

Synthesis and X-ray structures of mono- and bis-acetonitrile derivatives of the cationic rhenium allyl complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)]\text{[BF}_4\text{]}$

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Abstract

Replacement of CO ligands in the η^3 -allyl complex $[\text{Cp}^*\text{Re}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)]\text{[BF}_4\text{]}$ (**1**) has been accomplished by reacting **1** in acetonitrile with PhIO or Me_3NO to yield *endo* isomers of $[\text{Cp}^*\text{Re}(\text{CO})(\text{NCMe})(\eta^3\text{-C}_3\text{H}_5)]\text{[BF}_4\text{]}$ (**2**) and $[\text{Cp}^*\text{Re}(\text{NCMe})_2(\eta^3\text{-C}_3\text{H}_5)]\text{[BF}_4\text{]}$ (**3**) respectively. The assignment of the allyl proton resonances and the isomeric forms of **2** and **3** have been deduced with the aid of ^1H nuclear magnetic resonance nuclear Overhauser enhancement experiments. The X-ray crystal structures of **2** and **3** confirm that these are *endo* isomers. Poor quality crystals of **2** (with 0.5 toluene solvate) are monoclinic, of space group $P2_1/c$, with $Z = 4$, $a = 8.381(2)$ Å, $b = 15.389(2)$ Å, $c = 17.161(3)$ Å, $\beta = 91.71(2)^\circ$ and $V = 2212.4$ Å³. The structure refined to $R_F = 0.060$ for 1950 data ($I_o \geq 2.5\sigma(I_o)$). Crystals of **3** are orthorhombic, of space group $P2_12_12_1$, with $Z = 4$, $a = 11.296(2)$ Å, $b = 12.012(2)$ Å, $c = 14.760(2)$ Å and $V = 2002.7$ Å³. The structure refined to $R_F = 0.027$ for 1815 data ($I_o \geq 2.5\sigma(I_o)$). The rhenium atom is bonded to the allyl group in **3** with an Re–C(7) distance of 2.124(11) Å to the central carbon atom and an Re–C(6) distance of 2.177(12) Å and an Re–C(8) distance of 2.201(12) Å to the terminal carbon atoms. The acetonitrile groups are bound with an Re–N(1) distance of 2.089(7) Å and an Re–N(2) distance of 2.086(10) Å, and N=C with an N(1)–C(9) distance of 1.125(11) Å and an N(2)–C(11) distance of 1.134(14) Å.

Key words: Rhenium; Allyl; Acetonitrile; Pentamethylcyclopentadienyl; Nuclear magnetic resonance; Crystal structure

1. Introduction

Recently we [1,2] and others [3a] have reported the synthesis of the cationic cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp*) rhenium (dicarbonyl) allyl complexes $[\text{CpRe}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)]^+$ or $[\text{Cp}^*\text{Re}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)]^+$ using $[\text{Ph}_3\text{C}][\text{BF}_4]$ or $[\text{Ph}_3\text{C}][\text{PF}_6]$ to abstract hydride from the corresponding propene complexes. These cationic allyl complexes [3b] are of considerable interest with respect to (a) the barrier for *exo-endo* isomerization of the allyl group and (b) the possibility of further elaboration of the allyl group through reaction with nucleophiles, including which of the central or terminal carbon atoms is the preferred site for this addition.

In order to explore more widely the chemistry of the η^3 -allyl ligand in half-sandwich rhenium complexes of this type, we have sought to replace the CO group in

