Reactivity of [Cp*Re(η³-C₃H₅)(CO)₂][BF₄] towards oxygen, sulfur, nitrogen and carbon nucleophiles

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Abstract

The nucleophilic addition of oxygen, sulfur, nitrogen and carbon nucleophiles to [Cp*Re(η³-C₃H₅)(CO)₂][BF₄] (1) has been investigated. In all cases, addition of the nucleophile to the allyl ligand in 1 was observed to result, giving the substituted propene complexes with general formula Cp*Re(CO)₂(η²-C₃H₅R) (R = CH₃CO₂, C₂H₅S, C₆H₅S, NH₂, N₃, CHMe₂ and C₆H₅) and [Cp*Re(CO)₂]₂(η²:η²-C₃H₅S(CH₂)₃SC₃H₅). No product of attack at the central carbon was observed for any of the nucleophiles. In the cases where the nucleophile was NH₂⁻ or C₆H₅Li, nucleophilic addition occurred either at the η³-allyl or at a CO ligand. At low temperature (−78–0 °C) the CO was attacked and complexes with general formula Cp*Re(η³-C₃H₅)(CO)(COR) (R = NH₂ and C₆H₅) were produced. When R is C₆H₅, the product was stable and was observed along with the substituted propene complex in solution, but when NH₂⁻ was used, the carbamoyl complex converted completely to the substituted propene complex at room temperature. A by-product of the method used to synthesize Cp*Re(η²-C₃H₅SC₆H₅)(CO)₂ was a small amount of Cp*Re(η²-C₃H₅)(CO)(O₂CSC₆H₅) (7). The X-ray crystal structure of 7 has been determined.

Keywords: Rhenium; Cyclopentadienyls; Allyls; Nucleophilic substitution; Olefin complexes; X-ray structure

1. Introduction

Among carbon–carbon bond formation reactions promoted by transition metal compounds, allylic alkylation by nucleophilic addition to the η³-allyl group in cationic transition metal complexes has played an important role. Nucleophilic addition can occur at either the central or one of the terminal carbon atoms, depending on the metal and co-ligands. The terminal carbons are the preferred sites of attack in most cases [1,2], but the central carbon atom can also be attacked to give metal-lacyclobutanes [3,4]. Previously, we reported the reactions of the rhenium allyl complex [Cp*Re(η³-C₃H₅)(CO)₂][BF₄] (1) with H⁻, MeO⁻ and PMe₃. Each of these nucleophiles attacked the terminal carbon of the η³-allyl group to give substituted propene complexes, although with MeO⁻ the methoxycarbonyl complex 2 was also formed when the reaction was conducted at 0 °C, and slowly converted to the substituted

propene complex 3 at room temperature [5–8]. In this paper, we extend the reactions of the η³-allyl in 1 to include carbon, nitrogen, oxygen and sulfur nucleophiles.

2. Results and discussion

2.1. Reaction of [Cp*Re(η³-C₃H₅)(CO)₂][BF₄] (1) with CH₃CO₂Na

The reaction of 1 with CH₃CO₂Na was carried out at room temperature for 5 h, after which the IR spectrum showed ν(CO) absorptions for only Cp*Re(η²-C₃H₅O₂CCH₃)(CO)₂ (4) (Scheme 1) at 1956 and 1877 cm⁻¹ in CH₂Cl₂. The EIMS of 4 gave a strong parent peak at m/z 478 (52% intensity), and a fragment at m/z 378 corresponding to [M⁺–C₃H₅O₂CCH₃] (80% intensity).

The ¹H NMR spectrum of 4 in C₆D₆ showed Cp* and CH₃ resonances at δ 1.32 and 1.85, plus resonances for the substituted propene. For the assignments
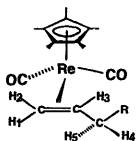
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Fig. 1. Structure of the substituted propene complexes 3–6, 8–11 and 13 with proton numbering scheme.

of the protons in the substituted propene ligand in this and subsequent compounds refer to Fig. 1. The H_4 and H_5 protons at δ 5.18 and 3.71 are diastereotopic, and each showed a doublet of doublets resulting from mutual coupling with H_3.

In the $^{13}C\{^1H\}$ NMR spectrum of 4, the three propene carbons gave resonances at δ 73.40, 37.33 and 26.62, which are in the same region as the literature data for similar complexes [9].

## 2.2. Reaction of [Cp*Re(η³-C₃H₅)(CO)₂][BF₄] (1) with CH₃CH₂SNa

In an attempt to coordinate a sulfur containing ligand to the rhenium η³-allyl complex, the cationic dicarbonyl complex 1 was reacted with PhIO in the presence of NaSCH₂CH₃ in CH₂Cl₂. The expected product is

Cp*Re(η³-C₃H₅)(CO)(SCH₂CH₃), if PhIO oxidatively removes one CO, as in the case of the reaction of PhIO with 1 in CH₃CN [10]. Although PhIO or Me₃NO have been extensively used to oxidatively remove coordinated CO from cationic carbonyl complexes, the reaction is usually carried out in coordinating solvents, such as CH₃CN, so that as soon as the carbonyl is removed, the solvent can coordinate to the metal [11,12]. Here, we were trying to extend the application of PhIO by utilizing a potential ligand C₂H₅S⁻ in a poor coordinating solvent CH₂Cl₂. However, the strong nucleophilic ability of C₂H₅S⁻ dominated the reaction, resulting in attack at the η³-allyl faster than the CO was removed by PhIO, to result in the complex Cp*Re(η²-C₃H₅SEt)(CO)₂ (5) (Scheme 1). In order to confirm this result, complex 1 was treated with NaSC₂H₅ in CH₂Cl₂ alone, and the reaction gave the same product.

The IR spectrum of 5 showed ν(CO) absorptions at 1964 and 1892 cm⁻¹ in hexane, and the EIMS gave a weak parent peak at m/z 480 (11%). The base peak was observed at m/z 439, which corresponds to the loss of C₃H₅ from M⁺. This is unusual compared with other allyl and substituted propene rhenium complexes we have characterized [5,6,10]. Normally, the η³-allyl or substituted propene is still coordinated to the metal in the base peak fragment. It is not common for C₃H₅ to be lost before a CO ligand. No [M⁺−CO] fragment was observed for 5. A coordination transformation, involv-
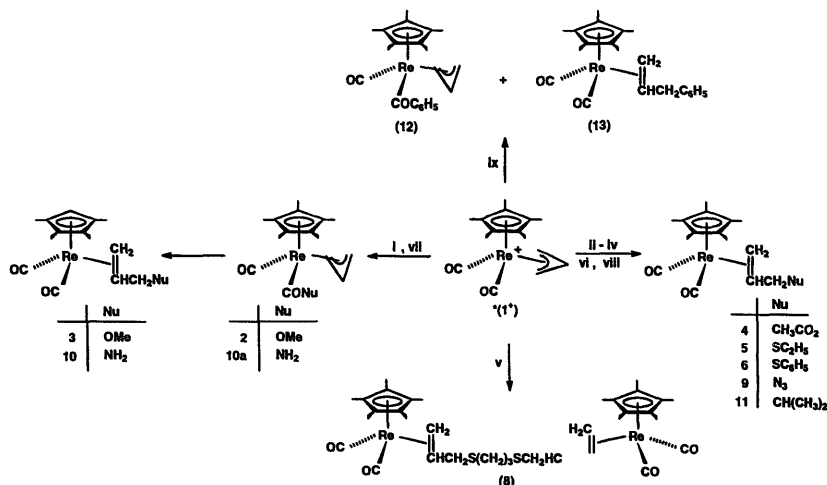
Scheme 1. Reactions of complex 1 (* mixture of *endo* and *exo*): (i) CH₃ONa/CH₃OH; (ii) CH₃COONa/CH₂Cl₂; (iii) NaSC₂H₅/CH₂Cl₂; (iv) NaSC₆H₅/CH₂Cl₂; (v) NaS(CH₂)₃SNa/CH₂Cl₂; (vi) NaN₃/CH₂Cl₂; (vii) NaNH₂/CH₂Cl₂; (viii) Me₂CHMgCl/CH₂Cl₂; (ix) C₆H₅Li/CH₂Cl₂.
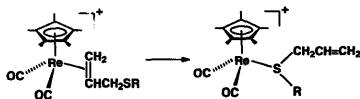
Scheme 2. Proposed transformation of $[Cp^*Re(\eta^2-C_3H_5SR)(CO)_2]^+$ in the mass spectra of **5** (R = C_2H_5) and **6** (R = C_6H_5).

ing a shift of Re from the C=C double bond to the sulfur atom, may explain why loss of C_3H_5 was preferred to loss of CO from M^+ (Scheme 2).

In the ^{1}H NMR spectrum of **5**, the SCH$_2$CH$_3$ gave the expected triplet at δ 1.20 for CH$_3$, and multiplet at δ 2.52 for CH$_2$. Two diastereotopic protons H$_4$ and H$_5$ gave two doublets of doublets at δ 3.71 and 2.52. The assignments were confirmed by ^{1}H NMR decoupling and ^{1}H–^{1}H correlation experiments.

The ^{13}C{^{1}H} NMR spectrum of **5** exhibited signals at 42.33 and 41.09 ppm assigned to the two sulfur-bound carbon atoms, and one at δ 26.41 assigned to the methyl of SCH$_2$CH$_3$.

