor hydride resonances at δ −9.51 and δ −9.33.

The protonation of **1** with CF_3CO_2D was conducted in C_6D_6 in an attempt to investigate the reaction pathway. A mixture of Cp*Re(η^2-C_3H_5D)(H)(CO)(CF_3CO_2) (**7**) and Cp*Re(η^2-C_3H_6)(D)(CO)(CF_3CO_2) (**8**) was obtained with the ratio **7**:**8** = 3.3:1 (see below). The ^{1}H-NMR spectrum of the mixture gave almost the same resonances as for complex **5**, except that the signal at δ 2.33 (assigned to $-CH_2D$ and $-CH_3$) is broad because of coupling with the single D atom, and the central proton H_3 also showed a broad multiplet at δ 3.20. The ^{2}H{^{1}H}-NMR of this mixture gave a broad signal at δ 2.24, which corresponds to the deuterium in a CH_2D group, and is at a chemical shift similar to the proton resonance of this group, confirming the presence of a CH_2D group in complex **7**. A resonance at δ −9.31, corresponding to Re–D, indicated the presence of complex **8**. The integration of the ^{2}H resonances indicated a ratio of **7**:**8** = 3.3:1.

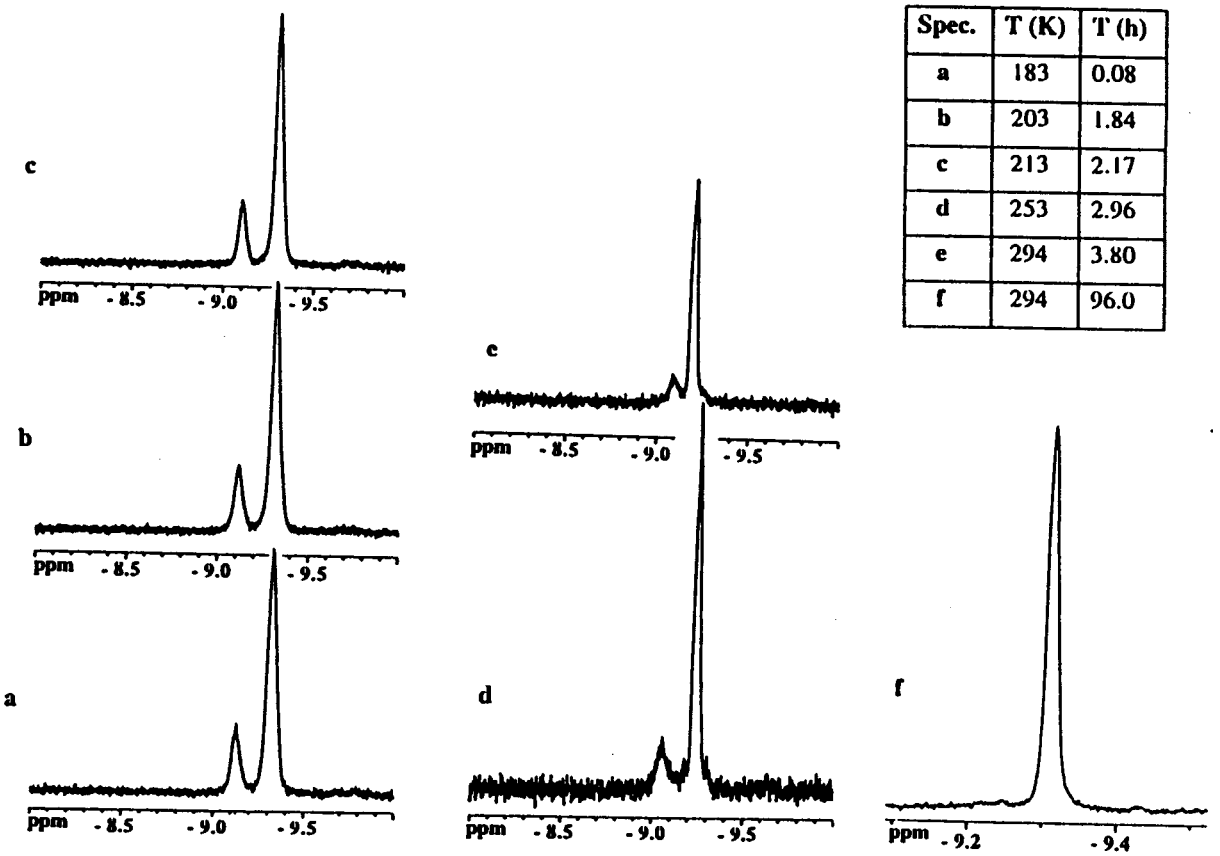
The protonation of **1** was also carried out with HBF_4 in an attempt to observe an intermediate (possibly a dihydrido complex) from proton addition prior to coordination of the anion, since BF_4^- may be a poorer ligand compared with $CF_3CO_2^-$ or $CF_3SO_3^-$. However, both the IR and the ^{1}H-NMR indicated that a hydrido propene complex was again produced which is formulated as Cp*Re(η^2-C_3H_6)(H)(CO)(FBF_3) (**9**).

*2.3. Low temperature ^{1}H-NMR study of the protonation of **1***

*2.3.1. Protonation of Cp*Re(η^3-C_3H_5)(CO)(H) (**1**) with CF_3CO_2H in CD_2Cl_2*

The above protonation of **1** with CF_3CO_2D gave results that could be accommodated by attack of D^+ at the metal or the metal–hydride bond with formation of a hydrido deuterio intermediate, followed by transfer of either H or D to the allyl group. The purpose of a low temperature study was therefore to try to observe any such dihydride intermediate produced in the protonation reaction. It was also hoped to observe whether different stereoisomers of a dihydride intermediate might be produced, and, if so, whether these might lead to different isomers of the hydrido propene complex product observable at the lower temperatures.