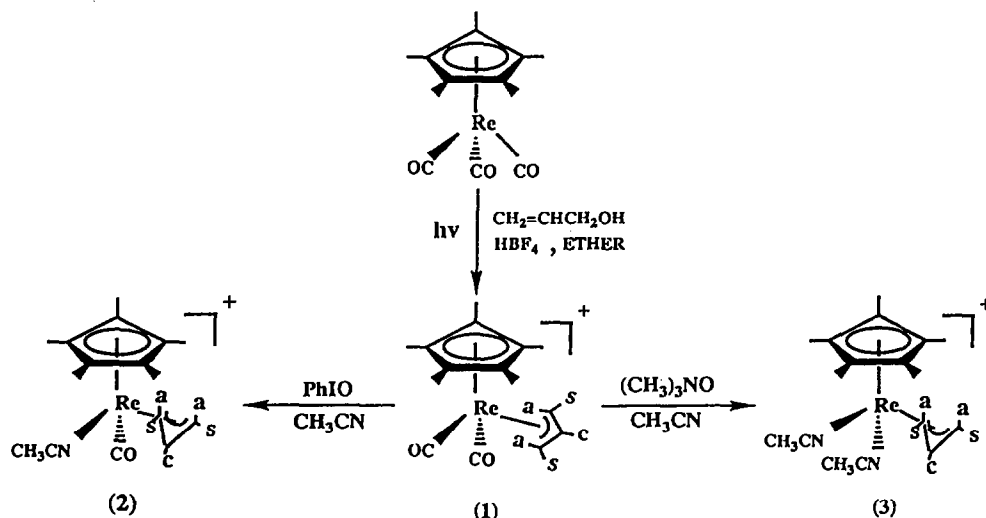
$[\text{Cp}^*\text{Re}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)]^+$ (**1**) to prepare derivatives of the composition $[\text{Cp}^*\text{Re}(\text{CO})(\text{L})(\eta^3\text{-C}_3\text{H}_5)]^+$ and $[\text{Cp}^*\text{Re}(\text{L})_2(\eta^3\text{-C}_3\text{H}_5)]^+$, where L is a $2e^-$ -donor ligand other than CO. This paper reports the results of our initial attempts in this direction. We describe the synthesis, characterization and X-ray structure determination of the mono- and bis-acetonitrile complexes $[\text{Cp}^*\text{Re}(\text{CO})(\text{NCMe})(\eta^3\text{-C}_3\text{H}_5)]\text{[BF}_4\text{]}$ (**2**) and $[\text{Cp}^*\text{Re}(\text{NCMe})_2(\eta^3\text{-C}_3\text{H}_5)]\text{[BF}_4\text{]}$ (**3**). Aspects of the chemistry of these complexes will be the subject of a subsequent paper.

2. Results and discussion

2.1. Synthesis

As mentioned in Section 1, the η^3 -allyl complex $[\text{Cp}^*\text{Re}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)]\text{[BF}_4\text{]}$ (**1**) can be generated by treating the propene complex $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-C}_3\text{H}_6)$ with $[\text{Ph}_3\text{C}][\text{BF}_4]$ [1,2]. We have not used this method in this work because the propene complex is available with only a low yield (about 28%) and must be sepa-

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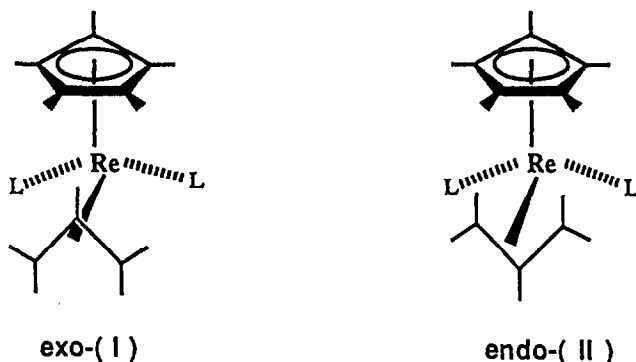


Scheme 1.

rated from secondary products (e.g. the hydrido(allyl) complex $\text{Cp}^*\text{Re}(\text{CO})(\text{H})(\eta^3\text{-C}_3\text{H}_5)$) formed in the photolysis of $\text{Cp}^*\text{Re}(\text{CO})_3$ with propene [1]. We have instead synthesized **1** by photolysing $\text{Cp}^*\text{Re}(\text{CO})_3$ with allyl alcohol in diethyl ether in the presence of HBF_4 (Scheme 1) [3b,4]. The dicarbonyl complex **1** is obtained as an equilibrium mixture of both *exo* and *endo* isomers [2].

Complex **1** reacted with iodosylbenzene (PhIO) in acetonitrile solution at 0°C over 2 h to effect the oxidative removal of only one CO group to produce *endo*- $[\text{Cp}^*\text{Re}(\text{CO})(\text{NCMe})(\eta^3\text{-C}_3\text{H}_5)][\text{BF}_4]$ (**2**) with an 80% yield after work-up as a yellowish solid. By contrast, trimethylamine oxide (Me_3NO) in acetonitrile solution reacted at room temperature with **1** to remove oxidatively both CO groups to give *endo*- $[\text{Cp}^*\text{Re}(\text{NCMe})_2(\eta^3\text{-C}_3\text{H}_5)][\text{BF}_4]$ (**3**) as a pale-yellow solid with a 90–94% yield after isolation (Scheme 1). Both **2** and **3** were obtained only as the *endo*- η^3 -allyl isomers, identified on the basis of ^1H nuclear magnetic reso-

nance (NMR) nuclear Overhauser enhancement (NOE) data and the X-ray structure determinations described below.