2.3. Reaction of $[Cp^*Re(\eta^3-C_3H_5)(CO)_2][BF_4]$ (1) with NaSC$_6$H$_5$

Complex **1** was treated with Me$_3$NO in the presence of NaSC$_6$H$_5$ in CH$_2$Cl$_2$ in an attempt to replace CO with C$_6$H$_5$S. However, the major product was Cp*Re(η^2-C$_3$H$_5$SC$_6$H$_5$)(CO)$_2$ (**6**), not Cp*Re(η^3-C$_3$H$_5$)(CO)(SC$_6$H$_5$). A small amount of Cp*Re(η^3-C$_3$H$_5$)(CO)(O$_2$CSC$_6$H$_5$) (**7**) was also produced. The nucleophilic addition of C$_6$H$_5$S$^-$ to the η^3-allyl in **1** to give **6** dominated the reaction, and the same product was obtained when **1** was reacted with NaSC$_6$H$_5$ alone in CH$_2$Cl$_2$. The IR spectrum of **6** in hexane showed two ν(CO) bands at 1964 and 1892 cm^{-1}, which are in similar positions to the ν(CO) bands in compounds **3**–**5**.

The EIMS of **6** gave only a weak parent peak at m/z 528 (5%), and again the fragment [M$^+$–C$_3$H$_5$] at m/z 487 was the base peak. This is similar to the result obtained for **5**, and a similar transformation of **6** is proposed to account for it (Scheme 2). This time, however, the fragment [M$^+$–CO] was observed at m/z 500 (19%).

The ^{1}H NMR spectrum of **6** showed resonances for the SC$_6$H$_5$ protons, and the two diastereotopic protons H$_4$ and H$_5$ again gave two doublets of doublets at δ 4.10 and 2.89. The other substituted propene protons gave much the same coupling pattern and chemical shifts as the complexes already discussed.

Although the ^{1}H NMR spectrum of **6** did not indicate the presence of any other product, such as Cp*Re(η^3-C$_3$H$_5$)(CO)(O$_2$CSC$_6$H$_5$) (**7**), the ^{1}H NMR sample (of **6**

synthesized using Me$_3$NO in the reaction) that was used subsequently for crystallization produced several crystals, which a subsequent X-ray structure determination showed to be Cp*Re(η^3-C$_3$H$_5$)(CO)(O$_2$CSC$_6$H$_5$) (**7**). We presume that **7** resulted as a by-product from the reaction of **1** with Me$_3$NO in the presence of C$_6$H$_5$SNa. A possible explanation for the formation of **7** is that, while not the major reaction, Me$_3$NO did react to some extent with a carbonyl ligand of **1**, and thus released CO$_2$. This CO$_2$ reacted with C$_6$H$_5$S$^-$ to give C$_6$H$_5$SCO$_2^-$, and addition of C$_6$H$_5$SCO$_2^-$ to the intermediate [Cp*Re(η^3-C$_3$H$_5$)(CO)]$^+$ (produced from the reaction of **1** with Me$_3$NO) gave complex **7**. Only a few crystals of **7** were obtained, and were consumed in the X-ray structure determination (see below). No spectroscopic data were obtained for **7**. We are unaware of any previous report in the literature to indicate the preparation and structure of C$_6$H$_5$SCO$_2$H or its anion, but the C$_6$H$_5$SCO$_2$ fragment is found in some organic polymers. The mother liquid, after the crystals were removed, was evaporated to dryness and redissolved in C$_6$D$_6$ to measure the ^{1}H NMR spectrum. Only complex **6** was detectable in solution within experimental limits.

C$_6$H$_5$S$^-$ has previously been used as a nucleophile to attack the η^3-allyl ligand in the Mo complex [(η^5-CH$_3$COC$_6$H$_4$)Mo(η^3-C$_3$H$_5$)(NO)(CO)][PF$_6$] to give the substituted complex (η^5-CH$_3$COC$_6$H$_4$)Mo(η^2-C$_3$H$_5$SC$_6$H$_5$)(NO)(CO) [13]. This is similar to the reaction reported here of **1** with C$_6$H$_5$SNa to give **6**.

2.4. Reaction of $[Cp^*Re(\eta^3-C_3H_5)(CO)_2][BF_4]$ (1) with NaS(CH$_2$)$_3$SNa

The reaction of **1** with the disulfur nucleophile NaS(CH$_2$)$_3$SNa in CH$_2$Cl$_2$ at room temperature gave Cp*Re(CO)$_2$(η^2-C$_3$H$_5$)S(CH$_2$)$_3$S(η^2-C$_3$H$_5$)(CO)$_2$Re-Cp* (**8**) (Scheme 1). In complex **8** the two sulfur atoms have attacked allyl groups in two different molecules of **1** to allow the ligand to bridge. The IR spectrum of **8** in hexane gave only two ν(CO) absorptions at 1962 and 1892 cm^{-1}, which indicates a symmetric structure for **8**. Unfortunately, there is no parent peak for **8** in the EIMS spectrum, but the fragment [Cp*Re(CO)$_2$-(C$_3$H$_5$SCH$_2$CH$_2$CH$_2$S)]$^+$ at m/z 525 was observed, which agrees with [M$^+$–Cp*Re(CO)$_2$(C$_3$H$_5$)]. The fragment at m/z 456, which is produced from the loss of the C$_3$H$_5$ unit from [Cp*Re(CO)$_2$-(C$_3$H$_5$SCH$_2$CH$_2$CH$_2$S)], is consistent with the results obtained for **5** and **6** (Scheme 2).

The ^{1}H NMR spectrum of **8** showed resonances at δ 3.73 and 2.51 for the two diastereotopic protons from the substituted propene, and a multiplet at δ 2.76 for the four protons from the two –CH$_2$– groups in –SCH$_2$CH$_2$CH$_2$S–; the equivalence of these four protons again suggested a symmetric structure for **8**. In

particular, a typical quintet for the central $-CH_2-$ protons (integrating for two protons) unambiguously supports a symmetrical dinuclear structure of complex **8**.

The $^{13}C\{^1H\}$ spectrum of **8** in C_6D_6 showed resonances for Cp^* ring and methyl carbons and the expected five signals for the propene and thioether group carbons were assigned by means of a $^1H-^{13}C$ correlation experiment.

2.5. Reaction of $[Cp^*Re(\eta^3-C_3H_5)(CO)_2][BF_4]$ (1) with NaN_3

Azide is a common nucleophile in addition reactions of cationic transition metal complexes [14]. Reaction of **1** with NaN_3 at room temperature in CH_2Cl_2 resulted in $Cp^*Re(\eta^2-C_3H_5N_3)(CO)_2$ (**9**) (Scheme 1). The IR spectrum of **9** in hexane showed $\nu(CO)$ absorptions at 1969 and 1898 cm^{-1}, and a $\nu(NN)$ absorption at 2101 cm^{-1}. This is an indication that the N_3^- was added to the allyl group in complex **1** [15]. Neither the EIMS nor the CIMS of **9** gave a parent peak for **9**. Instead, a fragment at m/z 433, corresponding to $[M^+-N_2]$, was the highest mass fragment in the mass spectrum of **9**. The base peak occurred at m/z 346, which corresponded to $[M^+-CO-C_3H_5N_3-4H]$.

Complex **9** was treated with $LiBEt_3H$ in ether at $-78°C$ in an attempt to reduce the $\eta^2-C_3H_5N_3$ ligand to $\eta^2-C_3H_5NH_2$ and give $Cp^*Re(\eta^2-C_3H_5NH_2)(CO)_2$ (**10**). However, the disappearance of the $\nu(CO)$ absorption in the IR spectrum, and loss of the Cp^* signal in the ^1H NMR spectrum, indicated that **9** decomposed in the presence of $LiBEt_3H$.

2.6. Reaction of $[Cp^*Re(\eta^3-C_3H_5)(CO)_2][BF_4]$ (1) with $NaNH_2$

Complex **1** reacted with $NaNH_2$ at room temperature to give two products: $Cp^*Re(\eta^3-C_3H_5)(CO)(CONH_2)$ (**10a**) and $(Cp^*Re(\eta^2-C_3H_5NH_2)(CO)_2$ (**10**) (Scheme 2). The IR spectrum of the solution showed three $\nu(CO)$ absorptions at 1950, 1927 and 1873 cm^{-1}. However, when the product was isolated after work-up at room temperature, only complex **10** was observed in both the IR and ^1H NMR spectra, indicating that any **10a** present converted to complex **10**. This is reminiscent of the conversion of the methoxycarbonyl complex **2** to the methoxypropene complex **3** reported previously [6].

The parent ion of **10** was not observed in the EIMS spectrum. Instead, the fragment at m/z 419 corresponding to loss of NH_2 from the M^+ is the base peak. The fragment at m/z 378, consistent with loss of $C_3H_5NH_2$ from M^+, is also very strong. The CIMS gave M^+ at m/z 435, and the base peak in this case is m/z 391, which is in agreement with loss of NH_2 and CO from the parent ion.

The ^1H NMR spectrum of **10** showed two NH_2 proton triplets at δ 3.45 and 3.27 respectively for inequivalent NH protons. The five protons from the substituted propene were assigned by $^1H-^1H$ correlation experiments.