The CF_3CO_2H was added to a solution of **1** (mixture of *exo* and *endo* isomers, ratio *endo*: *exo* ca. 3:1) in CD_2Cl_2 at 173 K in an NMR tube, and the ^{1}H-NMR spectrum was recorded 5 min later at 183 K. The hydride region of the spectrum showed two broad signals at δ −9.32 and δ −9.13 in a ratio of 3.9:1.0. The spectrum was obtained again at 183 K after a further 10 min. It showed that the resonance intensity at δ −9.13 had decreased slightly relative to that at δ −9.32. The ^{1}H-NMR spectrum was recorded at 203, 213 and 253 K over 3 h (Fig. 1), and the intensity ratio of these resonances continued to change in favour of the δ −9.32 resonance. When the temperature was increased to 294 K, the signal at −9.32



Spec.	T (K)	T (h)
a	183	0.08
b	203	1.84
c	213	2.17
d	253	2.96
e	294	3.80
f	294	96.0

Fig. 1. Variable temperature ^{1}H-NMR spectra (Re–H resonances) following the addition of CF_3CO_2H to **1** in CD_2Cl_2 at 173 K. Spectrum **f** was recorded in C_6D_6, all others in CD_2Cl_2).

shifted to δ −9.20, and the one at −9.13 shifted to δ −9.08, and was now of only small intensity (Fig. 1e). At all temperatures, only one Cp* resonance was observed, and was a singlet at δ 2.03 at 294 K. The resonances for the propene protons were very broad (possibly indicating exchange) and were difficult to assign. The sample was then pumped to dryness and redissolved in C_6D_6. The ^{1}H-NMR spectrum in C_6D_6 gave a spectrum essentially identical to the one observed for Cp*Re(η^2-C_3H_6)(CO)(H)(CF_3CO_2) (**5**) in the r.t. synthesis above. Only a single hydride resonance occurred at δ −9.33 (Fig. 1f), and the propene and Cp* resonances were well-resolved.

It is conceivable that the two hydride resonances initially observed result from inequivalent products formed from the *endo* and *exo* isomers of **1**, respectively as the initial ratio of the resonances is somewhat similar to the relative amounts of these isomers in the sample of **1** employed. However, there is no direct evidence for this. This, of course, could be tested by studying a pure isomer of **1**. This was done, as described next (but using CF_3SO_3H in acetone for the protonation), and two isomers of the propene complex again resulted, which argues against this idea.

*2.3.2. Protonation of Cp*Re(η^3-C_3H_5)(CO)(H) (**1**) with CF_3SO_3H in acetone-d_6*

The reaction of **1** with CF_3SO_3H was conducted in acetone-d_6 by using the pure *exo* isomer of **1**. The ^{1}H-NMR spectrum of **1** in acetone-d_6 was first recorded at 213 K, and showed only the hydride resonance for the *exo* isomer at δ −9.68. Then, CF_3SO_3H was added to a solution of **1** in acetone-d_6 in an NMR tube at 183 K. A spectrum taken at 213 K 5 min after CF_3SO_3H was added showed three hydride resonances at δ −9.19, δ −9.30 and δ −9.42 assigned to unknown hydride species i–iii (Table 1). A sequence of spectra with increasing temperature in the range 213–273 K was obtained, and showed changes in the hydride resonances as indicated in Table 1. The δ −9.19 and δ −9.42 resonances generally decayed away as the temperature was increased. At 273 K a further spectrum was obtained 0.8 h later, and showed that a further change had occurred with time while the temperature was held constant. The temperature was lowered again to 253 K, but the observed spectrum was not the same as previously obtained at this temperature, indicating that the changes were not reversible with temperature. Instead, it appeared that at 273 K two species were present (with hydride resonances at δ −9.24 and δ

Table 1
^{1}H-NMR data for the temperature and time dependence of the species produced from the protonation of the *exo* isomer of **1** in acetone-d_6 at 213 K

T (K)	Time (h)	Species[a]			
		i	ii	iii	**6**
		δ (ReH) (%)[b]	δ (ReH) (%)[b]	δ (ReH) (%)[b]	δ (ReH) (%)[b]
213	0.00	−9.19; 42.1	−9.30; 32.6	−9.42; 25.3	
223	0.50	−9.18; 36.7	−9.30; 30.1	−9.42; 33.2	
233	1.18	−9.18; 35.2	−9.30; 36.7	−9.39; 28.0	
243	1.68	−9.18; 15.4	−9.27; 62.0	−9.38; 22.5	
253	2.65	−9.16; 13.3	−9.24; 43.8	−9.35; 23.7	−9.45; 19.2
263	2.95	−9.16; 7.5	−9.24; 37.3	−9.34; 22.3	−9.44; 33.0
273	3.32	−9.16; 0.0	−9.24; 65.3	−9.34; 0.0	−9.44; 34.7
273	4.12		−9.24; 43.5		−9.44; 56.5
253	4.47		−9.24; 40.4		−9.44; 59.7
253	4.63		−9.24; 35.5		−9.44; 64.6
294	72.0				−9.44; 100

[a] Species i–iii are unknown intermediates or isomers of **6**, see text.
[b] The relative percentages of the species were obtained from the intensity of the hydride resonances.

−9.44), and on decreasing the temperature to 253 K, and then increasing it from 253 to 294 K, the ratio changed such that the resonance at δ −9.24 eventually disappeared, and only the one at δ −9.44 remained. The solvent was removed, and the spectrum was re-recorded in C_6D_6. The ^{1}H-NMR spectrum of this sample was identical to that previously recorded for complex **6**.

2.4. Reaction of Cp*Re(η^3-C_3H_5)(CO)(H) (**1**) with alkenes and alkynes

We anticipated that **1** might react with alkenes to give the corresponding alkyl complexes Cp*Re(η^3-C_3H_5)(CO)(R). Some of these are known complexes that have been synthesized in this laboratory from the chloro complex Cp*Re(η^3-C_3H_5)(CO)Cl [16]. Complex **1** was treated with ethylene, hexene or cyclohexene at r.t. in hexane. The IR spectrum showed no change in the ν(CO) absorption of **1** over 24 h. Similarly, **1** showed no reaction with PhC≡CMe or MeC≡CMe in hexane at r.t. for 24 h.

2.5. Reaction of Cp*Re(η^3-C_3H_5)(CO)(H) (**1**) with CH_3CN

A solution of **1** in pure CH_3CN was stirred at r.t. for 24 h and was monitored by IR. No reaction occurred.

2.6. Reaction of Cp*Re(η^3-C_3H_5)(CO)(H) (**1**) with PMe_3

Complex **1** was treated with PMe_3 overnight in an attempt to replace the CO to give Cp*Re(η^3-C_3H_5)(PMe_3)(H). No reaction occurred.