2.2. Spectroscopic properties

Complexes **2** and **3** have been characterized by microanalysis, IR, ^1H NMR and fast-atom bombardment (FAB) mass spectroscopy (MS) (Table 1). Com-

TABLE 1. Spectroscopic data for 1–3

Complex	IR (CH_2Cl_2) $\nu_{(\text{CO})}$ (cm^{-1})	FAB MS m/z (^{187}Re)	^1H NMR (CDCl_3) δ (ppm)
1 ^a	2053 s, 1999 s	419 (M^+), 391 ($\text{M}^+ - \text{CO}$) (base), 361 ($\text{M} - 2\text{CO} - 2\text{H}$)	4.73 (m, H_c), 3.82 (d, $J_{sc} = 5.6$ Hz, H_s), 2.21 (s, C_5Me_5), 1.87 (d, $J_{ac} = 9.9$ Hz, H_a)
2	1975 s	432 (M^+), 391 ($\text{M}^+ - \text{CH}_3\text{CN}$), 389 ($\text{M}^+ - \text{CH}_3\text{CN} - 2\text{H}$) (base), 361 ($\text{M}^+ - \text{CH}_3\text{CN} - \text{CO} - 2\text{H}$), 359 ($\text{M}^+ - \text{CH}_3\text{CN} - \text{CO} - 4\text{H}$)	4.85 (m, H_c), 3.21 (m, H'_s), 3.16 (m, H_s), 2.80 (s, CH_3CN), 2.04 (d, $J_{a'c} = 11.6$ Hz, $\text{H}_{a'}$), 1.98 (s, C_5Me_5), 1.33 (d, $J_{ac} = 9.28$ Hz, H_a)
3		445 (M^+), 404 ($\text{M}^+ - \text{CH}_3\text{CN}$) (base), 361 ($\text{M}^+ - 2\text{CH}_3\text{CN} - 2\text{H}$)	3.81 (m, H_c), 2.80 (s, CH_3CN), 2.47 (d, $J_{sc} = 5.04$ Hz, H_s), 1.71 (s, C_5Me_5), 1.47 (d, $J_{ac} = 6.30$ Hz, H_a)

^a IR and NMR data are for the *endo* isomer.

plex **2** exhibited the expected single $\nu(\text{CO})$ absorption in the IR spectrum and this occurs at 1975 cm^{-1} in CH_2Cl_2 solution, shifted to a lower wavenumber in comparison with that of the dicarbonyl complex **1** (2053 and 1999 cm^{-1} in CH_2Cl_2 [2]) because MeCN is a poorer π acid. Of course, no $\nu(\text{CO})$ absorption occurred for **3**, indicating complete replacement of the CO ligands and no contamination with **2**. Only very weak IR absorption bands were observed for **2** and **3** in the region of 2300 cm^{-1} where $\nu(\text{C}\equiv\text{N})$ would be expected to occur and none could be unambiguously assigned to this vibration.

The positive-ion FAB MS of **2** gave a strong parent M^+ peak at $m/z = 432$ for the cation, and the base peak at $m/z = 389$ corresponded to the loss of MeCN and 2H from M^+ . The loss of two H atoms from the C_5Me_5 ligand in the fragmentation of pentamethylcyclopentadienyl rhenium compounds is well documented [1,5]. Notably, there was no peak at $m/z = 404$ corresponding to loss of CO from M^+ . The FAB MS of **3** gave a parent M^+ peak at $m/z = 445$, but the intensity was weak in comparison with the parent peak for **2**, presumably reflecting greater lability with a second MeCN ligand. A peak at $m/z = 404$ resulted from loss of one MeCN and the base peak for **3** at $m/z = 361$ corresponded to the loss of two MeCN ligands and two H atoms.

The ^1H NMR spectrum for **3** is straightforward with singlets at $\delta = 1.71\text{ ppm}$ (Cp^*) and $\delta = 2.80\text{ ppm}$ (MeCN) and three resonances corresponding to the H_c (multiplet at $\delta = 3.81\text{ ppm}$), H_s (doublet at $\delta = 2.47\text{ ppm}$) and H_a (doublet at $\delta = 1.47\text{ ppm}$) protons of the allyl group because of the plane of symmetry. Notably, these resonances are all shifted upfield compared with the same resonances for **1** (*endo* isomer) (Table 1). The assignments for H_c , H_a and H_s are straightfor-

ward, and were confirmed by NOE experiments (see below).

