Cationic rhenium allyl complex $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)_2][BF_4]$ and its acetonitrile derivatives $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(NCMe)][BF_4]$ and $[Cp^*Re(\eta^3\text{-}C_3H_5)(NCMe)_2][BF_4]$. Products of reactions with borohydride, methoxide and trimethylphosphine, and the X-ray crystal structure of the bis-ethylamine complex $[endo\text{-}Cp^*Re(\eta^3\text{-}C_3H_5)(NH_2Et)_2][ReO_4]$.solv

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Abstract

By replacing one or both of the CO groups in $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)_2][BF_4]$ (1) by MeCN to give $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(NCMe)][BF_4]$ (3) or $[Cp^*Re(\eta^3\text{-}C_3H_5)(NCMe)_2][BF_4]$ (4), it was anticipated that the MeCN groups would be labile and would promote ligand substitution reactions, leading to a variety of new rhenium η^3-allyl half-sandwich derivatives. Instead, MeCN is found to be difficult to substitute, and nucleophiles often result in products that arise from attack at either the MeCN or allyl ligands. Complex 1 reacted with NaBH$_4$ to give the propene complex $Cp^*Re(\eta^2\text{-}CH_2CHCH_3)(CO)_2$ (2), with NaOMe to give the methoxycarbonyl complex $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(COOMe)$ (6) and the 3-methoxypropene complex $Cp^*Re(\eta^2\text{-}CH_2CHCH_2OMe)(CO)_2$ (5), and with PMe$_3$ to give $[Cp^*Re(\eta^2\text{-}CH_2CHCH_2PMe_3)(CO)_2][BF_4]$ (7). Complex 3 gave the ethylamine complex $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(NH_2Et)][BF_4]$ (8) when reacted with NaBH$_4$, $[Cp^*Re(\eta^2\text{-}CH_2CHCH_2PMe_3)(CO)(NCMe)][BF_4]$ (9) with PMe$_3$, and $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(NHCOMe)$ (10) with NaOH. Complex 4 similarly yielded the bis-ethylamine complex $[Cp^*Re(\eta^3\text{-}C_3H_5)(NH_2Et)_2][BF_4]$ (11) when reacted with NaBH$_4$, but with PMe$_3$ ligand substitution occurred, resulting in $[Cp^*Re(\eta^3\text{-}C_3H_5)(NCMe)(PMe_3)][BF_4]$ (12). Treating 12 with NaBH$_4$, or 11 with PMe$_3$, yielded the ethylamine complex $[Cp^*Re(\eta^3\text{-}C_3H_5)(PMe_3)(NH_2Et)][BF_4]$ (13). The X-ray crystal structure of $[endo\text{-}Cp^*Re(\eta^3\text{-}C_3H_5)(NH_2Et)_2][ReO_4]$.solv has been determined. This compound crystallizes in the space group $Pnma$ with $a = 8.6554(8)$ Å, $b = 11.729(2)$ Å, $c = 26.928(3)$ Å, $V = 2733.7$ Å^3, and $Z = 4$. The structure was refined to $R_F = 0.028$ for 1444 data ($I_0 \geqslant 2.5\sigma(I_0)$, $2\theta_{max} = 46°$) and 158 variables. The cation has a crystallographic mirror plane that relates the two EtNH$_2$ ligands and bisects the $endo\text{-}\eta^3$-allyl and Cp* ligands. Selected distances and angles are Re–N = 2.228(7) Å, Re–C(6) = 2.177(9) Å (allyl terminal carbon), Re–C(7) = 2.090(13) Å (allyl central carbon), N–C(4) = 1.470(10) Å, Re–N–C(4) = 125.2(6) Å, and C(6)–C(7)–C(6)' = 114.1(13) Å

1. Introduction

The synthesis and X-ray crystal structure of the cationic rhenium η^3-allyl complex $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)_2][BF_4]$ (1; Cp* = $\eta^5\text{-}C_5Me_5$) and its mono- and bis-acetonitrile derivatives $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(NCMe)][BF_4]$ (3) and $[Cp^*Re(\eta^3\text{-}C_3H_5)(NCMe)_2][BF_4]$ (4) (Scheme 1) have been reported in previous papers [1,2]. The acetonitrile derivatives 3 and 4 were synthesized in anticipation that the acetonitrile ligand would be more substitutionally labile than CO and would be readily substituted by neutral (L), or anionic (X) ligands, leading to a series of new half-sandwich rhenium η^3-allyl complexes of the type $[Cp^*Re(CO)(L)(\eta^3\text{-}C_3H_5)]^+$, $[Cp^*ReL_2(\eta^3\text{-}C_3H_5)]^+$, and $Cp^*Re(CO)X(\eta^3\text{-}C_3H_5)$.

In this paper we compare the reactions of the dicarbonyl compound 1 and the acetonitrile compounds 3

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and 4 with potential nucleophiles such as borohydride, trimethylphosphine and methoxide. Disappointingly, we find that acetonitrile in these rhenium complexes is not a good leaving group, and that ligand substitution does not usually occur preferentially. Instead, nucleophilic attack occurs at one or other of the possible ligand sites, and the result depends on the particular nucleophile employed.

There is currently considerable interest in nucleophilic additions to cationic cyclopentadienyl allyl complexes [3]. One of the most extensively explored is the molybdenum complex [CpMo(CO)(NO)(allyl)]$^+$ [4]. Rather less is known about the reactions of manganese [5] or rhenium [6] compounds, and there has been only a preliminary study of additions to pentamethylcyclopentadienyl rhenium allyl complexes [7].

2. Results and discussion

### 2.1. Reaction of [Cp*Re(η^3-C$_3$H$_5$)(CO)$_2$][BF$_4$] (1) with NaBH$_4$ and NaOMe

In an earlier paper we indicated briefly that at room temperature 1 reacts with NaBH$_4$ in THF to give the η^2-propene complex (2), and with NaOMe in methanol to give the η^2-methoxypropene complex (5) [7,8]. These results have been confirmed in the present work, but additionally we find that when the reaction of 1 with NaOMe is conducted at 0°C, both 5 and the methoxycarbonyl complex 6 are formed. By the time the products were purified and warmed to room temperature to get the ^{1}H NMR spectrum, 5 and 6 were present in

approximate 1:1 ratio (from Cp* ^{1}H NMR intensities). The IR spectrum of the methanol solution after 3 h reaction exhibited ν(CO) at 1956 and 1885 cm^{-1}, assigned to 5 [7], and at 1942 cm^{-1}, assigned to 6. After removal of the methanol, the IR spectrum of the hexane extract showed absorptions for 5 at 1964 and 1892 cm^{-1}, and absorptions at 1944 and 1634 cm^{-1} for the terminal CO and methoxycarbonyl groups of 6, respectively. The ^{1}H NMR spectrum in CDCl$_3$ gave all the expected resonances for 5 [7], and the presence of the η^3-allyl ligand in 6 was clearly evident: a multiplet at δ 4.20 (H$_c$), two doublets of doublets at δ 3.02 and δ 2.94 (inequivalent H$_s$ protons), and two doublets at δ 1.10 and δ 0.69 (inequivalent H$_a$ protons).

Interestingly, the reaction of 1 with NaBH$_4$ was highly regioselective, and there was no evidence of other products such as the known [7] hydrido(allyl) complex Cp*Re(CO)(H)(η^3-C$_3$H$_5$) (from CO substitution) or possibilities such as a formyl [9] or a metallacyclobutane [10] complex. By contrast, NaOMe resulted in products from elaboration of either the allyl or a carbonyl ligand. However, when the product mixture in CDCl$_3$ was maintained at room temperature for three days, the ^{1}H NMR then exhibited only the resonances for 5, suggesting that 6 slowly isomerized to 5 in solution.