In the $^{13}C\{^1H\}$ NMR spectrum of **10** the resonances for the substituted propene carbons were assigned as δ 78.91 for $-CH_2NH_2$, δ 40.59 for $=CH-$, and δ 27.76 for $=CH_2$. Both the ^1H and ^{13}C NMR resonances of **10** indicated that the coordination of $CH_2=CHCH_2NH_2$ to the rhenium center is through the $C=C$ bond rather than the nitrogen atom.

2.7. Reaction of $[Cp^*Re(\eta^3-C_3H_5)(CO)_2][BF_4]$ (1) with $(CH_3)_2CHMgCl$

When **1** was treated with $Me_2CHMgCl$ in CH_2Cl_2 at $-78°C$ for 2 h, complex $Cp^*Re(\eta^2-C_3H_5CHMe_2)(CO)_2$ (**11**) was produced (Scheme 2). The IR spectrum of **11** showed two $\nu(CO)$ bands at 1960 and 1888 cm^{-1}. The EIMS of **11** showed a strong parent peak at m/z 462. A fragment $[M^+-C_3H_5CHMe_2]$ at m/z 378 is the second highest peak in the mass spectrum. The base peak at m/z 348 is consistent with the fragment $[M^+-C_3H_5CHMe_2-CO-2H]$.

The ^1H NMR spectrum of **11** showed complicated coupling patterns for the two diastereotopic H_4 and H_5 protons. The resonance at δ 2.50 is assigned to H_4 and, interestingly, the eight lines generated from the doublet of doublets of doublets for this proton, with coupling constants $J_{45} = 13.6$, $J_{34} = 6.13$ and $J_{4-CH} = 3.37$ Hz, did not overlap. The other proton H_5 also gave the same coupling pattern with eight lines, but appeared at higher field (δ 1.27). The two isopropyl methyls are diastereotopic and gave two doublets at δ 1.08 and 1.04 respectively. The proton from $CHMe_2$ showed a multiplet at δ 1.77. Introduction of the $CHMe_2$ group to the η^3-allyl caused all the proton chemical shifts to move to higher field, an indication of the strong electron donating ability of the $CHMe_2$ group. As a result, the Cp^* signal of **11** appeared at δ 1.43, which is the highest field of all resonances for this series of complexes. These assignments were confirmed by $^1H-^1H$ NMR correlation experiments.

In the $^{13}C\{^1H\}$ NMR spectrum of **11** the two methyl carbons $CH(CH_3)_2$ showed very close resonances at δ 22.67 and 22.52, the CH carbon resonance appeared at δ 28.27, and the resonances at δ 49.04, 42.68 and 33.43 were assigned to the $-CH_2-$, $=CH-$ and $=CH_2$ carbons respectively. The ^{13}C NMR was not as sensitive as the ^1H NMR spectrum to the electron density changes in the complexes, as there was no obvious chemical shift difference of these signals compared with those of the other complexes already mentioned.

2.8. Reaction of [Cp*Re(η^3-C$_3$H$_5$)(CO)$_2$][BF$_4$] (1) with C$_6$H$_5$Li

Complex 1 was reacted with C$_6$H$_5$Li in CH$_2$Cl$_2$ at −78 °C for 4 h, and the CO and allyl were separately attacked to produce Cp*Re(η^3-C$_3$H$_5$)(CO)(COC$_6$H$_5$) (12) and Cp*Re(η^2-CH$_2$=CHCH$_2$C$_6$H$_5$)(CO)$_2$ (13). The ratio 12/13 was 1:1.33 from the integration of the ^{1}H NMR resonances. The IR spectrum of the mixture of 12 and 13 in hexane showed three ν(CO) bands in the region of 1600–2200 cm^{-1}, which were assigned as 1962 and 1890 cm^{-1} for 13 and 1919 cm^{-1} for 12.

A mixture of 12 and 13 in C$_6$D$_6$ (^{1}H NMR sample) was refluxed for 12 h in order to observe any conversion of 12 to 13. The IR spectrum was then measured at room temperature, and neither the position nor the intensity of the ν(CO) bands had changed.

The EIMS was obtained for the mixture of 12 and 13. The parent peak at m/z 496 is very strong in intensity (65%) in comparison with the base peak. The base peak at m/z 440 is consistent with loss of two CO from M$^+$. The fragment at m/z 378 is in agreement with the loss of C$_3$H$_5$C$_6$H$_5$ from the parent ion, and the other fragment at m/z 348 was generated from [M$^+$–C$_3$H$_5$C$_6$H$_5$–CO–2H]. These fragmentations are most reasonably produced from 13. The fragment at m/z 391 consistent with [M$^+$–COC$_6$H$_5$] is expected to arise from only 12, and it is very weak.

The ^{1}H NMR spectrum of the mixture of 12 and 13 showed all the resonances expected for both products. For the η^3-allyl group in 12, which has inequivalent protons, the proton resonances were assigned as a multiplet at δ 4.26 for H$_c$, a doublet of doublets at δ 2.83 and 2.74 for the two H$_s$, and two doublets at δ 0.83 and 0.66 for the two H$_a$. The Cp* signal gave a singlet at δ 1.66, while the proton signals for the phenyl group in ReC(O)C$_6$H$_5$ were overlapped with the signals from the phenyl protons in C$_3$H$_5$C$_6$H$_5$. The substituted propene resonances for 13 showed two diastereotopic proton signals at δ 3.85 and 2.57, which are doublets of doublets. H$_3$ gave a multiplet at δ 2.12, and H$_1$ and H$_2$ showed two doublets at δ 2.29 and 1.34. These assignments were confirmed by a ^{1}H–^{13}C correlation experiment.

The ^{13}C(^{1}H) spectrum showed resonances for the carbon signals of 13 at δ 46.5 for CH$_2$, δ 43.2 for =CH–, and δ 26.7 for =CH$_2$. The carbon signals for 12 were assigned as δ 81.1 for the central carbon, and δ 48.9 and 31.6 for the two terminal carbons of the η^3-allyl [16]. The methyl carbon signals of the Cp* group for both complexes were coincident at δ 9.80.

Although Cp*Re(η^3-C$_3$H$_5$)(CO)(COOCH$_3$) (2) and Cp*Re(η^3-C$_3$H$_5$)(CO)(CONH$_2$) (10a) were obtained when nucleophilic addition occurred at the CO ligand in 1, each converted to the dicarbonyl isomer. However, Cp*Re(η^3-C$_3$H$_5$)(CO)(COC$_6$H$_5$) (12) is stable at room

temperature, and it did not convert to Cp*Re(η^2-C$_3$H$_5$C$_6$H$_5$)(CO)$_2$ (13) even after refluxing in C$_6$D$_6$ for 12 h.

2.9. Stereochemical consideration of the substituted propene complexes Cp*Re(η^2-C$_3$H$_5$Nu)(CO)$_2$ (Nu = nucleophile)

The stereochemical selectivity of nucleophilic additions to the η^3-allyl ligand has been extensively studied. For [CpMo(η^3-C$_3$H$_5$)(NO)(CO)][BF$_4$], nucleophilic addition occurred trans to the NO ligand in an endo isomer, but cis to the NO in an exo isomer, and finally led to the same product [17,18].

Because of the plane of symmetry in 1, the nucleophilic additions at the two η^3-allyl carbon termini in any one isomer of 1 (i.e. exo or endo) are evenly preferred. Although four ways of attack of the nucleophile can be visualized as in Scheme 3, assuming the rotamers a and b can interconvert, and similarly c and d, the result is simply the formation of enantiomers of the product. They are not distinguishable in the ^{1}H NMR spectrum, and hence one isomer of each substituted propene complex was observed.
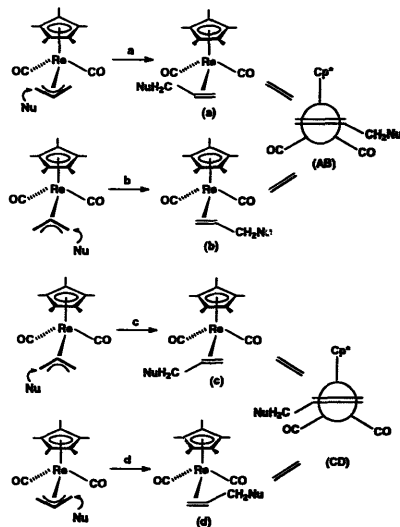
Scheme 3. Isomers produced from nucleophilic addition of Nu$^-$ to the η^3-allyl in 1.

2.10. Synthesis and reactions of [Cp*Re(η³-C₃H₄CH₃)(CO)₂][BF₄] (14)

*2.10. Synthesis and reactions of [Cp*Re(η³-C₃H₄CH₃)(CO)₂][BF₄] (14)*

Complex **14** was synthesized by the same procedure used for the preparation of complex **1** [10], but with allyl alcohol replaced by crotyl alcohol. Theoretically, complex **14** may occur as four isomers: *endo–syn* or *endo–anti* and *exo–syn* or *exo–anti* (Scheme 4). The ^{1}H NMR spectrum of complex **14** showed the presence of only two isomers. The major one is assigned as the *endo–syn* isomer, and the minor one as the *exo–syn* isomer according to the following ^{1}H NMR nuclear Overhauser enhancement (NOE) results. The isomeric mixture was not separated, and was used in subsequent reactions.