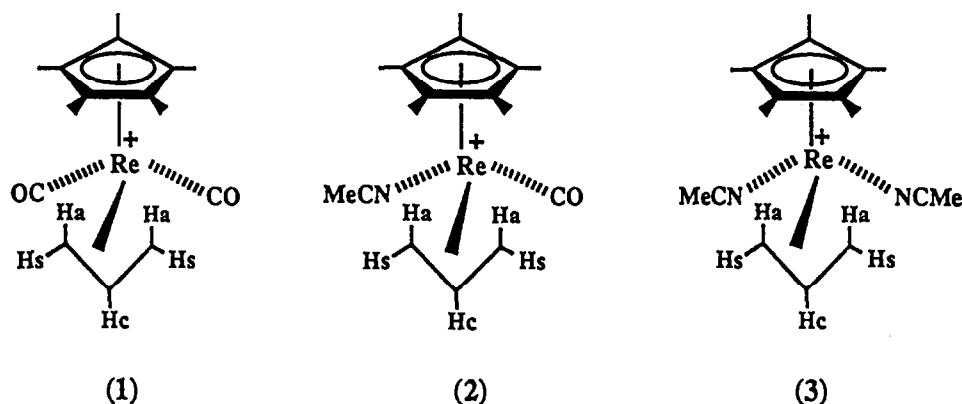
Complex **2** does not possess a plane of symmetry so that, in addition to the resonances for Cp^* ($\delta = 1.98\text{ ppm}$) and MeCN ($\delta = 2.80\text{ ppm}$), all five protons of the allyl group give individual resonances. Based on NOE data these have the assignments shown in Table 1, where H_a and H_s are the *anti* and *syn* protons on one terminal carbon atom and H'_a , H'_s are on the other terminal carbon atom.

2.3. ^1H nuclear magnetic resonance nuclear Overhauser enhancement experiments

It is possible for the η^3 -allyl ligand to adopt two different orientations with respect to the remaining ligand environment. These are termed *exo* (I) and *endo* (II) [6] as illustrated for piano-stool complexes of the type considered here.

In some cases, only one of these isomers is observed, but often both isomers occur in solution and frequently there is rapid interconversion between them. Additionally, stereochemical non-rigidity in a given isomer may interconvert the H_a and H_s protons. In the case of the dicarbonyl complex **1**, it was demonstrated that rapid interconversion of *exo* and *endo* isomers occurred in solution with no scrambling of the *syn* and *anti* protons, and the X-ray crystal structure indicated both isomers to be present in the solid [2]. It was therefore of considerable interest to compare these properties of **1** with those of the new cationic complexes **2** and **3** to evaluate the effect of replacing CO by MeCN in the rhenium coordination sphere.

For **3**, irradiation of the Cp^* resonance resulted in a strong NOE enhancement of the H_a resonance at $\delta = 1.47\text{ ppm}$, indicating that this is the *endo* isomer (Fig. 1). Irradiation of the H_s resonance at $\delta = 2.47$



ppm caused an enhancement of the H_c and H_a resonances and confirmed the correctness of the assignments. There was no indication of $\text{H}_a\text{-H}_s$ exchange.

For **2**, irradiation of the Cp^* resonance gave a strong enhancement of the H_a resonance at $\delta = 1.33$ ppm, indicating that the isomer is *endo* (Fig. 2). The resonance for the other *anti* proton H'_a is very close to the Cp^* resonance position, so no enhancement could be observed for this signal. In fact, when irradiation of Cp^* is conducted, H'_a is unavoidably irradiated also, and this gives rise to the observed enhancement of the geminal proton H'_s signal at $\delta = 3.21$ ppm. Similarly, irradiation of H_a at $\delta = 1.33$ ppm results in enhancement of the H_s signal at $\delta = 3.16$ ppm. Again, there is no indication of $\text{H}_a\text{-H}_s$ or $\text{H}'_a\text{-H}'_s$ exchange, nor exchange of the $\text{H}_a\text{-H}'_a$ or $\text{H}_s\text{-H}'_s$ protons (*i.e.* no end-to-end interchange of the terminal allyl protons).

We had hoped that irradiation of the MeCN methyl resonance would allow us to observe which terminal allyl proton signals are due to the protons closest in proximity to the MeCN ligand and therefore to assign uniquely all the allyl protons. Unfortunately, this assignment could not be made with any degree of certainty, because irradiation of the MeCN signal could not be achieved without irradiating also the closely adjacent H_s and H'_s signals, which inevitably produced NOEs to H_a and H'_a . In the inverse experiment, irradi-