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

When complex 1 was reacted with PMe$_3$ at room temperature in CH$_2$Cl$_2$ or acetone, PMe$_3$ acted as a nucleophile attacking the η^3-allyl ligand to give the
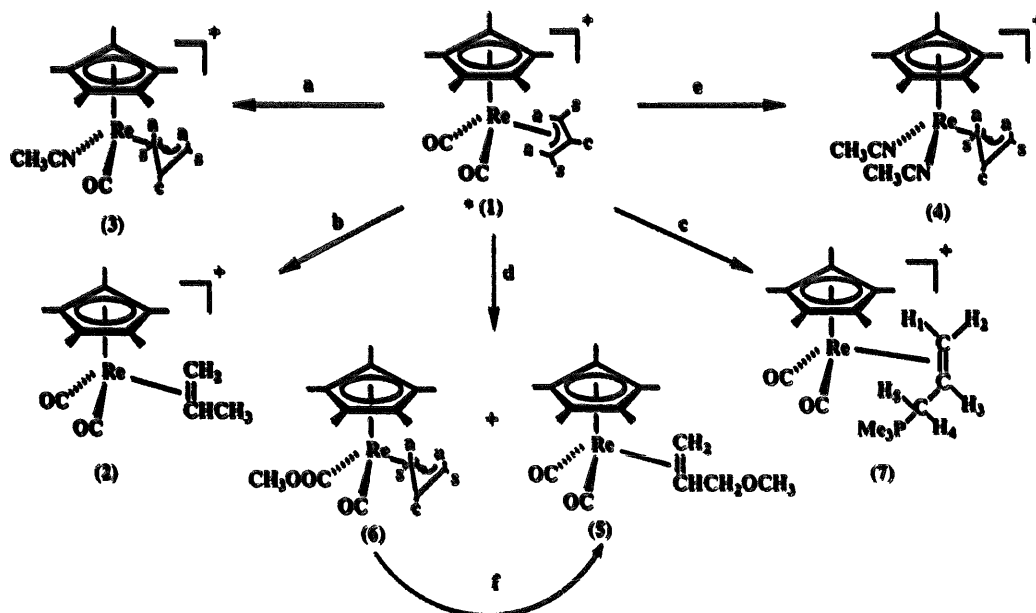
Scheme 1. Reactions of [Cp*Re(η^3-C$_3$H$_5$)(CO)$_2$][BF$_4$] (1) (BF$_4$ counter-ions omitted). Conditions: (a) PhIO/MeCN; (b) NaBH$_4$/THF/H$_2$O(trace); (c) PMe$_3$/CH$_2$Cl$_2$; (d) NaOMe/MeOH (0°C); (e) Me$_3$NO/MeCN; (f) In C$_6$D$_6$ for 72 h at RT. * 1 is a mixture of exo and endo isomers.

allyltrimethylphosphonium complex 7. The IR spectrum of 7 showed ν(CO) absorptions at 1964 and 1885 cm^{-1} in CH$_2$Cl$_2$. These values are much lower in comparison with complex 1, for which ν(CO) absorption is at 2053 and 1999 cm^{-1}, because the positive charge in 7 is now formally located on the phosphorus instead of the metal.

The ^{1}H NMR spectrum of 7 showed a strong doublet at δ 1.88 for the methyl protons, with $J_{PH} = 13.9$ Hz. This is a larger coupling constant than typically observed for *coordinated* PMe$_3$ (about 9 Hz), and is close to reported values (about 14.5 Hz) for the Me$_3$PCH$_2$ group in related ruthenium complexes [11]. The remaining resonances were assigned by a combination of phosphorus decoupling, ^{1}H NOE, ^{1}H–^{1}H correlation and ^{1}H–^{13}C correlation results. The ^{31}P{^{1}H} NMR spectrum gave a singlet at δ 29.73 ppm, in the range for -CH$_2$PMe$_3$ [11] and downfield from the region typical of *coordinated* PMe$_3$ [12]. The ^{13}C{^{1}H} NMR spectrum showed resonances at δ 208.87 and δ 207.08 for the two inequivalent CO groups, and a doublet at δ 34.98 with $J_{PC} = 42.3$ Hz, assigned to the -CH$_2$PMe$_3$ carbon, unambiguously shows that PMe$_3$ has attacked the allyl terminal carbon, resulting in this allyltrimethylphosphonium complex 7. There have been reported cases of PPh$_3$ undergoing nucleophilic attack at an η^3-allyl to give triphenylphosphonium complexes [5,13], so the present result is not unexpected, though we are not aware of previous ones involving PMe$_3$.

Complex 7 did not react with PhIO or Me$_3$NO in CH$_3$CN solution in attempts to substitute CO by MeCN, as occurs for 1 [2]. This also can be explained as a result of the positive charge being displaced from the metal center to the CH$_2$PMe$_3$ function, so that there is more back-bonding to the CO, and reduced propensity to react with the nucleophile.

2.3. Reaction of [Cp*Re(η^3-C$_3$H$_5$)(CO)(NCMe)][BF$_4$] (3) with NaBH$_4$

The reaction of complex 3 with NaBH$_4$ in THF/H$_2$O solution gave the ethylamine complex 8 (Scheme 2). The ^{1}H NMR spectrum of 8 showed that all five protons are inequivalent and exhibited a similar coupling pattern to that of 3. Consequently, the multiplet at δ 5.00 was assigned to H$_c$, the multiplets at δ 3.12 and δ 2.73 to H$_s$, and the doublets at δ 2.05 and δ 1.48 to H$_a$. Broad resonances at δ 3.95 and δ 3.76 were assigned to the diastereotopic NH$_2$ protons. No H–D exchange was observed for these protons over one week at room temperature after D$_2$O was added. The IR spectrum showed ν(CO) at 1937 cm^{-1} (in THF). This compares with ν(CO) of 1975 cm^{-1} (CH$_2$Cl$_2$) for 3 [2], and is an indication that the ethylamine ligand increases back-bonding to the carbonyl by being a stronger σ donor compared with CH$_3$CN, and by having no π-acceptor properties.

Surprisingly, there have been rather few previous reported examples of reduction of coordinated CH$_3$CN to ethylamine [14]. In one case, the CH$_3$CN ligand in a tungsten complex was reduced stepwise and the intermediate imine complex was observed [14b]. In our case, there was no evidence for the formation of an intermediate imine complex when the reaction was monitored at room temperature by IR.

When 8 was treated with PMe$_3$ at room temperature for 72 h, no substitution of EtNH$_2$ by PMe$_3$ occurred, nor was the η^3-allyl group attacked by PMe$_3$.Thus, the replacement of CH$_3$CN by EtNH$_2$ has made the complex inactive toward nucleophilic attack by PMe$_3$, probably owing to the increased electron density at the rhenium center as reflected by the above ν(CO) values
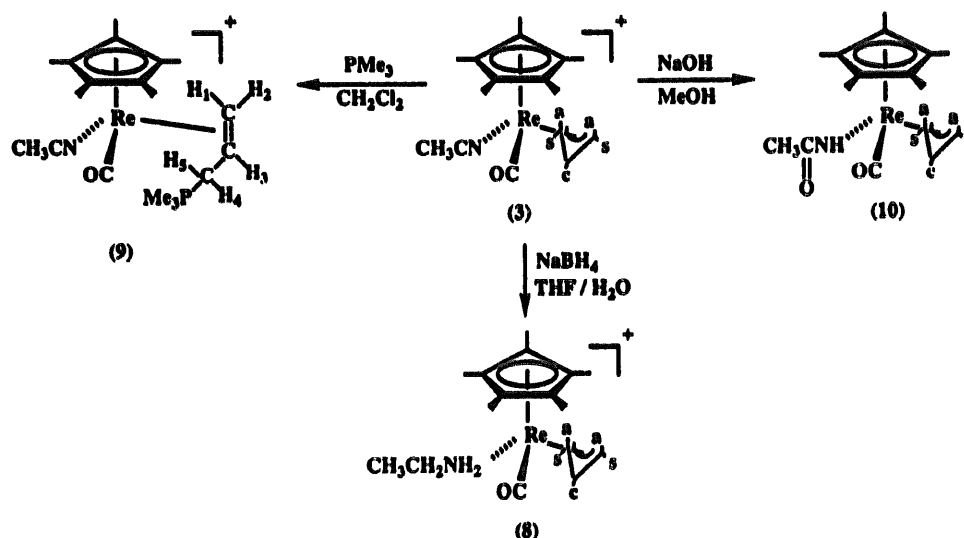
Scheme 2. Reactions of [Cp*Re(η^3-C$_3$H$_5$)(CO)(MeCN)][BF$_4$] (3) (BF$_4$ counter-ions omitted).

for 3 and 8. Attempts to deprotonate the EtNH$_2$ ligand in this cationic complex were carried out by using DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) or ^{t}BuLi. In each case, loss of ν(CO) in the IR spectrum and the disappearance of the Cp* resonance in the ^{1}H NMR spectrum indicated decomposition.