3. Discussion

In the reaction of **1** with $NOBF_4$ the ^{1}H-NMR spectrum of product **2** gave two sets of propene resonances. We assign these to the two possible diastereomers **2a** and **2b** illustrated in Scheme 2. These should ideally have different ν(CO) and ν(NO) IR bands, and we presume that these are not resolved in the polar solvents necessary to dissolve this ionic complex. Each diastereomer has a corresponding enantiomer **2a**′ and **2b**′. The sample of **1** used for this reaction was a mixture of both the *endo* and the *exo* isomers. Scheme 2 shows that each of these can generate both diastereomers of **2**. Theoretically, there are three possible interligand positions for NO^+ to attack the rhenium in **1**. These are numbered 1–3. We assume that a four-legged piano stool intermediate is formed after NO^+ attack, as shown in square brackets in Scheme 2. The NO ligand must be a bent 1e-donor at this stage, and we assume the η^3-allyl still adopts the same orientation as it had in **1**. (The formation of a bent NO ligand from electrophilic NO^+ attack at a basic metal site is well established) [24]. If the hydride transfers only to the nearest end of the allyl to produce the propene ligand together with conversion of the NO ligand from a 1e- to a 3e-donor to give **2**, only the reaction of **1** with NO^+ in positions 1 and 2 will be productive. This is because (assuming there is no fast stereochemical reorganisation) the hydride will be in a position *trans* to the allyl if NO^+ attacks **1** at position 3, which will preclude transfer of the hydride to the allyl. For a given enantiomer of *exo*-**1**, the two diastereomers **2a** and **2b** can be envisaged to result from NO^+ attacking at the different positions 1 and 2, respectively (Scheme 2). The other enantiomer of *exo*-**1**

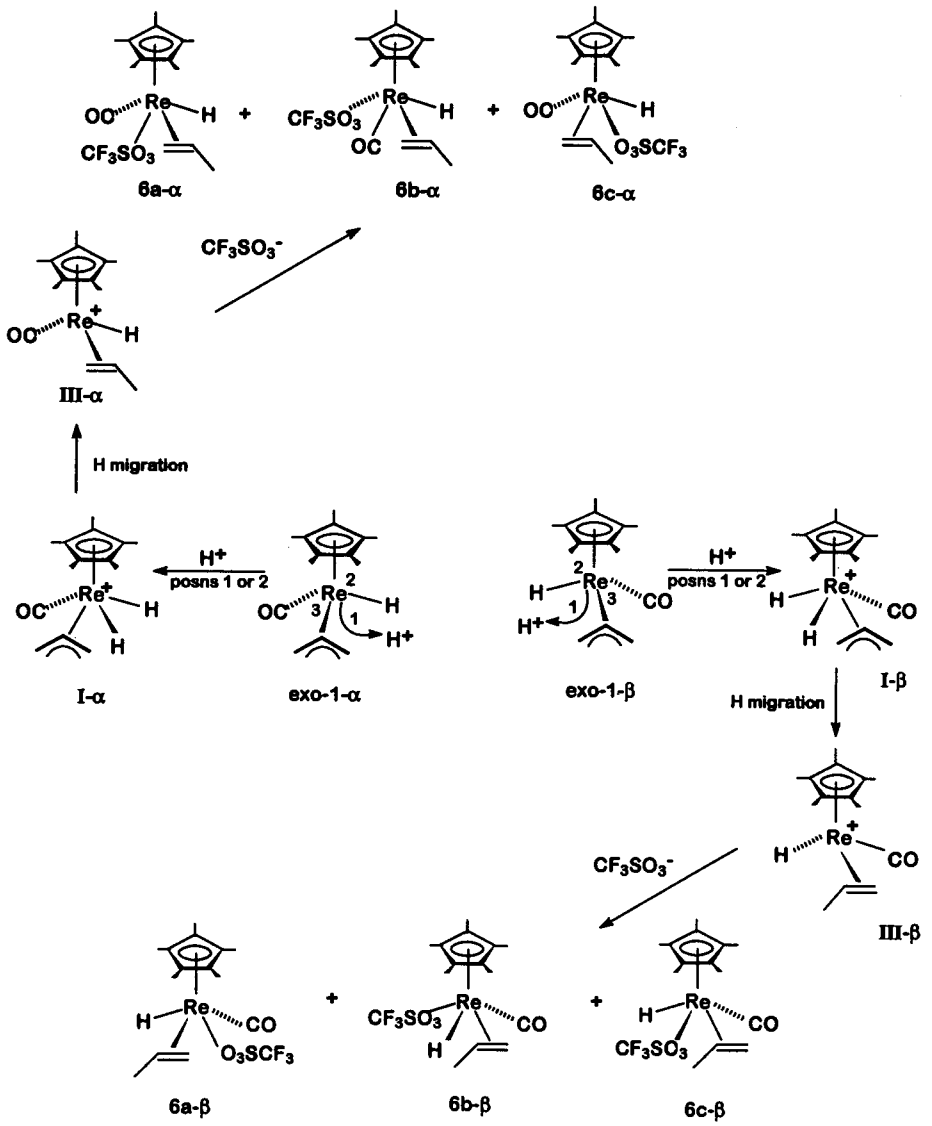
will then give the enantiomers **2a′** and **2b′**. These are all also formed in a corresponding way from the *endo* isomer of **1** as also shown in Scheme 2. It should perhaps be pointed out that additional isomers of **2** are possible if propene rotamers are considered. Chiral half-sandwich rhenium nitrosyl alkene complexes similar to **2**, but with PPh_3 replacing CO have been extensively studied by Gladysz and co-workers. The orientation of the alkene C=C vector is consistent with rhenium–alkene frontier orbital overlap considerations, and steric preferences with regard to the other co-ligands have been used to define the most likely alkene rotamer in the observed diastereomers [25]. Here, we have considered that the preferred rotamer has the methyl group avoiding the bulky Cp* ligand, as shown. It is also conceivable that alkene rotation scrambles any possible isomers based on alkene rotamers. An entirely different mechanism for the formation of **2** in which a hydride-to-allyl migration occurs first, followed by coordination of NO^+ as a 2e-donor is considered to be less likely, in view of the lack of reactivity of **1** with other 2e-donors.

Because of the presence of the Re–H bond, there was the possibility that **1** might react with an arenediazonium ion to give an aryldiazene or an arylhydrazide complex, formally the products of an insertion of the diazonium ion into the metal–hydride bond [26–28]. However, **1** reacted with $[N_2C_6H_4OMe][BF_4]$ in the way that it did with $NOBF_4$. The N_2Ar ligand is coordinated as a 3-electron donor and the H ligand has migrated to the allyl to give a propene ligand. Complexes containing an aryldiazenide ligand and an alkene are uncommon [29]. Complex **3** is an addition to a range of cationic rhenium half sandwich carbonyl aryldiazenido complexes of the type $[Cp^*ReLL'(N_2Ar)]^+$ synthesized in this laboratory [30]. The hydride in **1** exhibits hydridic character in the reaction of **1** with Ph_3C^+ and is simply abstracted to leave a vacant site that is filled by the solvent MeCN yielding **4**.