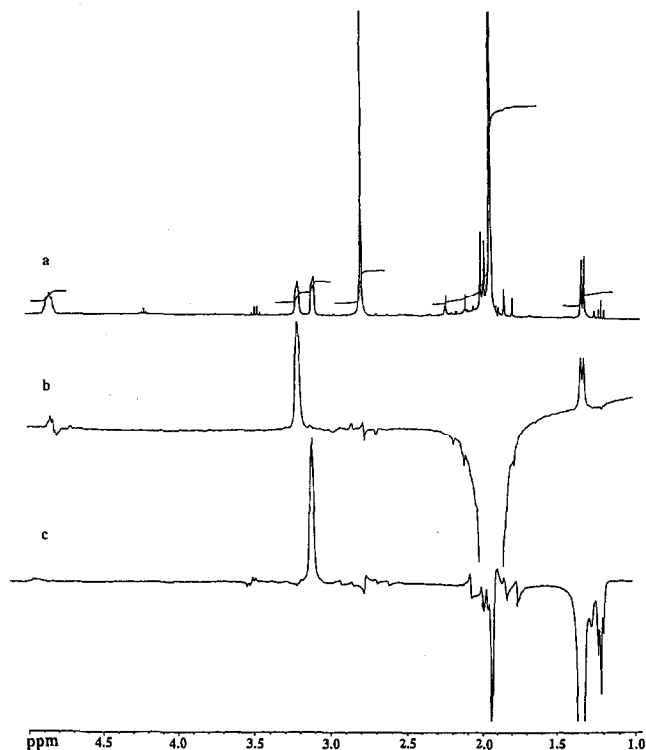


Fig. 2. Curve a, ^1H NMR spectrum of **2** in CDCl_3 ; curve b, NOE difference spectrum with irradiation of Cp^* at 1.98 ppm and H'_a at 2.04 ppm; curve c, NOE difference spectrum with irradiation of H_a at 1.33 ppm.

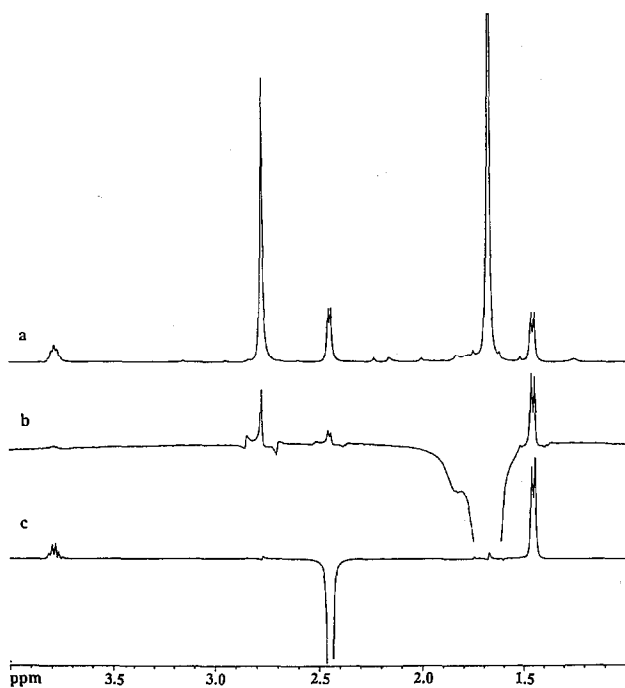


Fig. 1. Curve a, ^1H NMR spectrum of **3** in CDCl_3 ; curve b, NOE difference spectrum with irradiation of Cp^* at 1.71 ppm; curve c, NOE difference spectrum with irradiation of H_s at 2.47 ppm.

ation at $\delta = 1.33$ ppm (H_a) did not give any NOE of the MeCN methyl signal; however, neither did irradiation at Cp^* and H'_a (combined), and so no specific assignment of the two sets of allyl terminal protons can be made.

Irradiation of H_c at $\delta = 4.85$ ppm gave the expected enhancement of H_s and H'_s , confirming the assignment of the *syn* and *anti* protons. We conclude that both **2** and **3** are produced only as the *endo* isomers (in contrast with the dicarbonyl **1**) and that the allyl group in each case is undergoing no rearrangement within the time scale of the ^1H NMR experiment. In order to confirm that the *endo* isomer is thermodynamically preferred, **2** was heated in mixed solvents CDCl_3 -toluene (1.5:1 by volume) to reflux (at 110°C) for 12 h. The ^1H NMR confirmed the absence of the *exo* isomer.

2.4. X-ray crystal structures of **2** and **3**

The X-ray crystallographic structure determinations for **2** and **3** confirm the compositions indicated by the above spectroscopic data and demonstrate that these are *endo* stereoisomers in both cases. The structures of the cations are illustrated in Figs. 3 and 4, and selected