Saturation of the central proton signal at δ 4.62 induced a strong enhancement of the methyl group at δ 2.00, indicating the close proximity of these two groups; this can occur only when the methyl group is in a *syn* but not an *anti* position in the allyl ligand. No enhancement for the Cp* signal was observed, as would be expected to occur for the *exo* isomer. Saturation of the multiplet *anti* proton (the *anti* proton from the carbon terminus bearing the methyl group) at δ 2.69 caused a strong enhancement of the Cp* resonance at δ 2.18, indicating close proximity of the Cp* with the *anti* proton, and this corresponds to the case when the allyl adopts the *endo* structure.

The exchange of the *endo–exo* isomers in complex **1** has been reported in previous work [19]. Those studies indicated that **1** exists as a mixture of both the *endo* and the *exo* isomers in a ratio *endo/exo* of 6.4:1 (at room temperature in CD_2Cl_2). The interconversion of the *endo–exo* isomers occurs without scrambling of the *syn* and *anti* protons, consistent with a rotation mechanism but not an η^3-η^1-η^3 mechanism.

For complex **14**, saturation of the central proton signal at δ 4.62 for the *endo–syn* isomer caused saturation of a resonance at δ 4.20, which was assigned to the
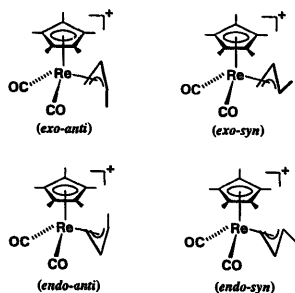
Scheme 4. Possible isomers of complex **14**.
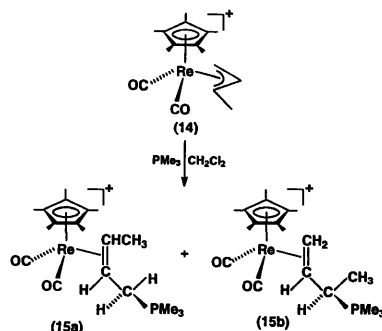
Scheme 5. Reaction of [Cp*Re(η³-C₃H₄CH₃)(CO)₂][BF₄] (**14**) with PMe₃.

central proton of the *exo–syn* isomer. This indicated fast *exo–endo* exchange, and magnetization transfer from H_c of the *endo–syn* to the H_c of the *exo–syn* isomers. Saturation of the *syn* proton resonance at δ 3.69 of the *endo–syn* isomer induced a saturation of H_s at δ 2.80, which is the *syn* proton resonance of the *exo–syn* isomer, but not the *anti* proton at δ 0.88, indicating no scrambling of the *syn* and *anti* protons. Saturation at δ 2.69 of the H_a resonance in the *endo–syn* isomer (from the same carbon terminus with the methyl group) caused a saturation of the H_a resonance at δ 3.35 for the *exo–syn* proton, and again indicated the magnetization transfer between these two protons because of the exchange of the *endo–exo* isomers.

The results from the ^{1}H NMR NOE experiments showed that the two isomers of complex **14** are the *endo–syn* and the *exo–syn*. The magnetization transfer of H_c–H_c, H_s–H_s and H_a–H_a between the two isomers indicated the exchange of the *endo–syn* with the *exo–syn* isomer. Since no scrambling of the *syn* to *anti* protons was observed, the exchange must occur via a rotation mechanism instead of the η^3-η^1-η^3 mechanism, in which the *syn* and *anti* protons of the allyl ligand would be exchanged. This is in agreement with the result obtained for complex **1** [19].

Complex **14** reacted with PMe₃ in CH_2Cl_2 to form two products, **15a** and **15b**, which resulted from the PMe₃ attacking different carbon termini of the methallyl ligand (Scheme 5).

The IR spectrum of the mixture of **15a** (67%) and **15b** (33%) in CH_2Cl_2 showed only two ν(CO) absorptions at 1964 and 1881 cm^{-1}, indicating that the absorptions of **15a** and **15b** were unresolved. The FABMS of this mixture showed a parent ion at m/z 509, and a base peak at m/z 433 due to [M⁺–PMe₃].

The ^{1}H NMR spectrum indicated that **15a** is the

major isomer, and **15b** is the minor one. The typical diastereotopic $-CH_2PMe_3$ proton resonances occurred at δ 3.04 and 2.15. The resonances for the minor isomer **15b** in the ^1H NMR spectrum overlapped with the major isomer, but two Cp^* signals for the two different isomers are apparent, being singlets at δ 1.99 for **15a** and δ 2.02 for **15b**. PMe$_3$ gave a doublet at δ 1.80 with a separation of 12.0 Hz. The $^{31}P\{^1H\}$ NMR spectrum showed two signals: δ 34.30 for **15a** and δ 29.27 for **15b**. The ^1H NMR resonances of **15a** and **15b** were not well separated in CDCl$_3$ or CD$_2$Cl$_2$. Thus, further distinction between the *cis* and *trans* isomers of CH(Me)=CHCH$_2$PMe$_3$ in **15a** was unsuccessful.

Nucleophilic addition to the methallyl ligand has been reported by Casey's group for [CpRe(CO)$_2$(η^3-C$_3$H$_4$CH$_3$)][BF$_4$] [20]. In their case, when LiCu(CH$_3$)$_2$ was used as the nucleophile, addition occurred only at the less substituted allyl carbon to give both the *cis* and *trans* isomers, with a ratio *cis/trans* of 65:35. The same regioselectivity of malonate to the less substituted allyl carbon of the methallyl was obtained, although addition to the substituted carbon also occurred. This is similar to the result obtained for **14** when PMe$_3$ was used as a nucleophile.

Upon treatment of complex **14** with PhIO in acetonitrile, one CO was substituted to give the mono acetonitrile complex [Cp*Re(η^3-C$_3$H$_4$Me)(CO)(NCMe)]-[BF$_4$] (**16**). When PhIO was replaced by Me$_3$NO, both CO groups were substituted by MeCN to give the bis-acetonitrile complex [Cp*Re(η^3-C$_3$H$_4$Me)-(NCMe)$_2$][BF$_4$] (**17**). This parallels results obtained previously for **1** [10].

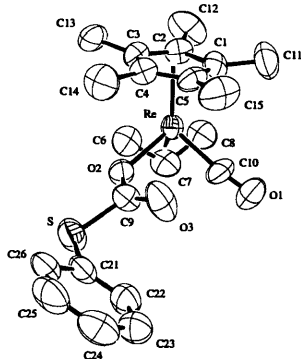The ^1H NMR spectrum of complex **16** showed resonances for only the *endo–syn* isomer. The resonance

Fig. 2. Structure of Cp*Re(η^3-C$_3$H$_5$)(CO)(OCOSC$_6$H$_5$) (**7**); 50% probability thermal ellipsoids are shown for all non-hydrogen atoms.

for Cp* occurred at δ 1.89, which is shifted to high field compared with **14**. The resonance for the coordinated acetonitrile occurred at δ 2.78, which is in a similar position to that of [Cp*Re(η^3-C$_3$H$_5$)(CO)-

Table 2
Fractional atomic coordinates and equivalent isotropic temperature factors (Å^2) for the non-hydrogen atoms of Cp*Re(η^3-C$_3$H$_5$)(CO)(O$_2$CSPh) (**7**)

Atom	x	y	z	U_{eq} [a]
Re	0.34057(4)	0.18932(6)	0.08491(3)	0.0469
S	0.2083(4)	−0.0439(5)	−0.12896(22)	0.073
O(1)	0.4482(10)	−0.1362(15)	0.1202(7)	0.091
O(2)	0.2816(7)	0.1093(10)	−0.0193(5)	0.056
O(3)	0.2426(11)	−0.1450(13)	0.0004(6)	0.079
C(1)	0.2903(10)	0.2003(18)	0.1858(8)	0.055
C(2)	0.2878(10)	0.3628(15)	0.1601(8)	0.051
C(3)	0.2125(10)	0.3761(16)	0.1006(8)	0.050
C(4)	0.1626(10)	0.2256(16)	0.0891(8)	0.053
C(5)	0.2077(11)	0.1146(15)	0.1387(8)	0.053
C(6)	0.4090(12)	0.3689(19)	0.0213(10)	0.070
C(7)	0.4887(11)	0.2664(21)	0.0522(9)	0.070
C(8)	0.5027(11)	0.2719(22)	0.1258(9)	0.072
C(9)	0.2480(11)	−0.0315(16)	−0.0358(8)	0.054
C(10)	0.4124(12)	−0.0163(21)	0.1031(9)	0.070
C(11)	0.3499(14)	0.1409(25)	0.2549(9)	0.088
C(12)	0.3488(16)	0.5020(21)	0.2005(10)	0.086
C(13)	0.1790(14)	0.5313(18)	0.0642(9)	0.076
C(14)	0.0733(11)	0.1882(22)	0.0275(9)	0.082
C(15)	0.1711(13)	−0.0545(18)	0.1500(10)	0.081
C(21)	0.1543(12)	−0.2447(19)	−0.1417(8)	0.058
C(22)	0.2130(13)	−0.3779(19)	−0.1180(8)	0.069
C(23)	0.1655(14)	−0.5291(20)	−0.1274(9)	0.075
C(24)	0.0674(14)	−0.5453(24)	−0.1636(9)	0.080
C(25)	0.0100(14)	−0.409(3)	−0.1891(9)	0.079
C(26)	0.0533(13)	−0.2613(22)	−0.1773(8)	0.067

[a] U_{eq} is the cube root of the product of the principal axes of the thermal ellipsoid.