The protonation of **1** with CF_3CO_2H and CF_3SO_3H resulted in the formation of the new rhenium hydrido propene complexes $Cp^*Re(\eta^2\text{-}C_3H_6)(CO)(H)(CF_3CO_2)$ (**5**) and $Cp^*Re(\eta^2\text{-}C_3H_6)(CO)(H)(CF_3SO_3)$ (**6**). This is the first time, to our knowledge, that protonation of a hydrido allyl complex has yielded a characterizable propene complex. In the two previous cases that we know of protonation has resulted in the elimination of the propene. Henderson and co-workers observed the production of propene in the protonation of $Mo(H)(\eta^3\text{-}C_3H_5)(dppe)_2$ with HCl at low concentration [31]. The protonation of $Os(CO)(H)(\eta^3\text{-}C_3H_5)(PR_3)_2$ ($R = P^iPr_3$, PMe^tBu_2) with CH_3CO_2H, HBF_4 and HCl was studied by Schlünken and Werner [5]. The elimination of propene resulted in all cases, no matter which acid was used for the protonation, and the formation of the hydrido complex $Os(CO)(H)(PR_3)_2(CH_3CO_2)$ was identified in the case of CH_3CO_2H. No intermediate propene complex was observed. In our case, the spectroscopic data clearly indicated the coordination of the propene ligand in complexes **5** and **6**.

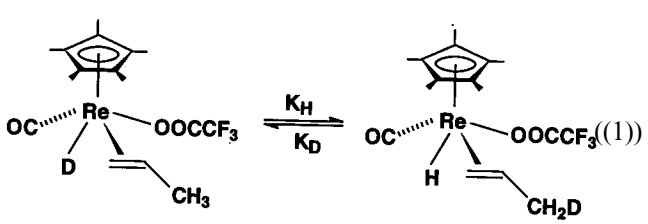
Because of the expected four-legged piano-stool geometry for complexes **5** and **6** there are three possible positional geometric isomers in which the hydride ligand is *trans* to either CO, propene, or the oxyanion ligand. In addition, each of these stereoisomers has a diastereomeric partner where the propene is bound by the opposite enantioface. For each of these six chiral isomers there is a corresponding enantiomer. We do not presently have enough evidence to assign the specific structure of the isomer ultimately obtained for **5** and **6**. It may be a single one of these six isomers or the ^{1}H-NMR could result from exchange between more than one isomer. As shown in Scheme 3 and Scheme 4, using *exo*-**1** and protonation with CF_3SO_3H for illustration, protonation at rhenium (or at the Re–H bond) can give two possible dihydride intermediates, in which the hydrides are either *cis* (Scheme 3) or *trans* (Scheme 4) in a four-legged piano-stool structure. The two Schemes depict the possible product isomers that can result in each case. In Scheme 3, two enantiomers **I-α** and **I-β** for the *cis* dihydride **I** arise from the enantiomers of *exo*-**1**. It is reasonable to assume that formation of the propene ligand results only from migration of a H atom *cis* to an allyl CH_2 group, and that migration of a H atom *trans* to the allyl ligand does not occur. Following H migration, attack of the oxyanion may then occur at a site opposite any one of the H, propene, or CO ligands in the unsaturated three-legged piano-stool cationic intermediate **III-α** or its enantiomer **III-β**. For **III-α** this generates isomers **6a-α–6c-α**, respectively. The enantiomer **III-β** produces the enantiomers **6a-β–6c-β**. In **6a-α–6c-α** the propene is bound to Re by the *si* face, whereas in **6a-β–6c-β** it is bound by the *re* face. In a similar fashion, as shown in Scheme 4, the *trans* dihydride **II** generates six corresponding diastereomers **6a′-α–6c′-α** and **6a′-β–6c′-β** of the above products, depending upon which of the two hydrogens migrates to the allyl group, followed by attack of the oxyanion as above. Thus, all six possible stereoisomers and their enantiomers of **6** can in principle result, depending upon which of sites 1–3 opposite the different basal ligands in *exo*-**1** is thought to be the site of initial proton attack. Note further that the allyl complex **1** exists in *exo* and *endo* isomeric forms, and each of these forms is capable of yielding all of the above stereoisomers of **5** and **6**, whether or not interconversion of these forms occurs.

The study done using CF_3CO_2D in C_6D_6 shows the formation of two singly D-labelled analogues of **6** in unequal amounts. In the major product (**7**) the D has been incorporated into the propene methyl group, while the other product (**8**) has D bound to Re. The first of

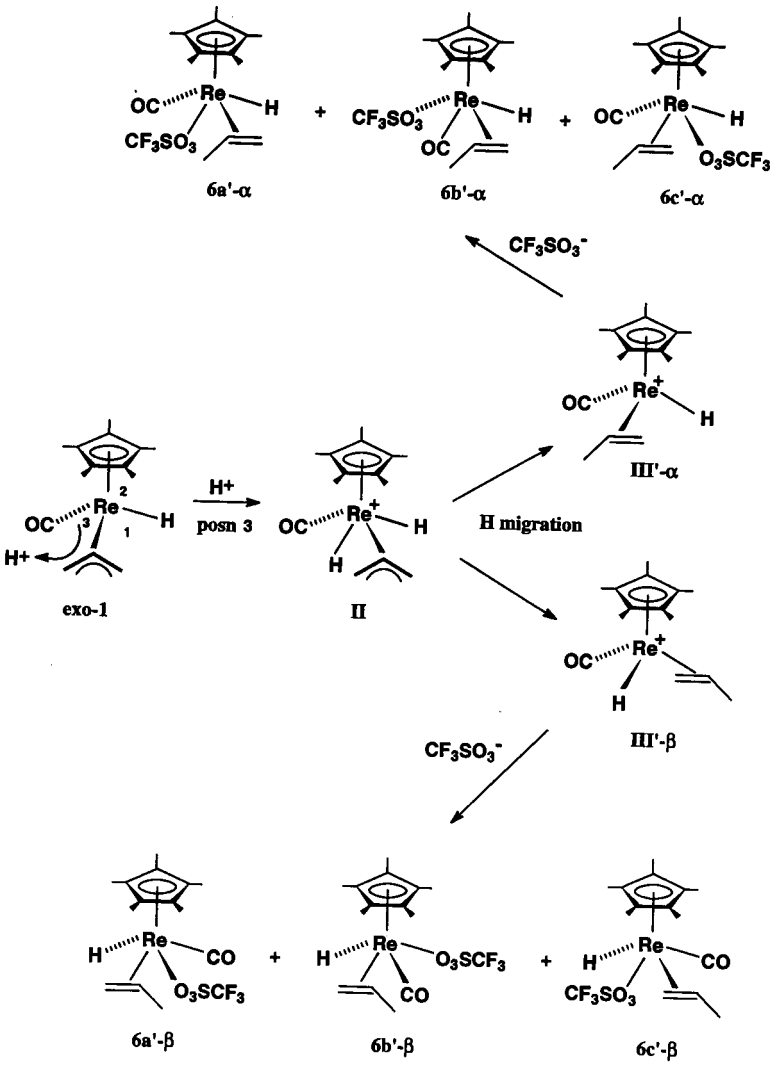


Scheme 3. Scheme illustarting the formation of isomers **6a-α–6c-α** from *exo*-**1-α** and the corresponding enantiomers **6a-β–6c-β** from *exo*-**1-β** following protonation of these enantiomers of *exo*-**1** at positions 1 or 2. Symbols α and β signify enantiomers.