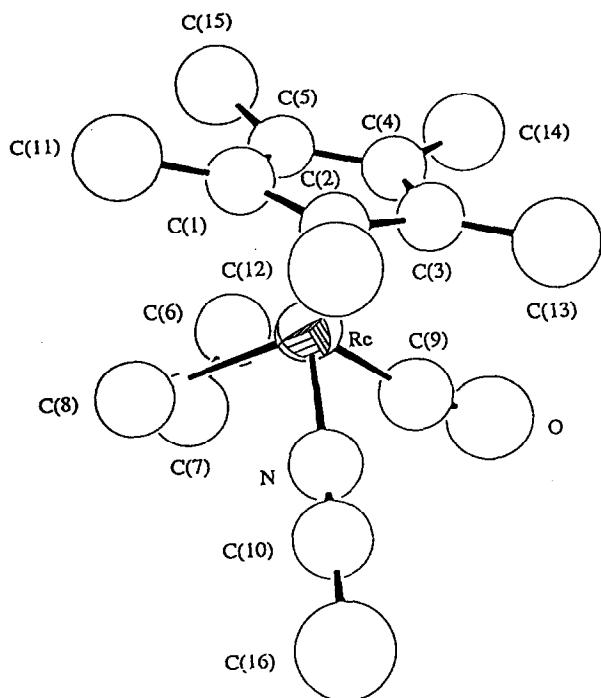


Fig. 3. The structure of the $[\text{Cp}^*\text{Re}(\text{CO})(\text{NCMe})(\eta^3\text{-C}_3\text{H}_5)]^+$ cation in **2**. 50% enclosure thermal ellipsoids or spheres are shown. Hydrogen atoms and one of the disordered orientations of the Cp^* ligand have been omitted for clarity.

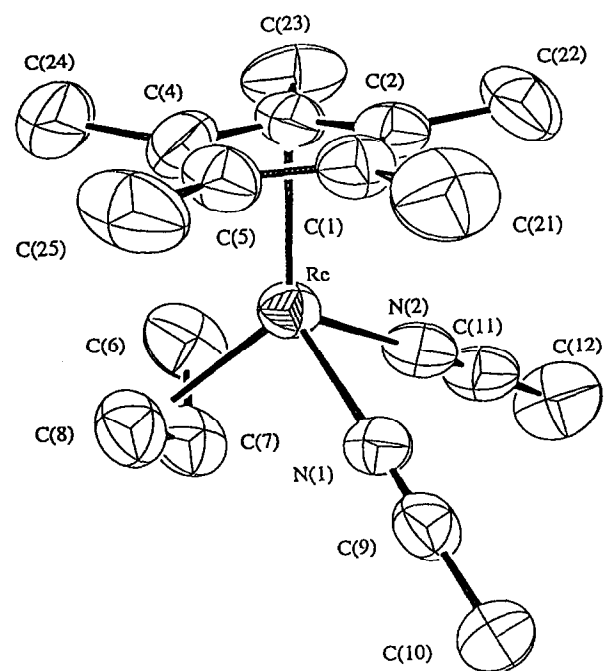


Fig. 4. The structure of the $[\text{Cp}^*\text{Re}(\text{NCMe})_2(\eta^3\text{-C}_3\text{H}_5)]^+$ cation in **3**. 50% enclosure thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity.

TABLE 2. Selected intramolecular distances and angles for the complex cation of $[\text{Cp}^*\text{Re}(\text{CO})(\text{NCMe})(\eta^3\text{-C}_3\text{H}_5)][\text{BF}_4] \cdot \frac{1}{2}\text{toluene}$

Distance (Å)		Distance (Å)	
Re–C(1)	2.26(1)	Re–C(105)	2.23(1)
Re–C(2)	2.21(1)	Re–Cp ^a	1.90
Re–C(3)	2.21(1)	Re–C(6)	2.24(2)
Re–C(4)	2.26(1)	Re–C(7)	2.21(2)
Re–C(5)	2.29(1)	Re–C(8)	2.27(2)
Re–C(101)	2.28(1)	Re–allyl ^b	1.99
Re–C(102)	2.29(1)	Re–C(9)	1.90(2)
Re–C(103)	2.23(1)	Re–N	2.06(2)
Re–C(104)	2.20(1)	O–C(9)	1.21(2)
C(10)–C(16)	1.55(3)	N–C(10)	1.09(2)
Angle (°)		Angle (°)	
N–Re–C(8)	79.4(6)	N–Re–allyl	100
N–Re–C(9)	84.5(7)	C(8)–C(7)–C(6)	124.(2)
Cp–Re–allyl	130	O–C(9)–Re	169.(2)
Cp–Re–C(9)	120	C(10)–N–Re	177.(2)
Cp–Re–N	115	C(16)–C(10)–N	179.(3)
C(9)–Re–allyl	97		

^a Cp denotes the centre of mass of the ten half-occupied ring carbon atom sites of the disordered Cp* ring.

^b allyl denotes the centre of mass of the carbon atoms of the allyl group.

bond lengths and interbond angles are listed in Tables 2 and 3.

The structures of **2** and **3** consist of discrete molecular ions with **2** having disordered solvent of crystallization. Although neither of the complex cations has crystallographic symmetry, there is, in **3**, an approximate mirror plane equating the two MeCN ligands and the two termini of the η^3 -allyl ligand. For **3** the Re–C(7) bond length to the central carbon of the allyl group is shorter than the Re–C(terminal) distances, as has been observed previously, for example in the *exo* isomer of $\text{Cp}^*\text{Re}(\text{CO})(\text{H})(\eta^3\text{-C}_3\text{H}_5)$ [7]. The dimensions for the coordinated MeCN groups are not exceptional [8*].