Table 3
Selected intramolecular distances (Å) and angles (°) for $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(O_2CSPh)$ (7)

Re–C(1)	2.182(15)	Re–C(6)	2.215(17)
Re–C(2)	2.242(15)	Re–C(7)	2.201(16)
Re–C(3)	2.311(14)	Re–C(8)	2.193(14)
Re–C(4)	2.312(13)	Re–Allyl [a]	1.96
Re–C(5)	2.241(15)	Re–O(2)	2.142(9)
Re–Cp [b]	1.91	Re–C(10)	1.934(17)
S–C(9)	1.800(15)	S–C(21)	1.797(16)
O(1)–C(10)	1.118(21)	C(6)–C(7)	1.377(22)
O(2)–C(9)	1.262(16)	C(7)–C(8)	1.417(22)
O(3)–C(9)	1.185(18)		
O(2)–Re–C(10)	88.7(6)	O(2)–Re–Cp	114.1
O(2)–Re–Allyl	97.7	C(10)–Re–Cp	121.5
C(10)–Re–Allyl	94.2	Cp–Re–Allyl	130.9
C(9)–S–C(21)	102.9(7)	Re–O(2)–C(9)	125.0(9)
C(6)–C(7)–C(8)	111.8(16)	S–C(9)–O(2)	109.4(10)
S–C(9)–O(3)	121.5(11)	O(2)–C(9)–O(3)	129.1(14)
Re–C(10)–O(1)	171.8(17)	S–C(21)–C(22)	121.6(12)
S–C(21)–C(26)	118.0(14)	C(22)–C(21)–C(26)	120.4(16)

[a] Allyl denotes the center of mass of the allyl carbon atoms.

[b] Cp denotes the center of mass of the carbon atoms of the C_5 ring.

$(NCMe)][BF_4]$ [10]. Complex 17 showed resonances for only the *endo–syn* isomer; these are assigned as: multiplet at δ 3.86 to H_c, singlet at δ 2.86 to CH_3CN, doublet at δ 2.35 to H_s, two H_a occurring at δ 2.00 and 1.33. The Cp^* resonance was a singlet at δ 1.67, which is shifted further to high field compared with complexes 14 and 16; this can be attributed to the s-donor ability of the acetonitrile ligand.

2.11. X-ray structure of $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(O_2\text{-} CSC_6H_5)$ (7)

The structure of complex 7 was undertaken to establish the identity of this unanticipated minor product, and is illustrated in Fig. 2. The crystallographic data, selected bond lengths and interbond angles are listed in Tables 1–3. The η^3-allyl adopts the *endo* structure in complex 7. There are no unusual dimensional parameters, and no chemically significant intermolecular contacts.

3. Conclusions

The nucleophilic addition of oxygen, sulfur, nitrogen and carbon nucleophiles to complex 1 has been investigated. In all cases, addition of the nucleophile to the allyl ligand in 1 was observed to result, giving the substituted propene complexes with general formula $Cp^*Re(CO)_2(\eta^2\text{-}C_3H_5R)$ (R = CH_3CO_2, C_2H_5S, C_6H_5S, $S(CH_2)_3S$, NH_2, N_3, $CHMe_2$ and C_6H_5). No product of attack at the central carbon was observed for any of the nucleophiles employed in this work. These

reactions provide an effective way to make new CX bonds (X = O, S, P, N and C) by utilizing the coordinated η^3-allyl ligand in the cationic rhenium complex 1. In the cases where the nucleophile was NH_2^- or $C_6H_5^-$, nucleophilic addition occurred either at the η^3-allyl or at a CO ligand. At low temperature ($-78\text{–}0\,^\circ C$) the CO was attacked and complexes with general formula $Cp^*Re(CO)(\eta^3\text{-}C_3H_5)(COR)$ (R = NH_2 and C_6H_5) were produced. When R is C_6H_5, the product was stable and was observed along with the substituted propene complex in solution, but when NH_2^- was used, the carbamoyl complex converted completely to the substituted propene complex at room temperature.

4. Experimental details

4.1. 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. Cp^*H, $Cp^*Re(CO)_3$ and PhIO were synthesized according to literature methods [21–23]. All other reagents were obtained from Aldrich. Melting points were determined with a Fisher–Johns melting point apparatus. Irradiation was carried out using a water-jacketed 200 W Hanovia Model 654A-0360 high pressure mercury vapor lamp. FTIR spectra were recorded on a Bomem Michelson-120 instrument in hexane, ether or CH_2Cl_2 solutions. ^1H NMR and NOE spectra were recorded by Mrs. M.M. Tracey at the SFU NMR Service using a Bruker WM-400 instrument operating at 400.13 MHz. For the numbering scheme for substituted propene protons see Fig. 1. The ^{13}C NMR spectra were recorded using the same machine as for the ^1H NMR but operating at 100.6 MHz. FABMS spectra were obtained by Mr. G. Owen on a Hewlett–Packard Model 5985 GC-MS instrument equipped with a Phrasor Inc. fast atom bombardment accessory. The source gas was xenon, and samples were dispersed in *m*-nitrobenzyl alcohol. Masses are given for the ^{187}Re isotope. Correct isotopic distribution patterns were observed for all parent peaks. Microanalyses were performed by Mr. M.K. Yang of the SFU Microanalytical Laboratory.

4.2. Preparation of NaSEt, $NaSC_6H_5$ and NaS-$(CH_2)_3SNa$

4.2.1. NaSEt

Sodium (0.3 mg, 0.01 mmol) was placed in a Schlenk tube, and C_2H_5SH (0.5 ml, 6.75 mmol) was added dropwise at $-78\,^\circ C$ until all the sodium disappeared. A white powder formed. Excess C_2H_5SH was removed, and the solid $NaSC_2H_5$ remaining was washed with ether (5×1 ml) and used for the preparation of 5.

4.2.2. NaSC$_6$H$_5$

Sodium (0.4 mg, 0.017 mmol) was placed in a Schlenk tube, and C$_6$H$_5$SH (0.5 ml, 4.86 mmol) was added dropwise. The mixture was heated to 80 °C and stirred for 5 h. The sodium disappeared, and a white powder formed. Excess C$_6$H$_5$SH was removed, and the solid was washed with benzene (5 × 1 ml) and used for the preparation of 6.

4.2.3. NaS(CH$_2$)$_3$SNa

Sodium (0.5 mg, 0.022 mmol) was placed in a Schlenk tube, and HS(CH$_2$)$_3$SH (0.5 ml, 3.19 mmol) was added dropwise and the mixture stirred at 100 °C for 3 h. The sodium was consumed and a white powder formed. Excess HS(CH$_2$)$_3$SH was removed by syringe, and the residue was washed with ether and used for the preparation of 8.

4.3. Preparation of Cp*Re(η^2-CH$_2$CHCH$_2$O-OCCH$_3$)(CO)$_2$ (4)

Complex 1 (30 mg, 0.059 mmol) and CH$_3$COONa (20 mg, 0.24 mmol) were placed in a Schlenk tube. CH$_2$Cl$_2$ (2 ml) was added to dissolve 1. This mixture was stirred at room temperature for 5 h, and the IR spectrum then showed the disappearance of the ν(CO) bands for 1, and new ν(CO) bands at 1956 and 1877 cm^{-1} were observed. The solution was filtered through Celite, the solvent was pumped off and the residue extracted with hexane (1 ml). The hexane solution crystallized at −78 °C overnight. Solvent was removed, and the white crystals were dried under vacuum to give pure 4 (25.8 mg, 0.054 mmol, 92%), m.p. 124–125 °C. IR (hex, cm^{-1}): ν_{CO} 1968, 1896, and 1739. EIMS (m/z): 478 (M$^+$), 422 (M$^+$-2CO), 378 (M$^+$-C$_3$H$_5$OOCCH$_3$), 360 (M$^+$-2CO-CH$_3$COOH-2H), 348 (M$^+$-C$_3$H$_5$OOCCH$_3$-CO-2H, base). ^{1}H NMR (C$_6$D$_6$, δ): 5.18 (1H, dd, J_{45} = 11.5, J_{34} = 3.5 Hz, H$_4$), 3.71 (1H, dd, J_{45} = 11.5, J_{35} = 9.5 Hz, H$_5$), 2.24 (1H, overlapped with H$_3$, H$_1$), 2.21 (1H, m, H$_3$), 1.85 (3H, s, OOCCH$_3$), 1.56 (15H, s, Cp*), 1.32 (1H, d, J_{23} = 6.5 Hz, H$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 206.00 (s, Re-CO), 170.00 (s, C$_3$H$_5$COOMe), 97.61 (s, C$_5$Me$_5$), 73.40 (s, -CH$_2$-), 37.33 (s, CH), 26.62 (s, CH$_2$), 20.93 (COCH$_3$), 9.73 (s, C$_5${CH$_3$}$_5$). Anal. Found: C, 42.53; H, 4.93. C$_{17}$H$_{23}$O$_4$Re Calc.: C, 42.75; H, 4.86%.