2.4. Reaction of [Cp*Re(η^3-C$_3$H$_5$)(CO)(NCMe)][BF$_4$] (3) with PMe$_3$

Complex 3 was allowed to react with PMe$_3$ in an attempt to substitute the MeCN ligand by PMe$_3$. Instead, it formed the allyltrimethylphosphonium complex 9 (Scheme 2). This is, of course, the MeCN derivative of 7, but it is not as stable as 7. It slowly decomposed in solution at 0°C, even under N$_2$. The IR spectrum of this complex showed ν(CO) at 1823 cm^{-1} (CH$_2$Cl$_2$). This can be compared with 3 (ν(CO) = 1975 cm^{-1} in CH$_2$Cl$_2$) [2] and, as discussed above for 7, this indicates more π back-donation to CO, since the formal positive charge is now located on the phosphorus atom. The FAB MS of 9 gave a parent peak at m/z = 508 for M$^+$ of the cation, and fragments at m/z = 467 and m/z = 432 which are consistent with the loss of CH$_3$CN and PMe$_3$ separately from the parent ion.

The ^{1}H NMR of 9 showed a multiplet at δ 3.01 which is assigned to one of the diastereotopic CH$_2$PMe$_3$ protons (H$_s$) and, as expected, it changed to a doublet of doublets after ^{31}P decoupling. The chemical shift and coupling pattern are similar to that of 7. The singlet resonance at δ 2.70 ppm integrating for three protons is assigned to the CH$_3$CN ligand. A doublet at δ 1.89 with J$_{PH}$ = 14.0 Hz is assigned to PMe$_3$ methyls, and multiplets at δ 1.93, 1.82, 1.71 and 1.43 to H(3), H(4), H(1) and H(2); these assignments were confirmed by

^{31}P, ^{1}H decoupling, ^{1}H-^{1}H and ^{1}H-^{13}C correlation experiments.

The ^{13}C NMR spectrum showed a resonance at δ 128.50 which is in a typical position for a nitrile carbon, supporting the presence of coordinated CH$_3$CN. A doublet at δ 25.85 with J$_{PC}$ = 44.2 Hz was assigned to the -CH$_2$PMe$_3$ carbon, and another doublet at δ 8.02 with J$_{PC}$ = 53.2 Hz to PMe$_3$ methyl carbons. These data are typical for the allyltrimethylphosphonium fragment by comparison with literature values [11] and our own results for 7.

Reactions of 9 with PhIO or Me3NO in CH$_3$CN or CH$_2$Cl$_2$ were attempted to see if CO could be oxidatively removed and lead to further CH$_3$CN coordination, or possibly a transfer of PMe$_3$ to the rhenium center. These resulted in loss of ν(CO) in the IR spectrum, indicating that oxidative removal of CO was successful, but the ^{1}H NMR appeared to indicate loss of the Cp* signal, and no identifiable products could be isolated from the resulting oily material obtained.

2.5. Reaction of [Cp*Re(η^3-C$_3$H$_5$)(CO)(NCMe)][BF$_4$] (3) with hydroxide

When 3 was treated with NaOH in MeOH at −78°C, a high yield of the acetamido complex 10 was obtained. The IR spectrum of 10 gave absorptions at 1952 cm^{-1} (coordinated CO, in hexane) and 1595 cm^{-1} (in hexane), assigned to the amide CO. The ^{1}H NMR in C$_6$D$_6$ showed a broad signal at δ 3.34, integrating for one proton, which is the range for δ (NH) by comparison with compound 8. The five inequivalent protons of the η^3-allyl group were assigned on the basis of NOE experiments. Saturation at δ 0.76 (H$_a$) induced enhancements at δ 1.54 (Cp*), δ 1.60 (H$_a$) and δ 2.48

(12)   (4)   (11)

(13)
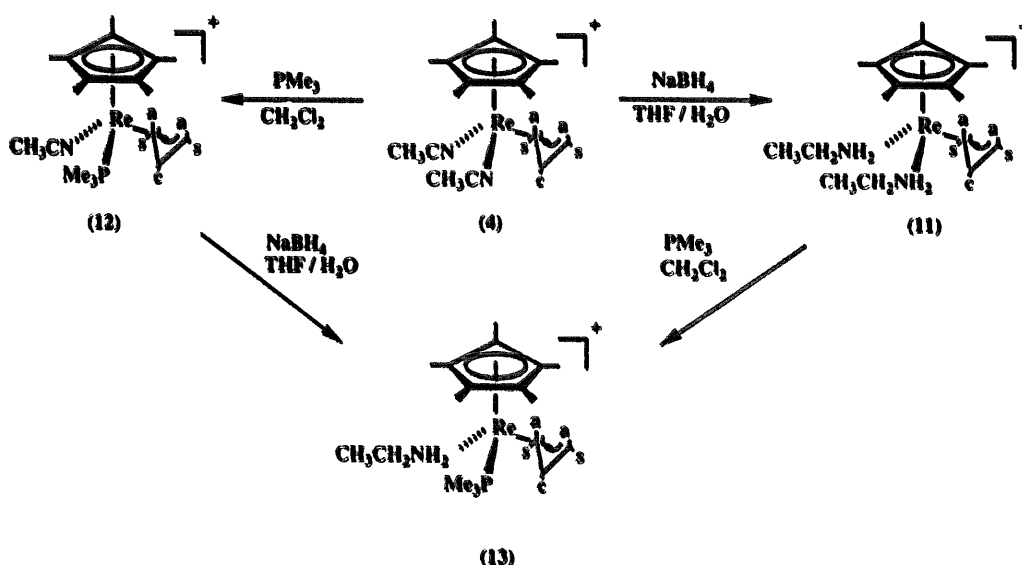
Scheme 3. Reactions of [Cp*Re(η^3-C$_3$H$_5$)(MeCN)$_2$][BF$_4$] (4) (BF$_4$ counter-ions omitted).

(H$_s$). Irradiation of Cp* at δ 1.54 gave an enhancement at δ 0.76 for H$_a$, and indicated the η^3-allyl group to be in the endo conformation. The EI MS gave strong peaks for M$^+$ and M$^+$-CO, but the peak for M$^+$-NHCOCH$_3$ at m/z 391 was hardly detectable. An attempt to protonate the coordinated amide with HBF$_4$ at −78°C resulted in loss of carbonyl IR absorption. No product was extracted into hexane or ether according to NMR spectra, and the residue left from these extractions did not give a clear Cp* signal.

Hydrolysis of coordinated acetonitrile has been commonly reported, and the mechanism has been discussed [15]. Recent examples for platinum [16] and tungsten [17] complexes have been reported.

2.6. Reaction of [Cp*Re(η^3-C$_3$H$_5$)(NCMe)$_2$][BF$_4$] (4) with NaBH$_4$

Complex 4 reacted with NaBH$_4$ under the same conditions used for 3 to give the bis-ethylamine complex [Cp*Re(η^3-C$_3$H$_5$)(NH$_2$Et)$_2$][BF$_4$] (11) (Scheme 3), where both CH$_3$CN ligands have been reduced. The FAB MS spectrum of 11 showed a parent peak for the cation at m/z = 453 and a base peak at m/z = 406 which results from the loss of one ethylamine ligand and 2H (presumably from Cp*)[18]. The ^{1}H NMR spectrum of 11 gave two broad signals at δ 3.50 and δ 3.38 which are assigned to the two diastereotopic NH$_2$ protons. The two ethylamine ligands are, however, equivalent by symmetry. Therefore the η^3-allyl protons gave, as expected, only three signals, assigned as: δ 3.77 (H$_c$), δ 2.44 (H$_s$), and δ 1.52 (H$_a$). All the assignments were confirmed by ^{1}H NMR decoupling experiments. Saturation of the CH$_2$ multiplet resulted in a broad AB quartet for the NH protons.