For **2** there are no significant intermolecular interactions. Such an open structure is consistent with the apparent high thermal motion and/or disorder found. For **3** there are a few interionic separations involving the disordered BF_4^- ion which are slightly less than the sum of the appropriate pairs of van der Waals radii, and one which appears to be markedly short: F(4)–C(10)* 2.59(3) Å (where the asterisk indicates the symmetry equivalent position $1+x, y, z$). Since F(4) belongs to the least partially occupied (0.18(1)) orientation of the disordered anion, it is unlikely that this represents a significant hydrogen-bonded interaction.

* A reference number with an asterisk indicates a note in the list of references.

TABLE 3. Selected intramolecular distances and angles for the complex cation of $[\text{Cp}^*\text{Re}(\text{NCMe})_2(\eta^3\text{-C}_3\text{H}_5)]\text{[BF}_4\text{]} (3)$

Distances (Å)		Distance (Å)	
Re–C(1)	2.313(9)	C(1)–C(21)	1.519(16)
Re–C(2)	2.285(10)	C(2)–C(3)	1.405(15)
Re–C(3)	2.196(11)	C(2)–C(22)	1.545(17)
Re–C(4)	2.199(12)	C(3)–C(4)	1.436(17)
Re–C(5)	2.249(10)	C(3)–C(23)	1.529(18)
Re–Cp ^a	1.898	C(4)–C(5)	1.472(16)
Re–C(6)	2.177(12)	C(4)–C(24)	1.502(20)
Re–C(7)	2.124(11)	C(5)–C(25)	1.505(18)
Re–C(8)	2.201(12)	C(6)–C(7)	1.439(19)
Re–allyl ^b	1.906	C(7)–C(8)	1.405(17)
Re–N(1)	2.089(7)	N(1)–C(9)	1.125(11)
Re–N(2)	2.086(10)	C(9)–C(10)	1.470(11)
C(1)–C(2)	1.382(15)	N(2)–C(11)	1.134(14)
C(1)–C(5)	1.394(15)	C(11)–C(12)	1.470(17)

Angle (°)		Angle (°)	
N(2)–Re–N(1)	80.6(3)	C(23)–C(3)–C(2)	125.3(11)
N(1)–Re–Cp	118.1	C(23)–C(3)–C(4)	126.3(11)
N(2)–Re–Cp	117.7	C(5)–C(4)–C(3)	105.9(10)
N(1)–Re–allyl	97.2	C(24)–C(4)–C(3)	126.2(12)
N(2)–Re–allyl	97.2	C(24)–C(4)–C(5)	126.9(13)
Cp–Re–allyl	132.6	C(4)–C(5)–C(1)	107.0(10)
C(5)–C(1)–C(2)	109.8(9)	C(25)–C(5)–C(1)	125.2(11)
C(21)–C(1)–C(2)	127.9(11)	C(25)–C(5)–C(4)	127.4(12)
C(21)–C(1)–C(5)	122.3(10)	C(8)–C(7)–C(6)	112.1(12)
C(3)–C(2)–C(1)	109.4(10)	C(10)–C(9)–N(1)	179.1(9)
C(22)–C(2)–C(1)	127.4(11)	C(12)–C(11)–N(2)	179.1(13)
C(22)–C(2)–C(3)	123.1(11)	C(9)–N(1)–Re	178.4(8)
C(4)–C(3)–C(2)	107.8(10)	C(11)–N(2)–Re	176.3(8)

^a Cp denotes the centre of mass of the five carbon atoms of the Cp* ring.

^b allyl denotes the centre of mass of the carbon atoms of the allyl group.

3. Experimental details

All reactions were carried out under dry nitrogen in a Schlenk apparatus. Solvents were purified by standard methods and were freshly distilled under dry nitrogen. $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ was obtained from Aldrich and was purified by sublimation. Fourier transform IR spectra were recorded on a Bomem Michelson-120 instrument for CH_2Cl_2 solutions. ^1H NMR and NOE spectra were recorded in the Simon Fraser University (SFU) NMR Service by Mrs. M.M. Tracey using a Bruker WM-400 instrument operating at 400.13 MHz. FAB mass spectra were obtained by Mr. G. Owen on a Hewlett–Packard model 5985 gas chromatography–MS instrument, equipped with a Phrasor Inc. FAB 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. Micro-

analyses were performed by Mr. M.K. Yang of the SFU Microanalytical Laboratory.