4.4. Preparation of Cp*Re(η^2-CH$_2$CHCH$_2$SCH$_2$CH$_3$)-(CO)$_2$ (5)

Complex 1 (50 mg, 0.1 mmol) and NaSCH$_2$CH$_3$ (16.8 mg, 0.2 mmol) were dissolved in acetone (4 ml) in a Schlenk tube, then stirred at room temperature for 0.5 h. By this time, the IR spectrum showed the disappearance of the ν(CO) bands for 1, and two new CO bands at 1950 and 1875 cm^{-1} appeared. The solvent was pumped off, and the residue extracted with hexane

(5 × 1 ml). The hexane solution was concentrated to 1 ml, then kept at −78 °C overnight, whereupon white crystals formed. The solvent was removed, and the solid dried under vacuum for 12 h to give the analytically pure sample (44.1 mg, 0.092 mmol, 92%), m.p. 67–68 °C. IR (hex, cm^{-1}): ν_{CO} 1964, 1892. EIMS (m/z): 480 (M$^+$), 439 (M$^+$-C$_3$H$_5$, base), 409 (M$^+$-C$_3$H$_7$-CO), 381 (M$^+$-2CO-C$_3$H$_7$), 353 (M$^+$-C$_3$H$_5$-C$_2$H$_6$-2CO). ^{1}H NMR (C$_6$D$_6$, δ): 3.71 (1H, dd, J_{45} = 12.4, J_{34} = 2.1 Hz, H$_4$), 2.53 (2H, m, SCH$_2$), 2.52 (1H, overlapped with -SCH$_2$-, H$_5$), 2.18 (1H, m, H$_3$), 2.16 (1H, m, H$_1$), 1.58 (15H, s, Cp*), 1.37 (1H, m, H$_2$), 1.20 (3H, t, J = 7.4 Hz, -CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 226.00, 207.00 (s, Re-CO), 97.29 (s, C$_5$Me$_5$), 42.33 (s, SCH$_2$), 41.09 (s, SCH$_2$), 27.04 (s, CH), 26.41 (s, CH$_3$), 15.02 (s, =CH$_2$), 9.80 (s, C$_5${CH$_3$}$_5$). Anal. Found: C, 42.80; H, 5.32. C$_{17}$H$_{25}$O$_2$SRe Calc.: C, 42.57; H, 5.25%.

4.5. Preparation of Cp*Re(η^2-CH$_2$CHCH$_2$SC$_6$H$_5$)-(CO)$_2$ (6)

Complex 1 (50 mg, 0.1 mmol) and NaSC$_6$H$_5$ (40 mg, 0.3 mmol) were dissolved in acetone (4 ml) in a Schlenk tube, then stirred at room temperature for 2 h. By this time, the IR spectrum showed the disappearance of the ν(CO) bands for 1, and two new CO bands at 1952 and 1877 cm^{-1} appeared. The solvent was pumped off, and the residue extracted with hexane (4 × 0.5 ml). The hexane solution was concentrated to 1 ml, then kept at −78 °C overnight to give greenish crystals, but the crystals changed to a sticky oil state when they were warmed to room temperature. The solvent was removed, and the green oil product was dried under vacuum overnight to give the sample used for spectroscopy and analysis (38.25 mg, 0.073 mmol, 72.5%). IR (hex, cm^{-1}): ν_{CO} 1964, 1892. EIMS (m/z): 500 (M$^+$-CO), 487 (M$^+$-C$_3$H$_5$, base), 470 (M$^+$-2CO-2H), 431 (M$^+$-2CO-C$_3$H$_5$), 419 (M$^+$-SC$_6$H$_5$), 389 (M$^+$-C$_6$H$_5$S-CO-2H). ^{1}H NMR (C$_6$D$_6$, δ): 7.48, 7.08 (4H, dd, C$_6$H$_5$), 6.90 (1H, m, C$_6$H$_5$), 4.10 (1H, dd, J_{45} = 12.3, J_{34} = 3.2 Hz, H$_4$), 2.89 (1H, dd, J_{45} = 12.3, J_{35} = 10.0 Hz, H$_5$), 2.20 (1H, m, H$_3$), 2.18 (1H, m, H$_1$), 1.54 (15H, s, Cp*), 1.26 (1H, dd, J_{23} = 7.2, J_{21} = 1.5 Hz, H$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 244.11, 238.00 (s, Re-CO), 130.84-125.99 (s, C$_6$H$_5$), 97.39 (s, C$_5$Me$_5$), 44.93 (s, -CH$_2$-), 39.49 (s, CH-), 26.80 (s, CH$_2$), 9.73 (s, C$_5${CH$_3$}$_5$). Anal. Found: C, 65.03; H, 5.22. C$_{21}$H$_{25}$O$_2$SRe Calc.: C, 47.80; H, 4.78%. The poor analytical result is attributed to difficulty in removing solvent from the sticky oily sample.

4.6. Preparation of {Cp*Re(CO)$_2$(η^2-CH$_2$CHCH$_2$-SCH$_2$)}$_2$CH$_2$ (8)

Complex 1 (23 mg, 0.05 mmol) and NaS(CH$_2$)$_3$SNa (20 mg, 0.13 mmol) were dissolved in CH$_2$Cl$_2$ (3 ml) in

a Schlenk tube, then stirred at room temperature for 5 h. By this time, the IR spectrum showed the disappearance of the ν(CO) bands for **1**, and two new CO bands appeared at 1950 and 1873 cm^{-1}. The solvent was pumped off, and the residue extracted with hexane (3 × 0.5 ml). The hexane solution was concentrated to 1 ml, then recrystallized at $-78\,^{\circ}$C overnight, whereupon some pink solid formed. The solvent was removed, and the solid changed into a sticky oil when it was warmed to room temperature. This product was dried overnight and used for spectroscopy and analysis (18.52 mg, 0.02 mmol, 86.24%). IR (hex, cm^{-1}): ν_{CO} 1962, 1892. EIMS (m/z): 525 (M$^+$– Cp*Re(C$_3$H$_5$)(CO)$_2$), 497 (M$^+$–Cp*Re(C$_3$H$_5$)(CO)$_2$– CO), 485 (M$^+$–Cp*Re(C$_3$H$_5$)(CO)$_2$–C$_3$H$_4$), 456 (M$^+$–Cp*Re(C$_3$H$_5$)(CO)$_2$–CO–C$_3$H$_5$), 419 (M$^+$– Cp*Re(C$_3$H$_5$)(CO)$_2$–SC$_3$H$_6$S, base), 389 (M$^+$– Cp*Re(C$_3$H$_5$)(CO)$_2$–SC$_3$H$_6$S–CO–2H), 359 (M$^+$– SC$_3$H$_6$S–2CO–Cp*Re(C$_3$H$_5$)(CO)$_2$–4H). ^{1}H NMR (C$_6$D$_6$, δ): 3.73 (1H, dd, J_{45} = 13.0, J_{34} = 3.0 Hz, H$_4$), 2.76 (4H, dt, J = 3.6, J = 1.3 Hz, –SCH$_2$– and –CH$_2$S–), 2.51 (1H, dd, J_{45} = 13.0, J_{35} = 10.0 Hz, H$_5$), 2.25 (1H, dd, overlapped with H$_3$, H$_1$), 2.22 (1H, m, H$_3$), 1.97 (2H, dq, J = 7.0, J = 1.1 Hz, CH$_2$), 1.60 (15H, s, Cp*), 1.42 (1H, d, J_{23} = 6.2 Hz, H$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 207.10 (s, Re–CO), 97.35 (s, C$_5$Me$_5$), 42.81 (s, CH$_2$S), 41.24 (s, =CH–), 31.64 (s, SCH$_2$), 30.42 (s, –CH$_2$–), 27.18 (s, CH$_2$), 9.84 (s, C$_5$(CH$_3$)$_5$). Anal. Found: C, 48.03; H, 5.62. C$_{33}$H$_{46}$O$_4$S$_2$Re$_2$ Calc.: C, 42.02; H, 4.92%. The poor agreement is attributed to contamination with solvent.

4.7. Preparation of Cp*Re(CO)$_2$(η^2-CH$_2$CHCH$_2$N$_3$) (9)

Complex **1** (25 mg, 0.05 mmol) and NaN$_3$ (20 mg, 0.31 mmol) were dissolved in CH$_2$Cl$_2$ (3 ml) in a Schlenk tube, then stirred at room temperature overnight. By this time, the IR spectrum showed the disappearance of ν(CO) for **1**, two new CO bands at 1956 and 1876 cm^{-1}, and a ν(NN) band at 2124 cm^{-1}. The solvent was pumped off, and the residue extracted with hexane (3 × 1 ml). By using the same method used for the purification of complex **6**, complex **9** was obtained as a white solid (20.28 mg, 0.044 mmol, 89%). IR (hex, cm^{-1}): ν_{CO} 1969, 1898, ν_{NN} 2101. EIMS (m/z): 433 (M$^+$–N$_2$), 419 (M$^+$–N$_3$), 405 (M$^+$–2CO), 375 (M$^+$– 2CO–N$_2$–2H), 373 (M$^+$–2CO–N$_2$–4H), 348 (M$^+$– CO–C$_3$H$_5$N$_3$–2H), 346 (M$^+$–CO–C$_3$H$_5$N$_3$–4H, base). ^{1}H NMR (C$_6$D$_6$, δ): 3.75 (1H, dd, J_{45} = 12.5, J_{34} = 3.5 Hz, H$_4$), 2.70 (1H, dd, J_{45} = 12.5, J_{35} = 10.0 Hz, H$_5$), 2.04 (1H, dd, J_{13} = 9.5, J_{12} = 2.6 Hz, H$_1$), 1.87 (1H, m, H$_3$), 1.50 (15H, s, Cp*), 1.22 (1H, dd, J_{23} = 7.5, J_{21} = 2.6 Hz, H$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 206.47, 205.68 (s, Re–CO), 97.60 (s, C$_5$Me$_5$), 60.99 (s, –CH$_2$–), 36.62 (s, =CH–), 25.48 (s, =CH$_2$), 9.66 (s,

C$_5$(CH$_3$)$_5$). Anal. Found: C, 42.44; H, 5.01; N, 7.22. C$_{15}$H$_{20}$N$_3$O$_2$Re Calc.: C, 39.12; H, 4.38; N, 9.12%. The C% and H% values are higher than theoretically, but the N% is lower. This may be attributed to some decomposition of **9**, resulting in partial loss of N$_2$ from the CH$_2$=CHCH$_2$N$_3$ ligand.