these products, **7**, (but clearly not **8**) could be accounted for by direct attack of D^+ on the allyl ligand. On the other hand, both products **7** and **8** are compatible with the mechanism discussed above, and shown in Scheme 3 and Scheme 4. In this case, attack of D^+ at the metal–hydrogen bond or at the metal is envisaged to give an intermediate cationic Re(H)(D) complex that can then transfer either H or D to the allyl group. If the different amounts of **7** and **8** observed to be produced are kinetic in origin, this may indicate that both mechanisms are operating. This possibility is consistent with Henderson's results on the protonation of $Mo(H)(\eta^3\text{-}C_3H_5)(dppe)_2$, with HCl [31]. In that case, protonation was proposed to occur at the metal center to give a dihydrido η^3-allyl cationic intermediate, or at the allyl ligand to give a hydrido propene cationic intermediate, and these intermediates lead to the elimination of the observed products propyne and propene, respectively. However, if D^+ attack is exclusively at the metal, or if **7** and **8** are in equilibrium, then the equilibrium deuterium isotope effect would also favor **7** (C–D bond) over **8** (Re–D bond) Eq. ((1)) A rough estimate of K_H/K_D for **7**:**8**, ignoring statistical effects, can be made by using ballpark wavenumber values ν(Re–H) ca. 2000 cm^{-1} and ν(C–H) ca. 3000 cm^{-1} and the formula $K_H/K_D = \exp\{(\varepsilon_H - \varepsilon_D)/K_BT\}$, where $\varepsilon_H - \varepsilon_D = hc/2 \times (1 - 1/1.40)(\nu_{CH} - \nu_{ReH})$ [32–36]. This gave a value of $K_H/K_D = 2$.



((1))



Scheme 4. Scheme illustrating the formation of isomers **6a′-α-6c′-α** and the corresponding enantiomers **6a′-β-6c′-β** following protonation of *exo*-**1** at position 3 and subsequent choice of migration of a H atom to the allyl group. Symbols α and β signify enantiomers. Primed labels (e.g. **6a′**) signify a diastereomer of the unprimed label (e.g. **6a**) arising from coordination of propene by the opposite enantioface.

Although it was hoped that the low temperature protonation studies would allow observation of intermediates such as the proposed *cis* or *trans* dihydride complexes **I** or **II**, these experiments did not yield unambiguously interpretable results, except to show that the final products were the same as those formed in the r.t. syntheses. While at the low temperatures two (in the case of protonation with CF_3CO_2H in CD_2Cl_2) or three (in the case of protonation with CF_3SO_3H in acetone) hydride resonances were initially observed, and converted to those of the final products on increasing the temperature, we cannot be sure of their assignment. There is no evidence specifically pointing to assignment as one or other of the dihydride intermediates **I** or **II**, though this is a possibility. In the low temperature protonation with CF_3SO_3H the resonance at δ −9.19 is very broad and could be composed of two inequivalent hydride resonances with unresolved mutual coupling and coupling to inequivalent allyl terminal protons consistent with assignment to the *cis* dihydride structure **I** in Scheme 3. The δ −9.42 resonance might therefore tentatively be assigned to the *trans* dihydride intermediate **II** in Scheme 4. As the temperature was changed, both of these decayed away and the hydride resonance at δ −9.30 underwent a complicated change in intensity. It is possible that this arises from one or more isomers of the propene complex $Cp^*Re(\eta^2\text{-}C_3H_6)(CO)(H)(CF_3SO_3)$ (**6**). Overall, this resonance eventually decreases as the resonance of δ −9.44 increases, and presumably represents an isomer that is unstable with respect to the final product.

As expected in view of the previous reports in which protonation of an allyl complex led to evolution of propene [5,31], the hydrido propene complexes **5** and **6** are not very stable, but were sufficiently so for full

spectroscopic characterization. It is likely that their decomposition also results from the elimination of the propene. Therefore, the protonation of **1** with CF_3CO_2H in acetone-d_6 at -78°C was also conducted in the presence of PMe_3, in an attempt to obtain a PMe_3 complex Cp*Re(CO)(H)(PMe_3)(CF_3CO_2) to stabilize the unsaturated species produced after the elimination. The product in this reaction was complex **5**, instead of the expected compound. Possibly the added PMe_3 was largely protonated by CF_3CO_2H to form the phosphonium ion $[HPMe_3]^+$.

The failure of **1** to react with alkenes, alkynes, MeCN or PMe_3 under the conditions utilized here contrasts with the reactivity shown towards the electrophilic unsaturated species NO^+ and N_2Ar^+. Presumably these are prevented from binding to the metal or inserting into the Re–H bond by the reluctance of **1** to provide a vacant site, either by an η^3-η^1 transition of the allyl group or ring slippage of the Cp*.

4. Conclusions

The most notable feature to emerge from this study is the electrophile-induced migration of the hydride ligand to the allyl group to give observable propene complexes. In the reactions with NO^+ and $[N_2C_6H_4OMe]^+$ attack occurs at the metal, and the nitrosyl and aryldiazenido ligands act as 3-electron donors, fulfilling the required electron count in the resulting propene complexes **2** and **3**. In the corresponding reactions with the strong acids CF_3CO_2H, CF_3SO_3H and HBF_4, the results are compatible with protonation at the metal center to give a dihydride intermediate, though protonation at the η^3-allyl or the Re–H bond must also be considered. Again, migration of hydride to the allyl group occurs and coordination of the anion is required to fulfil the required electron count of the resulting propene complex.