One ethylamine ligand in 11 can be substituted by PMe$_3$ to produce [Cp*Re(η^3-C$_3$H$_5$)(NH$_2$Et)(PMe$_3$)]-[BF$_4$] (13). A small impurity due to the bis-PMe$_3$ complex [Cp*Re(η^3-C$_3$H$_5$)(PMe$_3$)$_2$][BF$_4$] (M$^+$ = 515, very weak intensity) can be observed in FAB MS of isolated 13, but no matter how much excess PMe$_3$ was utilized or for how long the reaction was conducted at room temperature, all attempts to prepare the bis-PMe$_3$ complex were unsuccessful.

2.7. Reaction of [Cp*Re(η^3-C$_3$H$_5$)(NCMe)$_2$][BF$_4$] (4) with PMe$_3$

PMe$_3$ reacted with 4 to give 12, in which one CH$_3$CN has been substituted by PMe$_3$ (Scheme 3). Increasing the amount of PMe$_3$ and reaction time did not lead to the substitution of the second nitrile ligand to give the bis-PMe$_3$ complex. The FAB MS for 12 gave a parent peak at m/z = 480 for the cation M$^+$, and base peak at m/z = 439 which is consistent with the loss of CH$_3$CN from M$^+$. The ^{1}H NMR spectrum

for 12 gave a doublet at δ 2.84 (J_{PH} = 2.2 Hz) assigned to the coordinated CH$_3$CN, and a doublet at δ 1.38 (J_{PH} = 8.8 Hz) assigned to the PMe$_3$ ligand. The chiral rhenium center makes all five protons for the η^3-allyl ligand inequivalent, giving resonances for H$_c$ at δ 3.68, H$_s$ at δ 2.26 and δ 2.14 and H$_a$ at δ 1.45 and δ 1.03.

As in 3 and 4, the CH$_3$CN ligand in 12 can be reduced by NaBH$_4$ and this produced the ethylamine complex [Cp*Re(η^3-C$_3$H$_5$)(PMe$_3$)(EtNH$_2$)][BF$_4$] (13) previously mentioned above to result from substitution of one EtNH$_2$ ligand in 11 by PMe$_3$. The FAB MS spectrum of 13 showed M$^+$ for the cation at m/z = 484 and base peak at m/z = 439, which is in agreement with the loss of EtNH$_2$ from M$^+$. A comparison of the ^{1}H NMR spectrum of 13 with that of 12 showed that the CH$_3$CN resonance for 12 at δ 2.84 had disappeared, and there were two new broad resonances at δ 3.15 and δ 2.58 which are assigned to the NH$_2$ protons of the newly generated ethylamine ligand, which also exhibits the expected ethyl resonances. The PMe$_3$ resonance occurred at a similar position to that in 12, δ 1.39 (J_{PH} = 7.4 Hz). The presence of the PMe$_3$ ligand in 12 and 13 resulted in long-range coupling to the η^3-allyl protons, causing especially the resonance of the proximal H$_a$ proton to be a multiplet rather than the usual doublet. In 12 even the CH$_3$CN ligand methyl protons were weakly coupled to phosphorus, resulting in a doublet of separation 2.2 Hz.

2.8. X-Ray structure determination for [endo-Cp*Re(η^3-C$_3$H$_5$)(NH$_2$Et)$_2$][ReO$_4$].solv

Crystals for the X-ray structure determination were grown from a solution of 11 in acetone-toluene over a period of three months. The structure determination confirmed the presence of the cation of 11, [Cp*Re(η^3-C$_3$H$_5$)(NH$_2$Et)$_2$]$^+$, but the anion could not be satisfactorily modeled as the expected ion [BF$_4$]$^-$ based on the analysis and IR spectrum of the original material. The anion present in the crystal was best interpreted as [ReO$_4$]$^-$, and we presume that this has arisen from an unidentified reaction during the long period in solution prior to growth of crystals. The allyl group adopts the endo orientation, just as it has previously been shown to do in the crystal structures of 3 and 4 [2].

The molecular structure of [endo-Cp*Re(η^3-C$_3$H$_5$)(NH$_2$Et)$_2$]$^+$ is shown in Fig. 1. Selected intramolecular distances and angles are given in Table 1. The structure of the cation is closely comparable to that of [Cp*Re(η^3-C$_3$H$_5$)(NCMe)$_2$]$^+$ [2], and in fact there are no significant differences in the internal dimensions of the Cp*Re(η^3-C$_3$H$_5$) fragments in the two structures. Even the placement of the nitrogen atoms in the Re-atom coordination sphere is closely similar, with the exception that the Re-N bond lengths, as expected, are longer (2.228(7) Å) for ethylamine, than acetonitrile (2.089(7) and 2.086(10) Å).

Table 1
Crystallographic data for the structure determination of [Cp*Re(η^3-C$_3$H$_5$)(NH$_2$Et)$_2$][ReO$_4$].solv

Formula	Re$_2$O$_5$N$_2$C$_{20}$H$_{40}$ [a]	Crystal system	Orthorhombic
F.W. [a]	761	Space group	*Pnma*
a (Å) [b]	8.6554(8)	ρ_c (g cm^{-3}) [a]	1.85
b (Å)	11.729 (2)	λ (Mo Kα_1) (Å)	0.70930
c (Å)	26.928(3)	μ (Mo Kα) (cm^{-1}) [a]	90.0
V (Å^3)	2733.7	Min–max 2θ (°)	4–46
Z	4	Transmission [c]	0.325–0.532
R_F [d]	0.028	Crystal dim. (mm^3)	0.09 × 0.16 × 0.21 [e]
R_{wF} [f]	0.029	GoF [g]	1.37

[a] Formula weight, density and absorption coefficient calculated on the basis of: solv = C$_3$H$_6$O; ReO$_4^-$ anion (see text).
[b] Cell dimensions were determined from 25 reflections (35° $\leqslant 2\theta \leqslant$ 39°).
[c] All data were corrected for the effects of absorption by the gaussian integration method.
[d] $R_F = \Sigma |(|F_o| - |F_c|)|/\Sigma |F_o|$ for 1444 data ($I_o \geqslant 2.5\sigma$ (I_o)).
[e] A second crystal of dimensions 0.08 × 0.14 × 0.16 (mm^3) was used to remeasure 73 reflections (see text).
[f] $R_{wF} = [\Sigma(w(|F_o| - |F_c|)^2)/\Sigma(wF_o^2)]^{1/2}$ for 1444 data ($I_o \geqslant 2.5\sigma(I_o)$); $w = [\sigma(F_o)^2 + 0.0001F_o^2]^{-1}$.
[g] $GoF = [\Sigma(w(F_o - F_c)^2)/\text{degrees of freedom}]^{1/2}$.

There are no significant intermolecular contacts involving either the cation or anion, with the possible exception of some rather weak hydrogen bonds from the perrhenate anion to the amine ligand (O(1)–H(1)' = 2.13 Å, where ' indicates 1 − x, 1 − y, 2 − z, and O(2)–H(2) = 2.28 Å).

2.9. Stereochemical considerations

The X-ray structure determination shows that the allyl ligand adopts the endo configuration in the bis-ethylamine complex cation [Cp*Re(η^3-C$_3$H$_5$)(NH$_2$Et)$_2$]$^+$ of 11, just as it does in the mono- and bis-acetonitrile cations [Cp*Re(η^3-C$_3$H$_5$)(CO)(NCMe)]$^+$ and [Cp*Re-(η^3-C$_3$H$_5$)(NCMe)$_2$]$^+$ in 3 and 4 [2]. The ^{1}H NMR spectra of 11 indicate the presence of only one isomer in solution also, and because the chemical shifts and coupling constants of the allyl protons in 11 are very similar to those of 3 and 4, which have been previously established to be endo isomers in solution by NOE [2], it is highly probable that 11 is present as the endo isomer in solution. Similarly, we assign all the other allyl complexes in this study, i.e. 6, 8, 10, 12 and 13, to be endo isomers. Therefore, there seems to be a general tendency for the endo isomer to be preferred when the

electron-withdrawing CO groups in 1 are replaced by the better donors MeCN, EtNH$_2$, etc.