4.8. Preparation of Cp*Re(CO)$_2$(η^2-CH$_2$CHCH$_2$NH$_2$) (10)

Complex **1** (30 mg, 0.059 mmol) and NaNH$_2$ (10 mg, 0.26 mmol) were dissolved in CH$_2$Cl$_2$ (3 ml) in a Schlenk tube, then stirred at room temperature overnight. By this time, the IR spectrum showed the disappearance of the ν(CO) for **1**, and new CO bands at 1950, 1927 and 1873 cm^{-1} were observed. By using the same method used for the purification of **9**, complex **10** was obtained as a white solid (21.5 mg, 0.05 mmol, 84%), m.p. 121–122 °C. IR (hex, cm^{-1}): ν_{CO} 1964, 1892. CIMS (m/z): 435 (M$^+$), 419 (M$^+$–NH$_2$), 391 (M$^+$– CO–NH$_2$, base). ^{1}H NMR (C$_6$D$_6$, δ): 4.64 (1H, dd, J_{45} = 10.0, J_{34} = 3.9 Hz, H$_4$), 4.53 (1H, dd, J_{45} = 10.0, J_{35} = 3.9 Hz, H$_5$), 3.45, 3.27 (2H, t, J = 10.0 Hz, NH$_2$), 2.40 (1H, m, H$_1$), 2.29 (1H, m, H$_3$), 1.60 (15H, s, Cp*), 1.49 (1H, d, J_{13} = 8.1 Hz, H$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 206.77, 203.88 (s, Re–CO), 97.30 (s, C$_5$Me$_5$), 78.89 (s, –CH$_2$–), 40.59 (s, =CH–), 27.76 (s, =CH$_2$), 9.82 (s, C$_5$(CH$_3$)$_5$). Anal. Found: C, 41.36; H, 4.98; N, 3.01. C$_{15}$H$_{22}$NO$_2$Re Calc.: C, 41.46; H, 5.10; N, 3.22%.

4.9. Preparation of Cp*Re(CO)$_2$(η^2-CH$_2$CHCH$_2$-CHMe$_2$) (11)

Complex **1** (40 mg, 0.079 mmol) was dissolved in CH$_2$Cl$_2$ (3 ml) in a Schlenk tube at $-78\,^{\circ}$C and 0.2 ml Me$_2$CHMgCl (1 M ether solution) was added by syringe. The reaction was continued at $-78\,^{\circ}$C for 2 h. Two new CO bands at 1946 and 1865 cm^{-1} were observed in the IR spectrum. By using the same method used for the purification of **9**, complex **11** was obtained as a white solid (31.85 mg, 0.069 mmol, 87%). IR (hex, cm^{-1}): ν_{CO} 1960, 1888. EIMS (m/z): 462 (M$^+$), 432 (M$^+$–CO–2H), 419 (M$^+$–CH(CH$_3$)$_2$), 402 (M$^+$–2CO– 4H), 376 (M$^+$–C$_3$H$_5$CH(CH$_3$)$_2$–2H), 348 (M$^+$–CO– C$_3$H$_5$CH(CH$_3$)$_2$, base). ^{1}H NMR (C$_6$D$_6$, δ): 2.50 (1H, m, H$_4$), 2.17 (1H, dd, J_{13} = 10.5, J_{12} = 1.9 Hz, H$_1$), 2.02 (1H, m, H$_3$), 1.77 (1H, m, –CH), 1.54 (15H, s, Cp*), 1.43 (1H, dd, J_{12} = 1.9, J_{23} = 8.1 Hz, H$_2$), 1.27 (1H, m, H$_5$), 1.08, 1.04 (6H, d, J = 6.5 Hz, CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 207.47, 207.09 (s, Re–CO), 96.87 (s, C$_5$Me$_5$), 49.04 (s, –CH$_2$–), 42.68 (s, =CH–), 33.43 (s, –CHMe$_2$), 28.27 (s, =CH$_2$), 22.67, 22.52 (s, CH$_3$), 9.89 (s, C$_5$(CH$_3$)$_5$). Anal. Found: C, 46.68; H, 6.00. C$_{18}$H$_{27}$O$_2$Re Calc.: C, 46.83; H, 5.90%.

4.10. Preparation of $Cp^*Re(CO)(\eta^3$-$C_3H_5)(COC_6H_5)$ (12) and $Cp^*Re(CO)_2(\eta^2$-$CH_2CHCH_2C_6H_5)$ (13)

Complex **1** (25 mg, 0.049 mmol) was dissolved in CH_2Cl_2 (3 ml) in a Schlenk tube at $-78\,°C$ and 0.3 ml C_6H_5Li (1 M) ether solution was added by syringe, then stirred at $-78\,°C$ for 4 h. The IR spectrum showed only three new CO bands at 1950, 1913 and 1871 cm^{-1} by this time. By using the same method as used for the purification of complex **9**, a mixture of **12** and **13** was obtained as a white solid (22.53 mg, 0.046 mmol, 93%). EIMS (m/z, mixture of **12** and **13**): 496 (M^+), 466 (M^+-CO-2H), 440 (M^+-2CO, base), 419 (M^+-C_6H_5), 391 (M^+-COC_6H_5), 378 (M^+-$C_3H_5C_6H_5$), 348 (M^+-CO-$C_3H_5C_6H_5$-2H). Spectroscopic data for **12**: IR (hex, cm^{-1}): ν_{CO} 1919. ^{1}H NMR (C_6D_6, δ): 7.5–7.05 (5H, m, C_6H_5), 4.26 (1H, m, H_c), 2.83, 2.74 (2H, dd, J_{sc} = 5.6, J_{ss} = 2.9 Hz, H_s), 1.66 (15H, s, Cp*), 0.83 (1H, d, J_{ac} = 9.5 Hz, J_{ac} = 8.0 Hz, H_a). ^{13}C{^{1}H} NMR (C_6D_6, δ): 129.0 (s, C_6H_5), 81.1 (s, CH=), 48.9 (s, CH_2), 31.6 (s, =CH_2), 9.80 (s, $C_5(CH_3)_5$). Spectroscopic data for **13**: IR (hex, cm^{-1}): ν_{CO} 1962, 1890. ^{1}H NMR (C_6D_6, δ): 7.5–7.05 (5H, m, C_6H_5), 3.85 (1H, dd, J_{45} = 14.0, J_{34} = 3.2 Hz, H_4), 2.57 (1H, dd, J_{45} = 14.0, J_{35} = 10.1 Hz, H_5), 2.29 (1H, dd, J_{13} = 10.5, J_{12} = 2.0 Hz, H_1), 2.12 (1H, m, H_3), 1.60 (15H, s, Cp*), 1.34 (1H, dd, J_{23} = 8.0, J_{21} = 2.0 Hz, H_2). ^{13}C{^{1}H} NMR (C_6D_6, δ): 129.0 (s, C_6H_5), 46.5 (s, $-CH_2-$), 43.2 (s, =CH–), 26.7 (s, =CH_2), 9.80 (s, $C_5(CH_3)_5$). The ^{13}C data were obtained from the ^{13}C–^{1}H correlation experiment, no ^{13}C resonance of the Cp* ring carbon was obtained because there is no proton bonded to these carbons. Anal. Found: C, 50.78; H, 5.15. $C_{21}H_{25}O_2Re$ Calc.: C, 50.89; H, 5.09%.