5. Experimental section

5.1. General procedures

All reactions were carried out under dry nitrogen in Schlenk apparatus. Solvents were purified by standard methods and were freshly distilled under dry nitrogen. All reagents were obtained from Aldrich except where mentioned. FT-IR spectra were recorded on a Bomem Michelson-120 instrument in hexane, ether or C_6D_6 solutions. ^{1}H- and ^{13}C-NMR spectra were recorded by M.M. Tracey of the SFU NMR Service using a Bruker WM-400 instrument operating at 400.13 and at 100.6 MHz. MS spectra were obtained by G. Owen on a Hewlett-Packard Model 5985 GC-MS instrument equipped with a Phrasor Inc. fast atom bombardment accessory. Masses are given for the ^{187}Re isotope. Correct isotopic distribution patterns were observed for all parent peaks. Microanalyses were performed by M.K. Yang of the SFU Microanalytical Laboratory.

5.2. [Cp*Re(η^2-C_3H_6)(CO)(NO)][BF_4] (2)

Complex **1** (mixture of *endo*/*exo* ca. 4/1, 13 mg, 0.033 mmol) was dissolved in acetone (2 ml). At -78°C, $NOBF_4$ (10 mg, 0.086 M in acetone) was added, and the mixture was stirred for 10 min. By this time, the solution changed from colorless to yellow, and the temperature increased to -60°C. The solvent was pumped off, the residue was extracted with CH_2Cl_2, then recrystallized from ether/hexane. The pure product was obtained as yellow crystals (16.1 mg, 0.032 mmol, 74%), m.p.: decomposed at 149°C. IR (CH_2Cl_2, cm^{-1}): $\nu_{CO} = 2047$, $\nu_{NO} = 1765$. FAB-MS (m/z): 422 (M^+, base), 380 ($M^+ - C_3H_6$), 350 ($M^+ - C_3H_6 - CO - 2H$). ^{1}H-NMR ($CDCl_3$, δ), isomer **2a** (or **2b**): 4.27, (1H, m, H_3), 3.59 (1H, dd, $J_{12} = 2.5$ Hz, $J_{13} = 15.0$ Hz, H_1), 3.29 (1H, d, $J_{23} = 13.5$ Hz, H_2), 2.52 (3H, d, $J = 6.5$ Hz, CH_3), 2.23 (15H, s, Cp*). Isomer **2b** (or **2a**): 3.93, (1H, m, H_3), 3.00 (1H, dd, $J_{12} = 2.5$ Hz, $J_{13} = 9.0$ Hz, H_1), 2.78 (1H, d, $J_{23} = 9.0$ Hz, H_2), 2.22 (15H, s, Cp*), 2.12 (3H, d, $J = 6.5$ Hz, CH_3). Anal. Calc. for $C_{14}H_{21}BF_4NO_2Re$: C, 33.08; H, 4.16; N, 2.76. Found: C, 32.85; H, 3.95; N, 3.06.

5.3. [Cp*Re(η^2-C_3H_6)(CO)($N_2C_6H_4OCH_3$)][BF_4] (3)

Complex **1** (mixture of *endo*/*exo* ca. 8/1, 15 mg, 0.038 mmol) was dissolved in 2 ml acetone. At -78°C, [p-$N_2C_6H_4OCH_3$][BF_4] (10 mg, 0.09 M in 0.5 ml acetone) was added to this solution. The solution immediately changed from colorless to orange and the IR showed the disappearance of the ν(CO) for **1**, and a new CO absorption at 1995 cm^{-1} for **3**. The solvent was pumped off, and the residue was recrystallized from CH_2Cl_2/ether to give the pure product as brown solid (12.3 mg, 0.021 mmol, 63%). IR (CH_2Cl_2, cm^{-1}): $\nu_{CO} = 1982$, $\nu_{NN} = 1711$. ^{1}H-NMR ($CDCl_3$, δ): 7.04 (4H, m, C_6H_4), 4.10 (1H, m, H_3), 3.87 (3H, s, OCH_3), 3.47 (1H, m, H_2), 3.10 (1H, dd, $J_{13} = 13.0$ Hz, $J_{21} = 2.0$ Hz, H_1), 2.17 (15H, s, Cp*), 2.16 (3H, d, $J = 3.6$ Hz, CH_3).

5.4. [Cp*Re(η^3-C_3H_5)(CO)($NCCH_3$)][BF_4] (4)

Complex **1** (mixture of *endo*/*exo* ca. 7/1, 12 mg, 0.031 mmol) was dissolved in 3 ml of freshly distilled CH_3CN. At -35°C, [Ph_3C][BF_4] (10 mg, 0.11 M in 0.5 ml CH_3CN) was added to this solution, then stirred for 10 min. The IR showed disappearance of the ν(CO) band from **1**, and a new ν(CO) at 1971 cm^{-1} appeared.

the solvent was pumped off, and the residue was recrystallized from CH_2Cl_2/ether to give **4** as a yellowish solid. IR (CH_3CN, cm^{-1}): $\nu_{CO} = 1971$. ^{1}H-NMR ($CDCl_3$, δ): 4.83, (1H, m, H_c), 3.26 (1H, dd, $J_{sc} = 6.0$ Hz, $J_{ss} = 3.5$ Hz, H_s), 3.11 (1H, dd, $J_{sc} = 6.0$ Hz, $J_{ss} = 3.5$ Hz, H_s), 2.80, (3H, s, CH_3CN), 2.03 (1H, d, $J_{ac} = 11.6$ Hz, H_a), 1.96 (15H, s, Cp*), 1.32 (1H, d, $J_{ac} = 9.0$ Hz, H_a).

5.5. Cp*Re(η²-C₃H₆)(H)(CO)(CF₃CO₂) (5)

Complex **1** (mixture of *endo*/*exo* ca. 5/1, 20 mg, 0.051 mmol) was dissolved in acetone-d_6. At −78°C, five drops of CF_3CO_2H were added to the solution, which was then stirred for 1 h. The IR showed that the reaction was not finished at this time. The reaction was continued for another hour while the temperature was raised to −60°C. The IR showed the disappearance of the CO absorption from **1**, and appearance of a new CO band at 1962 cm^{-1} for **5**. The solvent was pumped off, and the residue was extracted with hexane. This hexane solution was pumped dry for 12 h, and the pure product was obtained as a yellowish solid. IR (hexane, cm^{-1}): $\nu_{CO} = 1981$. CI-MS (m/z): 506 (M^+), 505 ($M^+ - H$), 465 ($M^+ - C_3H_5$), 463 ($M^+ - C_3H_6 - H$), 421 ($M^+ - C_3H_5 - CO_2$), 391 ($M^+ - CF_3CO_2H - H$, base). ^{1}H-NMR (C_6D_6, δ): 3.22, (1H, m, H_3), 2.60 (1H, d, $J_{13} = 12.0$ Hz, H_1), 2.36 (3H, d, $J = 6.7$ Hz, CH_3), 2.20 (1H, d, $J_{23} = 8.5$ Hz, H_2), 1.59 (15H, s, Cp*), −9.28 (1H, s, Re–H).