Where the allyl group in the dicarbonyl 1 is converted to a substituted propene complex, as in 2, 5 and 7, the ground-state structure is expected to have the propene C=C axis parallel to the Cp* plane, as shown in Scheme 4 (a, b), and the preferred rotamer is expected to be b, in which the propene substituent avoids the bulky Cp*. As far as we can ascertain from the NMR spectra, complexes 2, 5 and 7 exhibit only a single set of resonances at room temperature, consistent with the presence of only one rotamer (presumed to be the less sterically congested one b) or possibly because of fast alkene rotation interconverting a and b.

When one CO has been replaced by MeCN, four possibilities exist for the stereochemistry of the result-
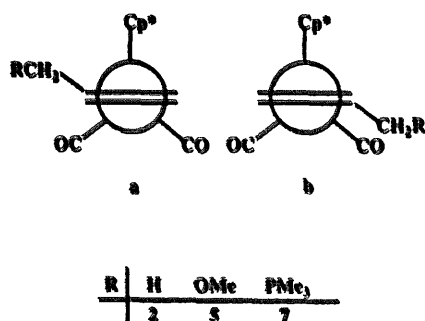
Scheme 4. Rotamers (a, b) for alkene complexes 2, 5 and 7.

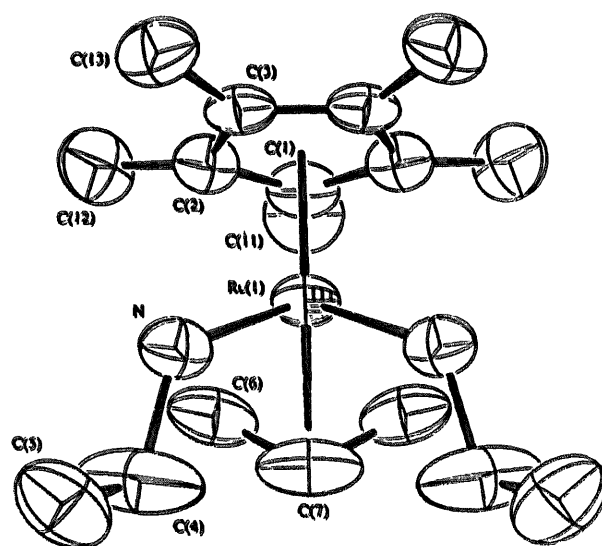| R	H	OMe	PMe$_3$
	2	5	7

Fig. 1. The molecular structure of the cation [Cp*Re(η^3-C$_3$H$_5$)(NH$_2$Et)$_2$]$^+$. 50% probability thermal ellipsoids are shown for the non-hydrogen atoms. The unlabeled atoms are related to the labeled ones by crystallographic mirror symmetry.
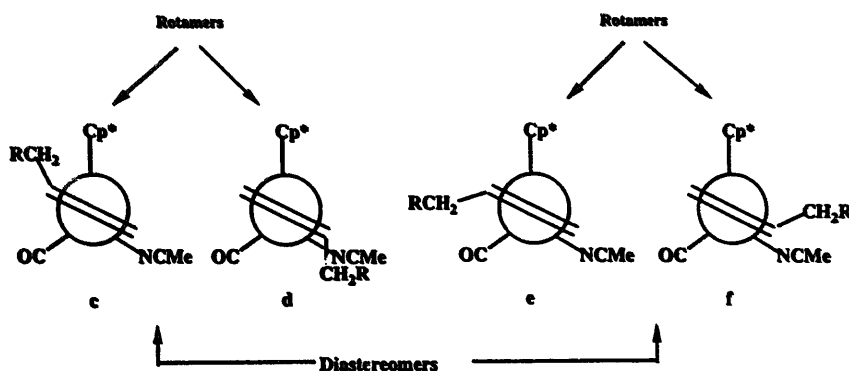
Scheme 5. Possible structures for the alkene complex [Cp*Re(η^2-CH$_2$CHCH$_2$PMe$_3$)(CO)(NCMe)]$^+$ (9) (R = PMe$_3$).

ing complex 9, which will depend on the site of nucleophilic attack and the most stable alkene rotamer. These possibilities are shown in Scheme 5 (c–f). Now, the C=C axis of the alkene is expected to be tilted toward the poorest π-accepting substituent, which in this case is MeCN. There is both theoretical [19a] and experimental support for alkene tilting in this way in, for example, CpMo(NO)(CO)(alkene) [20] and, more importantly, the rhenium complexes [CpRe(NO)(PPh$_3$)(alkene)]$^+$ [21] and [Cp*Re(NO)(PPh$_3$)(alkene)]$^+$ [22]. For [CpMo-(NO)(CO)(allyl)]$^+$, nucleophilic addition to the allyl group results in the formation of only a single diastereomer, and the product observed is that which could result from nucleophilic addition syn to the better π-accepting nitrosyl group in the exo isomer, or anti to the nitrosyl in the endo isomer [19,20,23]. If this regioselectivity can legitimately be extended to the present rhenium carbonyl acetonitrile complexes, it would predict that nucleophilic addition to the endo–allyl would occur anti to the carbonyl, as depicted in Scheme 5, and would lead, for 9, to formation of the diastereomer f (or its rotamer e) rather than configurations c or d (which would arise from addition syn to CO in the endo allyl group).

The pattern of allyl proton chemical shifts that we observe, i.e. δH$_2$ < δH$_1$ < δH$_3$ (for numbering scheme, see g in Scheme 6) is similar to the pattern carefully established for the thermodynamically preferred conformer in [Cp*Re(NO)(PPh$_3$)(alkene)]$^+$ by Gladysz (shown in Scheme 6, h) and on this basis we propose that the observed rotamer is e. However, we

cannot rule out rapid interconversion of e and f. (Notably, CpMo(NO)(CO)(propene) was observed to give a single set of propene resonances at room temperature, indicating a single diastereomer, but two sets of resonances corresponding to individual propene rotamers at −80°C [20].)

3. Conclusions

The acetonitrile ligands in [Cp*Re(η^3-C$_3$H$_5$)(CO)-(NCMe)][BF$_4$] (3) and [Cp*Re(η^3-C$_3$H$_5$)(NCMe)$_2$]-[BF$_4$] (4) are strong competitors with the allyl ligand as targets in the regiochemistry of nucleophilic attack, and are a poor choice of leaving group as regards ligand substitution at the metal. The coordinated acetonitrile has been observed to be reduced to coordinated ethylamine, and indeed both such groups were reduced in the case of the bis-acetonitrile complex 4. The only displacement of CH$_3$CN by PMe$_3$ we have observed is from 4, and, even then, only one of the acetonitriles could be easily substituted. This is in stark contrast with what might be thought (on the basis that N$_2$Ar and C$_3$H$_5$ are both 3e-donor ligands) to be rather closely related aryldiazenido complexes [Cp*Re(CO)(NCMe)-(N$_2$Ar)][BF$_4$] and [Cp*Re(NCMe)$_2$(N$_2$Ar)][BF$_4$] that we have studied. In these complexes, one or both acetonitrile groups can be readily substituted by a range of trialkyl or triaryl phosphines [24,25].

Clearly, replacing one or two CO groups by MeCN dramatically lowers the electrophilicity of the allyl
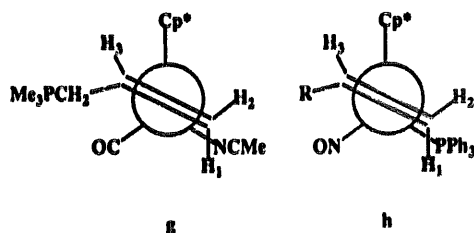
Scheme 6. Comparison of proposed thermodynamically preferred structure of 9 (g) with the thermodynamically preferred structure of monosubstituted alkene (R = CH$_2$) complex of [Cp*Re(NO)PPh$_3$)]$^+$ fragment (h) [22], with NMR proton labeling scheme.

group, and it is decreased further in the bis ethylamine complex 11, to the point that now no attack of PMe$_3$ occurs at the allyl group. Even so, only one of the two possible EtNH$_2$ ligands is substituted by PMe$_3$. One of the target compounds that prompted this work is the interesting stable hydrido allyl complex Cp*ReH(CO)-(η^3-C$_3$H$_5$) [26] and we were seeking a possible alternative method of synthesis by substituting acetonitrile in 3 by hydride. In view of the outcome, other strategies for its synthesis have needed to be developed, and will be reported in a future article.