4.11. Preparation of $[Cp^*Re(CO)_2(\eta^3$-$C_3H_4Me)][BF_4]$ (14)

A solution of $Cp^*Re(CO)_3$ (562.7 mg, 1.38 mmol) in freshly distilled ether (150 ml) was placed in a Schlenk tube equipped with an inner condenser. Crotyl alcohol (0.12 ml, 1.41 mmol) and $HBF_4 \cdot O(C_2H_5)_2$ (0.2 ml, 85%) were added, and the solution photolyzed under UV light at the temperature of refluxing ether for 5 h. By using the same purification method used for **1** [10], the pure product was obtained as a white solid (mixture of the *endo–syn* and *exo–syn*, 169.4 mg, 0.33 mmol, 24%), m.p. 275 °C (decomp.). IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2047, 1991. FABMS (m/z): 433 (M^+ and base), 405 (M^+-CO), 375 (M^+-2CO-2H). ^{1}H NMR (δ, $CDCl_3$), *endo–syn* isomer: 4.62 (m, H_c), 3.69 (d, $J_{s'c}$ = 6.5 Hz, $H_{s'}$), 2.69 (m, H_a), 2.00 (d, J = 7.4 Hz, CH_3), 2.18 (s, Cp*), 1.70 (d, $J_{a'c}$ = 9.3 Hz, $H_{a'}$). *Exo–syn* isomer: 4.20 (m, H_c), 3.35 (m, H_a), 2.80 (d, $J_{s'c}$ = 6.5 Hz, $H_{s'}$), 2.20 (s, Cp*), 1.98 (d, J = 7.4 Hz, CH_3), 0.88 (d, $J_{a'c}$ = 9.3 Hz, $H_{a'}$). Anal. Found: C, 37.33; H, 4.37. $C_{16}H_{22}BF_4O_2Re$ Calc.: C, 37.00; H, 4.27%.

4.12. Preparation of $[Cp^*Re(CO)_2(\eta^2$-CH_2CHCH-$(CH_3)PMe_3)][BF_4]$ (15)

Complex **14** (20 mg, 0.039 mmol) was dissolved in CH_2Cl_2 (3 ml), and excess PMe_3 (0.2 ml, 1.93 mmol) was added by syringe. The reaction mixture was stirred at room temperature for 1 h. The IR then showed two new CO bands at 1964 and 1881 cm^{-1} due to complex **15**. The solvent and excess PMe_3 were pumped off. The residue was washed with 2 ml ether, then recrystallized from CH_2Cl_2/hexane (1:6). The product was obtained as a white solid which is a mixture of **15a** (67%) and **15b** (33%) (14.9 mg, 0.025 mmol, 65%), m.p. 202–203 °C. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1964, 1881. FABMS (m/z): 509 (M^+ of cation), 433 (M^+-PMe_3, base), 405 (M^+-PMe_3-CO), 375 (M^+-PMe_3-2CO-2H). Spectroscopic data for **15a**: ^{1}H NMR (CD_3CN, δ): 3.04 (1H, dd, CH_2PMe_3), 2.15 (1H, m, –CH_2PMe_3), 1.99 (15H, s, Cp*), 1.96 (1H, m, =CH–), 1.80 (9H, d, J_{PH} = 12.0 Hz, PMe_3), 1.58 (1H, m, =CH_2), 1.45 (3H, d, J = 6.0 Hz, CH_3). ^{13}C{^{1}H} NMR (CD_3CN, δ): 207.65 (s, Re–CO), 99.91 (s, C_5Me_5), 38.56 (d, J_{PC} = 42.40 Hz, –CH_2PMe_3), 26.73 (s, =CH–), 19.78 (s, =$CHCH_3$), 10.92 (s, =$CHCH_3$), 10.42 (s, $C_5(CH_3)_5$), 7.25 (d, J_{PC} = 55.12 Hz, $P(CH_3)_3$). ^{31}P{^{1}H} NMR (CD_3CN, δ): 34.30 (s, –CH_2PMe_3). Spectroscopic data for **15b**: ^{1}H NMR (CD_3CN, δ): 2.61 (1H, m, –$CH(Me)PMe_3$), 2.02 (15H, s, Cp*). ^{31}P{^{1}H} NMR (CD_3CN, δ): 29.27 (s, –$CH(Me)PMe_3$). Anal. Found: C, 38.61; H, 5.40. $C_{19}H_{31}BF_4O_2PRe$ Calc.: C, 38.32; H, 5.25%.

4.13. Preparation of $[Cp^*Re(CO)(NCMe)(\eta^3$-$C_3H_4Me)][BF_4]$ (16)

To a solution of **14** (26.8 mg, 0.052 mmol) in freshly distilled acetonitrile (5 ml) was added PhIO (22.2 mg, 0.1 mmol). The reaction was stirred at 0 °C for 1 h and monitored by IR spectroscopy. The solution was filtered through Celite, the solvent pumped off and the residue recrystallized from THF/ether to give **16** as a pale yellow solid (*endo–syn*, 25.2 mg, 0.047 mmol, 91%), m.p. 129–130 °C. IR (CH_3CN, cm^{-1}): ν_{CO} 1962. FABMS (m/z): 446 (M^+), 405 (M^+-CH_3CN, base), 375 (M^+-CH_3CN-CO-2H). ^{1}H NMR ($CDCl_3$, δ): 4.78 (m, H_c), 3.07 (d, $J_{s'c}$ = 6.9 Hz, $H_{s'}$), 2.78 (s, CH_3CN), 2.53 (m, H_a), 1.89 (s, Cp*), 1.86 (d, J = 6.7 Hz, CH_3), 1.32 (d, $J_{a'c}$ = 6.9 Hz, $H_{a'}$). Anal. Found: C, 38.20; H, 4.84; N, 2.67. $C_{17}H_{25}BF_4NORe$ Calc.: C, 38.35; H, 4.73; N, 2.63%.

4.14. Preparation of $[Cp^*Re(NCMe)_2(\eta^3$-$C_3H_4Me)]$-$[BF_4]$ (17)

A solution of **14** (15.8 mg, 0.03 mmol) in freshly distilled acetonitrile (2 ml) was placed in a Schlenk

tube, and a solution of Me_3NO in acetonitrile (14 mg, 0.19 mmol) was added. The reaction was stirred at room temperature for 5 h, and monitored by IR; all CO bands of **14** disappeared during this time. The solvent was removed under vacuum and the residue recrystallized from CH_2Cl_2/ether to give the pure product as a yellowish solid (*endo–syn*, 12.4 mg, 0.023 mmol, 76%), m.p. 123–124 °C. FABMS (*m/z*): 459 (M$^+$), 418 (M$^+$–CH_3CN), 375 (M$^+$–$2CH_3CN$–2H). ^{1}H NMR (δ, $CDCl_3$): 3.86 (m, H$_c$), 2.86 (s, CH_3CN), 2.35 (d, $J_{s'c}$ = 6.0 Hz, H$_{s'}$), 2.00 (m, H$_a$), 1.67 (s, Cp*), 1.33 (d, $J_{a'c}$ = 6.6 Hz, H$_{a'}$), 1.12 (d, J = 6.0 Hz, CH_3). Anal. Found: C, 39.38; H, 4.94; N, 4.87. $C_{18}H_{28}BF_4N_2Re$ Calc.: C, 39.63; H, 5.18; N, 5.14%.

4.15. Crystal structure of $Cp^*Re(CO)(\eta^3\text{-}C_3H_5)\text{-}(O_2CSC_6H_5)$ (7)

The ^{1}H NMR sample of impure **6** (mixed with the product obtained from the reactions of **1** with $NaSC_6H_5$ in the presence of Me_3NO in CH_2Cl_2) was dissolved in a solvent mixture (ether/hexane 1:5), and kept in the refrigerator to crystallize (3–5 °C). Two weeks later, some yellowish crystals had formed. These crystals were kept in the refrigerator until the sample was used for X-ray analysis. Only a few crystals of **7** were obtained, and all were used for the X-ray structure determination.

A very pale greenish colored plate was removed from the viscous mother liquor and gently wedged in a glass capillary tube. Data were recorded with an Enraf–Nonius CAD4F diffractometer using graphite monochromated Mo Kα radiation. Absorption corrections were made by the Gaussian integration method. Data reduction included corrections for intensity scale variations and for Lorentz and polarization effects.

Coordinates and anisotropic thermal parameters for all non-hydrogen atoms were refined subject to soft null-relative thermal-motion restraints for bonded atom pairs and for pairs of adjacent methyl carbon atoms of the Cp* group. Hydrogen atoms were placed in calculated positions 0.95 Å from their respective carbon atoms and with isotropic temperature factors initially proportional to the carbon atom equivalent isotropic temperature factors. In subsequent cycles of refinement the coordinate shifts for the hydrogen atoms and their respective carbon atoms were constrained to be the same. The isotropic temperature factors of the hydrogen atoms were refined but constrained such that the shifts for all those on the Cp* group were the same as all those of the allyl group and all those of the phenyl group. Final full-matrix least-squares refinement of 238 parameters for 1987 data ($I_o \geq 2.5\sigma(I_o)$) and 38 restraints converged at $R = 0.047$. The final maximum |shift/error| was 0.03.

Crystallographic details are summarized in Table 1.

Final fractional atomic coordinates for the non-hydrogen atoms are listed in Table 2. Selected intramolecular distances and angles are listed in Table 3. The programs used for absorption corrections, data reduction, structure solution, refinement and plot generation were from the NRCVAX Crystal Structure System [24]. Final refinement was made using CRYSTALS [25]. Complex scattering factors for neutral atoms [26] were used in the calculation of structure factors. Computations were carried out on MicroVAX-II, 80486 and Pentium computers.

5. Supplementary material

Additional crystallographic details (one page), hydrogen atom parameters (one page), anisotropic thermal parameters (one page), additional bond lengths and angles (two pages), torsion angles (one page), least-squares planes (two pages) and observed and calculated structure factors (13 pages) are available from the authors.

Acknowledgements

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