5.6. Cp*Re(η²-C₃H₆)(H)(CO)(CF₃SO₃) (6)

Complex **1** (mixture, *endo*/*exo* ca. 5/1, 18 mg, 0.046 mmol) was dissolved in C_6D_6 (2 ml). At r.t., CF_3SO_3H (three drops) was added to this solution, which was then stirred for 10 min. The IR of the solution showed a new ν(CO) band at 1975 cm^{-1}, and the ν(CO) of **1** disappeared. The solvent was pumped off, and the residue was dried under vacuum for 3 h. The product was obtained as a brownish solid (18.5 mg, 0.034 mmol, 74%). IR (C_6D_6, cm^{-1}): $\nu_{CO} = 1975$. CI-MS (m/z): 542 (M^+), 541 ($M^+ - H$), 407 ($M^+ - CF_3SO_2 - 2H$), 391 ($M^+ - CF_3SO_3H - H$, base). ^{1}H-NMR (C_6D_6, δ): 4.00, (1H, m, H_3), 2.63 (1H, d, $J_{13} = 12.2$ Hz, H_1), 2.39 (3H, d, $J = 6.0$ Hz, CH_3), 2.19 (1H, dd, $J_{23} = 8.8$ Hz, $J_{21} = 1.0$ Hz, H_2), 1.58 (15H, s, Cp*), −9.68 (1H, s, Re–H). There were two minor hydride resonances at −9.51 and δ −9.33.

5.7. Cp*Re(η²-C₃H₅D)(H)(CO)(CF₃CO₂) (7) and Cp*Re(η²-C₃H₆)(D)(CO)(CF₃CO₂) (8)

Complex **1** (mixture of *endo*/*exo* ca. 3/1, 18 mg, 0.046 mmol) was dissolved in 2 ml C_6D_6 at r.t., CF_3CO_2D (five drops) was added, and the mixture stirred for 10 min. The IR showed only one new CO band at 1971 cm^{-1}. The solvent was pumped off, and the residue was dried for 5 h. The pure product was obtained as a yellowish solid (mixture of **7** and **8**, ratio **7**:**8** = 3:1; 18.9 mg, 0.037 mmol, 81%). IR (C_6D_6, cm^{-1}): $\nu_{CO} = 1971$. CI-MS (m/z): 465 ($M^+ - C_3H_6$), 463 ($M^+ - C_3H_6 - D$, base), 394 ($M^+ - CF_3CO_2$), 393 ($M^+ - CF_3CO_2H$), 392 ($M^+ - CF_3CO_2D$). ^{1}H-NMR (C_6D_6, δ): 3.20, (1H, m, H_3), 2.59 (1H, d, $J_{13} = 12.0$ Hz, H_1), 2.33 (2H, br, CH_2D), 2.18 (1H, d, $J_{23} = 8.8$ Hz, H_2), 1.55 (15H, s, Cp*), −9.32 (1H, s, Re–H). ^{2}H{^{1}H}-NMR (C_6D_6, δ): 2.24 (s, CH_2D), −9.31 (s, Re–D).

5.8. Cp*Re(η²-C₃H₆)(H)(CO)(FBF₃) (9)

Complex **1** (mixture of *endo*/*exo* ca. 4/1, 15 mg, 0.038 mmol) was dissolved in C_6D_6 (2 ml). At r.t., HBF_4 (three drops, 48% ether solution) was added and the solution was stirred for 5 min. The IR of the solution showed a new ν(CO) band at 1971 cm^{-1} for the product, and the ν(CO) of **1** disappeared. The solvent was pumped off, and the residue was dried under vacuum for 8 h. The product was obtained as a brownish solid. IR (C_6D_6, cm^{-1}): $\nu_{CO} = 1971$. CI-MS (m/z): 393 ($M^+ - FBF_3$, base). ^{1}H-NMR (C_6D_6, δ): 2.73, (1H, m, H_3), 2.69 (1H, d, $J_{13} = 13.0$ Hz, H_1), 2.47 (1H, d, $J_{23} = 5.8$ Hz, H_2), 2.33 (3H, d, $J = 6.0$ Hz, CH_3), 1.60 (15H, s, Cp*), −9.45 (1H, s, Re–H). There are two minor hydride resonances at −9.30 and δ −9.26.

5.9. Protonation of 1 with CF₃COOH in CD₂Cl₂ at low temperature

Complex **1** (mixture, *endo*/*exo* ca. 3/1, 15 mg, 0.038 mmol) was dissolved in 1 ml CD_2Cl_2 in a ^{1}H-NMR tube. This was then placed in a Schlenk tube, degassed three times, cooled to 173 K, and then placed in the probe. The ^{1}H-NMR spectrum was recorded at 183 K, which showed a mixture of *endo* and *exo* isomers of **1** in a ratio of *endo*/*exo* = 3/1. The sample was removed from the probe, and five drops of CF_3CO_2H were immediately added to this solution at 173 K. The NMR tube was again placed in the probe, and the ^{1}H-NMR spectrum was recorded at 183 K after 5 min and showed two hydride resonances at δ −9.32 and δ −9.13. The spectrum was obtained again 10 min later, and showed only a slight decrease of the signal at δ −9.13. The temperature was then raised to 203, 213, 253, and 294 K, and the ^{1}H-NMR spectra at these temperatures were recorded. As the temperature increased, the resonance at δ −9.13 decreased, and the one at δ −9.32 increased. At 294 K, the signal at δ −9.13 disappeared, and the one at δ −9.32 was the only remaining hydride resonance. The resonances of the propene and the allyl protons of the possible isomers were broad and overlapped, which made the

assignments of these signals impossible. Only one Cp* resonance was observed in all the temperature range, it was a singlet at δ 2.03. The product resulting from the low temperature protonation was pumped to dryness, and redissolved in C_6D_6. The ^{1}H-NMR spectrum of it in C_6D_6 was identical to that of obtained for complex **5**.