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. All reagents were obtained from Aldrich except where mentioned. FTIR spectra were recorded on a Bomem Michelson-120 instrument. NMR spectra were recorded in the SFU NMR service by Mrs. M.M. Tracey using a Bruker WM-400 instrument operating at 400.13 MHz (for ^{1}H). Mass 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. Samples for FAB MS were dispersed in m-nitrobenzyl alcohol (NOBA). 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. Compounds 1, 3 and 4 were synthesized as described previously [2].

4.2. Preparation of Cp*Re(CO)$_2$(η^2-CH$_2$CHCH$_2$OMe) (5) and Cp*Re(η^3-C$_3$H$_5$)(CO)(COOMe) (6)

NaOMe (10 mg, 0.19 mmol) was added to a solution of complex 1 (11.9 mg, 0.024 mmol) in MeOH (3 ml) at 0°C and the solution was stirred for 3 h. The IR spectrum showed the appearance of new ν(CO) absorptions at 1956, 1942 and 1885 cm^{-1}. Solvent was pumped off and the solid residue was extracted with hexane (2 ml × 3), filtered through Celite and the solution was pumped to dryness at 0°C. The white solid obtained was shown by ^{1}H NMR and IR spectroscopy to be a mixture of isomers 5 and 6. In attempted separation of 5 and 6 by room-temperature chromatography on neutral alumina, the fraction that eluted with hexane contained pure 5, and that which eluted with ether contained a mixture of 5 and 6. Upon repeated chromatographing again, a fraction containing both 5 and 6 was obtained showing successively decreasing 6 (from IR) indicating that 6 is isomerizing to 5 and the equilibrium is being

displaced as 5 is removed. Pure 6 could not be obtained. Data for 5 were identical with those reported previously [7,8]. Spectroscopic data for 6: IR (hexane): ν(CO) 1944, 1634 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 4.20 (m, H$_c$), 3.40 (s, COOCH$_3$), 3.02 (dd, J_{sc} = 5.1 Hz, J_{ss} = 3.7 Hz, H$_s$), 2.94 (dd, J_{sc} = 5.1 Hz, J_{ss} = 3.7 Hz, H$_s$), 1.91 (s, Cp*), 1.10 (d, J_{ac} = 9.0 Hz, H$_a$), 0.69 (d, J_{ac} = 9.0 Hz, H$_a$).

4.3. Preparation of [Cp*Re(η^2-CH$_2$CHCH$_2$PMe$_3$)-(CO)$_2$][BF$_4$] (7)

Complex 1 (40 mg, 0.08 mmol) was dissolved in CH$_2$Cl$_2$ (4 ml), and excess of 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 1885 cm^{-1} due to complex 7. Solvent and excess PMe$_3$ were pumped off over 2 h. The residue was washed with 2 ml ether then recrystallized from CH$_2$Cl$_2$-hexane (1:6). The product was obtained as a white solid: m.p. 210-211°C. Yield: 41 mg (0.07 mmol, 88%). IR (CH$_2$Cl$_2$): ν(CO) 1885, 1964 cm^{-1}. FAB MS (m/z): 495 (M$^+$ of cation), 419 (M$^+$-PMe$_3$, base), 391 (M$^+$-PMe$_3$-CO), 389 (M$^+$-PMe$_3$-CO-2H), 361 (M$^+$-PMe$_3$-2CO), 359 (M$^+$-PMe$_3$-2CO-2H). ^{1}H NMR (CD$_2$Cl$_2$): δ 3.18 (m, H$_s$), 1.97 (s, Cp*), 1.88 (d, J_{PH} = 13.9 Hz, PMe$_3$), 1.86 (m, H$_1$), 1.64 (m, H$_3$ and H$_4$, overlapped), 1.37 (m, H$_2$). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 208.87 (s, CO), 207.08 (s, CO), 99.73 (s, C$_5$Me$_5$), 34.98 (d, J_{PC} = 42.3 Hz, -CH$_2$PMe$_3$), 27.49 (s, d in ^{1}H-coupled spectrum, =CH-), 26.47 (s, t in ^{1}H-coupled spectrum, =CH$_2$), 10.37 (s, C$_5$(CH$_3$)$_5$), 8.24 (d, J_{PC} = 53.3 Hz, P(CH$_3$)$_3$). ^{31}P{^{1}H} NMR (CD$_3$CN): δ 29.73 (s, PMe$_3$). Anal. Found: C, 37.30; H, 4.91. C$_{18}$H$_{29}$BF$_4$O$_2$PRe. Calc.: C, 37.18; H, 5.03%.

4.4. Preparation of [Cp*Re(η^3-C$_3$H$_5$)(CO)(NH$_2$Et)]-[BF$_4$] (8)

Complex 3 (63.9 mg, 0.12 mmol) was dissolved in THF (5 ml) at 0°C. NaBH$_4$ (6 mg, 0.16 mmol) and two drops of H$_2$O were added to the solution. The ν(CO) band from 3 disappeared after the solution was stirred for 3 h at 0°C and was replaced by a new ν(CO) absorption at 1937 cm^{-1}. The reaction mixture was filtered through Celite, and the solvent pumped off. The residue was extracted with THF-hexane (5:1) and re-crystallized from THF-hexane (1:6). A yellowish solid was obtained in analytical purity. Yield: 30 mg (0.058 mmol, 48%). m.p.: at 180°C, the sample decomposed and gave a black solid. IR (THF): ν(CO) 1937 cm^{-1}. FAB MS (m/z): 436 (M$^+$ of cation), 391 (M$^+$-EtNH$_2$), 389 (M$^+$-EtNH$_2$-2H, base), 361 (M$^+$-EtNH$_2$-CO-2H). ^{1}H NMR (acetone-d$_6$, δ): 5.00 (m, H$_c$), 3.95 (br, NH$_2$), 3.76 (br, NH$_2$), 3.12 (m, H$_s$), 2.73 (m, H$_s$), 2.55 (m, CH$_2$), 2.05 (d, J_{ac} = 9.7 Hz, H$_a$), 1.98 (s, Cp*),

1.48 (d, J_{ac} = 8.5 Hz, H$_a$), 1.05 (t, CH$_3$). Anal. Found: C, 37.01; H, 5.15; N, 2.62. C$_{16}$H$_{27}$BF$_4$NRe. Calc.: C, 36.79; H, 5.20; N, 2.67%.

4.5. Preparation of [Cp*Re(η²-CH₂CHCH₂PMe₃)-(CO)(NCMe)][BF₄] (9)

Complex 3 (20 mg, 0.04 mmol) was dissolved in CH$_2$Cl$_2$ (4 ml), and PMe$_3$ (0.1 ml, 0.97 mmol) was added to this solution. The mixture was stirred at room temperature for 30 min, at the end of which the IR showed a ν(CO) band at 1823 cm^{-1}. Excess PMe$_3$ and solvent were pumped off and the residue was recrystallized from THF–hexane (2:5). A yellow solid was obtained, m.p. 85–86°C. Yield: 15.6 mg (0.026 mmol, 65%). IR (CH$_2$Cl$_2$): ν(CO) 1823 cm^{-1}. FAB MS (m/z): 508 (M$^+$ of cation), 467 (M$^+$-MeCN), 432 (M$^+$-PMe$_3$, base), 391 (M$^+$-PMe$_3$-MeCN), 389 (M$^+$-PMe$_3$-MeCN-2H). ^{1}H NMR (CD$_2$Cl$_2$): δ 3.01 (m, H$_5$), 2.70 (s, CH$_3$CN), 1.93 (m, H$_3$), 1.89 (d, J_{PH} = 14.0 Hz, PMe$_3$), 1.82 (m, H$_4$), 1.79 (s, Cp*), 1.71 (m, H$_1$), 1.43 (m, H$_2$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 128.50 (s, CN), 96.14 (s, C$_5$Me$_5$), 31.78 (s, =CH–), 26.02 (s, =CH$_2$), 25.85 (d, J_{PC} = 44.2 Hz, -CH$_2$PMe$_3$), 9.75 (s, C$_5$(CH$_3$)$_5$), 8.02 (d, J_{PC} = 53.2 Hz, PMe$_3$), 5.13 (s, CH$_3$CN). Anal. Found: C, 38.35; H, 5.54; N, 2.11. C$_{19}$H$_{32}$BF$_4$NOPRe. Calc.: C, 38.39; H, 5.43; N, 2.36%.

4.6. Preparation of Cp*Re(η³-C₃H₅)(CO)(NHCOCH₃) (10)

Complex 3 (30 mg, 0.058 mmol) was dissolved in MeOH (4 ml) at –78°C, and NaOH (10 mg, 0.25 mmol) was added to the solution, which was then stirred for 2 h. The solvent was pumped off, and the residue was extracted with hexane (2 ml × 3). The hexane solution was cooled to –78°C and pumped overnight to give the analytically pure product as a white solid, m.p. 148–149°C. Yield: 24 mg (0.054 mmol, 92%). IR (hexane): ν(CO) 1952, 1595 cm^{-1}. EI MS (m/z): 449 (M$^+$), 421 (M$^+$-CO), 379 (M$^+$-CO-C$_3$H$_6$, base), 360 (M$^+$-NH$_2$COMe-CO-2H). ^{1}H NMR (C$_6$D$_6$): δ 4.39 (m, H$_c$), 3.34 (br, NH), 2.48 (m, H$_s$), 2.08 (s, CH$_3$CO), 1.92 (m, H$_s$), 1.60 (d, J_{ac} = 5.5 Hz, H$_a$), 1.54 (s, Cp*), 0.76 (d, J_{ac} = 4.2 Hz, H$_a$). Anal. Found: C, 43.12; H, 5.59; N, 3.11. C$_{16}$H$_{24}$NO$_2$Re. Calc.: C, 42.84; H, 5.39; N, 3.12%.

4.7. Preparation of [Cp*Re(η³-C₃H₅)(NH₂Et)₂][BF₄] (11)

Complex 4 (50 mg, 0.094 mmol) was dissolved in THF (2 ml), and NaBH$_4$ (15 mg, 0.40 mmol) and two drops of H$_2$O were added and the solution was stirred for 4 h. The reaction mixture was filtered through Celite, and solvent was pumped off. The residue was

extracted with THF–hexane (6:1), and recrystallized from THF–hexane (1:5), m.p. 132–133°C. Yield: 46 mg (0.085 mmol, 90%). FAB MS (m/z): 453 (weak, M$^+$ of cation), 408 (M$^+$-NH$_2$Et), 406 (M$^+$-NH$_2$Et-2H), 362 (M$^+$-2NH$_2$Et-H, base). ^{1}H NMR (acetone-d_6): δ 3.77 (m, H$_c$), 3.50 (br, NH$_2$), 3.38 (br, NH$_2$), 2.50 (m, CH$_2$), 2.44 (d, J_{sc} = 4.9 Hz, H$_s$), 1.67 (s, Cp*), 1.52 (d, J_{ac} = 6.7 Hz, H$_a$), 1.10 (t, J_{H-H} = 7.0 Hz, CH$_3$). Anal. Found: C, 37.62; H, 6.07; N, 4.86. C$_{17}$H$_{34}$BF$_4$N$_2$Re. Calc.: C, 37.85; H, 6.35; N, 5.19%.

4.8. Preparation of [Cp*Re(η³-C₃H₅)(NCMe)(PMe₃)]-[BF₄] (12)

PMe$_3$ (0.5 ml, 4.83 mmol) was added to a solution of complex 4 (50.2 mg, 0.097 mmol) in CH$_2$Cl$_2$, then stirred overnight at room temperature, to give a yellow solution. The solvent and excess PMe$_3$ were pumped off and the residue was recrystallized from THF–hexane (1:6) to give a pale yellow solid, m.p. 133–134°C. Yield: 32.7 mg (0.058 mmol, 60%). FAB MS (m/z): 480 (M$^+$ of cation), 439 (M$^+$-CH$_3$CN, base), 437 (M$^+$-MeCN-2H), 419 (M$^+$-PMe$_2$), 405 (M$^+$-PMe$_2$CH$_2$). ^{1}H NMR (CDCl$_3$): δ 3.68 (m, H$_c$), 2.84 (d, J_{PH} = 2.2 Hz, CH$_3$CN), 2.26 (m, H$_s$), 2.14 (m, H$_a$), 1.73 (s, Cp*), 1.45 (m, H$_a$), 1.38 (d, J_{PH} = 8.8 Hz, PMe$_3$), 1.03 (m, H$_a$). Anal. Found: C, 38.06; H, 5.85; N, 2.20. C$_{18}$H$_{32}$BF$_4$NRe. Calc.: C, 38.17; H, 5.70; N, 2.47%.

4.9. Preparation of [Cp*Re(η³-C₃H₅)(NH₂Et)(PMe₃)][BF₄] (13)

Method A

Complex 12 (36 mg, 0.064 mmol) was dissolved in THF (3 ml), NaBH$_4$ (10 mg, 0.26 mmol) and two drops of H$_2$O were added to the solution, which was then stirred for 3 h. The solvent was pumped off and the residue was extracted with THF, and recrystallized from THF–hexane (1:5) to give a yellowish solid, m.p. 163–164°C. Yield: 31 mg (0.054 mmol, 84%). FAB MS (m/z): 484 (M$^+$ of cation), 439 (M$^+$-NH$_2$Et, base), 437 (M$^+$-NH$_2$Et-2H). ^{1}H NMR (CDCl$_3$): δ 3.67 (m, H$_c$), 3.15 (br, NH$_2$), 2.58 (br, NH$_2$), 2.25–2.20 (m, CH$_2$), 1.92 (m, H$_s$), 1.83 (m, H$_s$), 1.69 (s, Cp*), 1.43 (m, H$_a$), 1.39 (d, J_{PH} = 7.4 Hz, PMe$_3$), 1.17 (t, J_{H-H} = 7.0 Hz, CH$_3$), 1.13 (m, H$_a$). Anal. Found: C, 37.75; H, 6.63; N, 2.35. C$_{18}$H$_{36}$BF$_4$NPRe. Calc.: C, 37.90; H, 6.36; N, 2.46%.

Method B

PMe$_3$ (0.25 ml, 2.4 mmol) was added to a solution of 11 in CH$_2$Cl$_2$ (22 mg, 0.04 mmol) stirred at room temperature overnight. IR showed the ν(CO) band for 13. Solvent was pumped off, the residue was recrystallized from CH$_2$Cl$_2$/hexane (1:8) to give pure complex 13.

4.10. X-Ray structure determination for [endo-Cp*Re(η³-C₃H₅)(NH₂Et)₂][ReO₄].solv

4.10. X-Ray structure determination for [endo-Cp*Re(η³-C₃H₅)(NH₂Et)₂][ReO₄].solv

A solution of 11 in acetone–toluene (2:1) was kept at 0–5°C in the refrigerator over a period of 3 months. Yellow crystals were isolated and were stored in the refrigerator for a further six months before the structure determination. Crystals were sealed in glass capillary tubes with a trace of apiezon grease as adhesive. Data were recorded at ambient temperature with an Enraf Nonius CAD4F diffractometer, using graphite-monochromatized Mo K α radiation. Two intensity standards were measured every hour of exposure time, and showed no significant variations in intensity until very near the end of the data collection (96% complete), when the diffracted intensities declined precipitously in a few hours to effectively zero. Visual examination of the sample revealed no crystal movement, but no diffraction maxima could be located again by using the automatic searching routine. A second crystal, which yielded an identical unit cell (within e.s.d.s) was used to remeasure (and replace in the analysis) the 73 reflections affected by this decay. A few strong reflections of common indices for the two crystals showed relative intensities (prior to the decay) proportionate to the estimated crystal volumes. No significant variations in the intensities of the standard reflections for the second crystal were observed. All data were corrected for absorption by the gaussian integration method and corrections were carefully checked against measured psi scans for both crystals. Data reduction included corrections for Lorentz and polarization effects. The structure was solved by using only the data from the first crystal. An independent scale factor for the data from the second crystal was refined when these data were included in the refinement.