*5.10. Protonation of **1** with CF_3SO_3H in acetone-d_6 at low temperature*

Complex **1** (pure *exo* isomer, 15 mg, 0.038 mmol) was dissolved in acetone-d_6 in an NMR tube, degassed as above, and the ^{1}H-NMR spectrum of it was recorded at 213 K, which showed only one resonance in the hydride region as expected for the pure *exo* isomer of **1**. The sample was then removed from the probe, and five drops of CF_3SO_3H were added at 183 K. This gave a suspension because of the insolubility of CF_3SO_3H. The sample was replaced in the probe set at 213 K, and the spectrum was recorded after 5 min at 213 K, which showed three hydride resonances at δ −9.19, δ −9.30 and δ −9.42. The temperature was then raised in 10°C steps to 273 K, and the spectrum was recorded. As the temperature increased, the resonances at δ −9.19 and δ −9.42 decreased, and the one at δ −9.30 showed a complicated change. At 253 K, there were four hydride resonances at δ −9.16, δ −9.24, δ −9.35 and δ −9.45, respectively. At 273 K, the ^{1}H-NMR spectrum was recorded twice at different times, and the result indicated that the resonance at δ −9.30 decreased as the time increased, and the one at δ −9.44 increased. At 294 K, the other three resonances disappeared, and the one at δ −9.44 was the only signal in the hydride region (Table 1). The resonances of the propene and the allyl protons of the species were broad and overlapped, which made the assignments of these signals impossible. Several Cp* resonances were observed in all the temperature range, and they were at δ 2.0–δ 2.1. Finally, the ^{1}H-NMR spectrum of the ultimate product from this low temperature protonation was measured in C_6D_6 at r.t., and was found to be identical to that of obtained for complex **6**.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada through a research grant to D.S., and by the Simon Fraser University through a Graduate Research Fellowship to Y.H. We are indebted to Professors J.M. Mayer and A. Bennet for advice on the calculation of equilibrium isotope effects.

References

[1] R.J. Batchelor, F.W.B. Einstein, R.H. Jones, J.M. Zhuang, D. Sutton, J. Am. Chem. Soc. 111 (1989) 3468.
[2] J.M. Zhuang, D. Sutton, Organometallics 10 (1991) 1516.
[3] R.C. Schnabel, D.M. Roddick, Organometallics 15 (1996) 3550.
[4] M. Schulz, H. Werner, J. Organomet. Chem. 470 (1994) 243.
[5] C. Schlunken, H. Werner, J. Organomet. Chem. 454 (1993) 243.
[6] J.E. Bercaw, J.R. Moss, Organometallics 11 (1992) 639.
[7] W.D. McGhee, R.G. Bergman, J. Am. Chem. Soc. 110 (1988) 4246.
[8] W.D. McGhee, R.G. Bergman, J. Am. Chem. Soc. 107 (1985) 3388.
[9] R.H. Heyn, K.G. Caulton, J. Am. Chem. Soc. 115 (1993) 3354.
[10] T.H. Tulip, J.A. Ibers, J. Am. Chem. Soc. 101 (1979) 4201.
[11] E.O. Sherman, M. Olson, J. Organomet. Chem. 172 (1979) C13.
[12] G. Carturan, A. Scrivanti, F. Morandini, Angew. Chem. Int. Ed. Engl. 20 (1981) 112.
[13] R. Bertani, G. Carturan, A. Scrivanti, Angew. Chem. Int. Ed. Engl. 22 (1983) 246.
[14] J. Schwartz, J. Mol. Catal. 72 (1992) 373.
[15] M.D. Fryzuk, X. Gao, S.J. Rettig, J. Am. Chem. Soc. 117 (1995) 3106.
[16] Y. He, D. Sutton, J. Organomet. Chem. 538 (1997) 49.
[17] C. Roger, T.S. Peng, J.A. Gladysz, J. Organomet. Chem. 439 (1992) 163.
[18] J.R. Sweet, W.A.G. Graham, Organometallics 1 (1982) 982.
[19] J.R. Sweet, W.A.G. Graham, Organometallics 2 (1983) 135.
[20] J.R. Sweet, W.A.G. Graham, J. Organomet. Chem. 217 (1981) C37.
[21] B.L. Haymore, J. Organomet. Chem. 137 (1977) C11.
[22] G.C-Y. Kim, R.J. Batchelor, X. Yan, F.W.B. Einstein, D. Sutton, Inorg. Chem. 34 (1995) 6163.
[23] R.J. Batchelor, F.W.B. Einstein, Y. He, D. Sutton, J. Organomet. Chem. 468 (1994) 183.
[24] (a) D.J. Hodgson, N.C. Payne, J.A. McGinnety, R.G. Pearson, J.A. Ibers, J. Am. Chem. Soc. 90 (1968) 4486. (b) D.J. Hodgson, J.A. Ibers, Inorg. Chem. 7 (1968) 2345. (c) B.F.G. Johnson, B.L. Haymore, J.R. Dilworth in: G. Wilkinson, R.D. Gillard, J.A. McCleverty, (Eds.), Comprehensive Coordination Chemistry, vol. 2, Pergamon Press, Oxford, England, 1987, p. 99.
[25] (a) J.A. Gladysz, B.J. Boone, Angew. Chem. Int. Ed. Engl. 36 (1997) 550. (b) T.-S. Peng, J.A. Gladysz, J. Am. Chem. Soc. 114 (1992) 4174. (c) G.S. Bodner, T.-S. Peng, A.M. Arif, J.A. Gladysz, Organometallics 9 (1990) 1191.
[26] G.W. Parshall, J. Am. Chem. Soc. 89 (1967) 1822.
[27] J.A. Carroll, D. Sutton, Inorg. Chem. 19 (1980) 3137.
[28] F.W.B. Einstein, T. Jones, A.J.L. Hanlan, D. Sutton, Inorg. Chem. 21 (1982) 2585.
[29] X. Yan, F.W.B. Einstein, D. Sutton, Can. J. Chem. 73 (1995) 939.
[30] A. Cusanelli, R.J. Batchelor, F.W.B. Einstein, D. Sutton, Organometallics 13 (1994) 5096.
[31] K.E. Oglieve, R.A. Henderson, J. Chem. Soc. Chem. Commun. (1993) 474.
[32] E. Buncel, C.C. Lee (Eds.), Isotopes in Organic Chemistry, vol. 6, Elsevier, Amsterdam, 1984, p. 161.
[33] H.C. Urey, D. Rittenberg, J. Chem. Phys. 1 (1933) 137.
[34] J. Bigeleisen, M.G. Mayer, J. Chem. Phys. 15 (1947) 261.
[35] J. Bigeleisen, J. Chem. Phys. 17 (1949) 675.
[36] B.R. Bender, J. Am. Chem. Soc. 117 (1995) 11239.