Appropriate coordinates and anisotropic thermal parameters, according to the site symmetry, for all non-hydrogen atoms of the cation and perrhenate anion were refined. Hydrogen atoms were placed in calculated positions 0.95 Å from their respective carbon atoms or 0.92 Å from the nitrogen atom, and with isotropic temperature factors initially proportional to the C- or N-atom equivalent isotropic temperature factors. In subsequent cycles of refinement, the coordinate shifts for the hydrogen atoms were linked with those for their respective host atoms. A mean isotropic temperature factor for the hydrogen atoms of the Cp*, another for those of the allyl group, and two others for the methyl and methylene groups, of the ethylamine ligand were refined, and the shifts applied to the individual values.

The most significant peak (2.4(3) e Å⁻³) in an electron density difference map was situated on the mirror plane about 0.8 Å from the rhenium atom, Re(2), of the perrhenate anion. Given the method of synthesis, this peak may represent the occasional presence of an

alternate anion (iodide or iodate) or perhaps an alternate orientation of the perrhenate anion. A partial rhenium atom (Re(3)) was included at this site and the occupancy of the original perrhenate atoms were modified accordingly, so that the total anion site occupancy remained one. The relative occupancy and the position of Re(3) were then included in the refinement, and its thermal parameters were constrained to those of Re(2). The occupancy ratio refined to 0.977(3)/0.023 for Re(2)/Re(3). The electron density in this region was thus reasonably accounted for. Clearly, if we had posited an iodine atom for the Re(3) site, then this occupancy ratio would have been a little smaller, but it was not reasonable to attempt to distinguish between these two possibilities solely on the basis of the diffraction data. (The IR spectrum of the crystal sample gave a strong absorption band at 920 cm⁻¹ in KBr, which is in agreement with the literature value of ν_3 (Re–O) 918 cm⁻¹ for ReO₄⁻ [27].)

The electron density difference map also revealed peaks which we associate with disordered multiple orientations of solvent molecules of crystallization about the mirror plane, which did not lead to a simple interpretation. An NMR spectrum of redissolved crystals from the same sample showed the presence of both acetone and toluene in about 2:1 ratio. In view of the complexity of the disorder, this region was finally treated by refining the positions and occupancies of seven carbon atoms located at the major peak positions (five on the mirror plane and two general) and a single isotropic temperature factor for the set. This adequately accounted for the electron density in this region. The refined occupancies indicate there to be approximately

Table 2
Fractional atomic coordinates and equivalent isotropic temperature factors (Å)² for the non-hydrogen atoms of the complex cation and perrhenate anion of [Cp*Re(η³-C₃H₅)(NH₂Et)₂][ReO₄].solv

Atom	x	y	z	U_{eq} [a]
Re(1)	0.24053(5)	0.2500	0.87857(2)	0.0432
Re(2)	0.33405(10)	0.7500	0.95296(3)	0.0529
O(1)	0.4644(11)	0.7500	1.0008(4)	0.072
O(2)	0.3598(9)	0.6300(5)	0.9177(2)	0.080
O(3)	0.1532(12)	0.7500	0.9771(4)	0.092
N	0.2847(8)	0.3718(6)	0.9405(2)	0.054
C(1)	0.2848(14)	0.2500	0.7996(4)	0.050
C(2)	0.3588(10)	0.3504(8)	0.8202(3)	0.051
C(3)	0.4824(9)	0.3104(7)	0.8508(3)	0.046
C(11)	0.1754(18)	0.2500	0.7559(5)	0.080
C(12)	0.3332(12)	0.4704(8)	0.8045(4)	0.083
C(13)	0.5982(9)	0.3834(8)	0.8767(3)	0.066
C(4)	0.1724(13)	0.4035(12)	0.9790(4)	0.090
C(5)	0.2416(12)	0.4588(9)	1.0238(3)	0.075
C(6)	0.0328(10)	0.1489(10)	0.8667(4)	0.066
C(7)	0.0037(14)	0.2500	0.8937(5)	0.057

[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(η^3-C$_3$H$_5$)(NH$_2$Et)$_2$][ReO$_4$].solv

Re(1)-N	2.228(7)	N-Re(1)-N' [a]	79.8(4)
Re(1)-C(1)	2.160(11)	N-Re(1)-Cp* [b]	114.5
Re(1)-C(2)	2.215(8)	N-Re(1)-Allyl [c]	101.7
Re(1)-C(3)	2.333(8)	Cp*-Re(1)-Allyl	132.0
Re(1)-Cp*	1.892	C(4)-N-Re(1)	125.2(6)
Re(1)-C(6)	2.177(9)	C(2)-C(1)-C(2)'	108.6(10)
Re(1)-C(7)	2.090(13)	C(11)-C(1)-C(2)	125.0(5)
Re(1)-Allyl	1.884	C(3)-C(2)-C(1)	106.5(8)
N-C(4)	1.470(10)	C(12)-C(2)-C(1)	126.5(8)
C(1)-C(2)	1.451(11)	C(12)-C(2)-C(3)	125.9(9)
C(1)-C(11)	1.511(16)	C(3)'-C(3)-C(2)	109.2(5)
C(2)-C(3)	1.430(11)	C(13)-C(3)-C(2)	125.7(8)
C(2)-C(12)	1.486(12)	C(13)-C(3)-C(3)'	125.0(5)
C(3)-C(3)'	1.418(17)	C(5)-C(4)-N	114.5(9)
C(3)-C(13)	1.490(11)	C(6)-C(7)-C(6)'	114.1(13)
C(4)-C(5)	1.495(12)	O(2)-Re(2)-O(1)	109.3(3)
C(6)-C(7)	1.412(12)	O(2)-Re(2)-O(2)' [d]	110.6(5)
Re(2)-O(1)	1.712(9)	O(3)-Re(2)-O(1)	108.6(5)
Re(2)-O(2)	1.713(6)	O(3)-Re(2)-O(2)	109.5(3)
Re(2)-O(3)	1.695(10)		

[a] indicates (x, $1/2 - y$, z).

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

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

[d] indicates (x, $3/2 - y$, z).

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one molecule (acetone or toluene) in the site, i.e. 0.5 solvent molecules in the asymmetric unit.

A weighting scheme based on counting statistics was applied such that $\langle w(|F_o| - F_c|)^2\rangle$ was near constant as a function of both $|F_o|$ and $\sin\theta/\lambda$. Final full matrix least-squares refinement of 158 parameters (including an extinction parameter) [28] for 1444 data ($I_o \geqslant 2.5\sigma(I_o)$) converged at $R = 0.028$. Crystallographic details are summarized in Table 2. Final fractional atomic coordinates for the non-hydrogen atoms of the cation and the perrhenate anion are listed in Table 3. The programs used for absorption corrections, data reduction, structure solution, initial refinement and plot generation were from the NRCVAX Crystal Structure System [29]. Final refinement was made using CRYSTALS [30]. Complex scattering factors for neutral atoms [31] were used in the calculation of structure factors. Computations were carried out on MicroVAX-II and 80486 computers.

5. Supplementary material

5.1. For [Cp*Re(η^3-C$_3$H$_5$)(NH$_2$Et)$_2$][ReO$_4$].solv

Additional crystallographic details (one page), coordinates and isotropic temperature factors for the atomic sites of varied occupancy associated with the disordered anion and solvent, and hydrogen atoms of the cation (one page), anisotropic thermal parameters (one page), intramolecular torsion angles (one page) and table of observed and calculated structure factors (13 pages).

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