3.1. Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)]\text{[BF}_4\text{]} (1)$

A solution of $\text{Cp}^*\text{Re}(\text{CO})_3$ (216 mg, 0.53 mmol) in freshly distilled ether (40 ml) was placed in a Schlenk tube equipped with an inner condenser. 0.1 ml of allyl alcohol (Aldrich; 1.47 mmol) and 0.1 ml of $\text{HBF}_4 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ (Aldrich; 85%; 0.68 mmol) were added to this solution and then photolysed under UV light at the temperature of refluxing ether for 8 h. The resulting white precipitate was filtered off, washed with ether and recrystallized from CH_2Cl_2 –hexane as a white solid (yield, 140 mg, 0.277 mmol (52.2%)).

3.2. Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})(\text{NCMe})(\eta^3\text{-C}_3\text{H}_5)]\text{[BF}_4\text{]} (2)$

To a solution of **1** (79 mg, 0.156 mmol) in 8 ml of acetonitrile (which was dried with CaH_2 and freshly distilled under dry nitrogen) was added 93.3 mg (0.424 mmol) of PhIO [9]. The mixture was stirred for 2 h at 0 °C and monitored by IR spectroscopy. The solution was filtered through Celite; then the solvent was pumped off and the residue was washed with ether. Recrystallization from CH_2Cl_2 –hexane gave the product as a yellowish solid (yield, 65.1 mg, 0.126 mmol (80.6%); melting point (m.p.), 132–133 °C). Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{ONReBF}_4$: C, 37.01; H, 4.47; N, 2.70. Found: C, 37.04; H, 4.50; N, 2.68%.

3.3. Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{NCMe})_2(\eta^3\text{-C}_3\text{H}_5)]\text{[BF}_4\text{]} (3)$

A solution of **1** (75 mg, 0.148 mmol) in freshly distilled acetonitrile (5 ml) was placed in a Schlenk tube and 4.5 ml (0.34 mmol) of Me_3NO solution in acetonitrile (5.71 mg ml^{-1}) was added during 0.5 h. The solution was stirred at room temperature for 2 h and was monitored by IR spectroscopy, which showed disappearance of the $\nu(\text{CO})$ absorption bands for **1** and the growth and subsequent disappearance of the $\nu(\text{CO})$ absorption for **2** (1971 cm^{-1} in CH_3CN) by this time. The solvent was pumped off and the residue was washed with ether. It was then dissolved in tetrahydrofuran (THF) and recrystallized by careful addition of hexane. The product was obtained as a pale-yellow solid (yield, 90–94%; m.p. 142–143 °C). Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{N}_2\text{ReBF}_4$: C, 38.36; H, 4.92; N, 5.27%. Found: C, 38.36; H, 4.94; N, 5.38.

3.4. X-ray crystallography

Crystals of **2** were grown as small colourless plates, and **3** as yellow needles, both from solutions in THF–toluene (1:5 by volume). Those of **2** were of low

quality and proved to be the 0.5 toluene solvate by the subsequent structure determination. The presence of toluene in the sample from which the crystal was selected was confirmed by ^1H NMR spectroscopy (integration, 0.5). Numerous attempts to grow crystals of $[\text{Cp}^*\text{Re}(\text{CO})(\text{NCMe})(\eta^3\text{-C}_3\text{H}_5)][\text{BF}_4]$ using various solvent systems (CH_2Cl_2 -hexane; CH_2Cl_2 -ether; CH_2Cl_2 -THF) failed to yield good single crystals.

A crystal of **2** was mounted on a glass filament using epoxy resin as adhesive. A crystal of **3** was cleaved and a fragment was mounted in a glass capillary using Apiezon grease as adhesive. Data were recorded at ambient temperature with an Enraf-Nonius CAD4F diffractometer using graphite monochromated Mo K α radiation. Unit-cell dimensions were determined from 25 well-centred reflections (**2**, $30^\circ \leq 2\theta \leq 34^\circ$; **3**, $36^\circ \leq 2\theta \leq 44^\circ$). Two intensity standards were measured every hour of exposure time and those for **2** declined systematically in intensity by 23% while those for **3** showed no significant variations during the course of the measurements. The data were corrected for absorption by the gaussian integration method, and corrections were carefully checked against measured ψ scans. Data reduction also included corrections for intensity scale variation and for Lorentz and polarization effects.

The programs used for absorption corrections, data reduction, structure solution, refinement and plot generation were from the NRCVAX Crystal Structure System [10]. Final refinement was made using CRYSTALS [11]. Complex scattering factors for neutral atoms [12] were used in the calculation of structure factors. Computations were carried out on a MicroVAX-II and on 80486 processor-based computers. Crystallographic details are summarized in Table 4. Final fractional atomic coordinates for the non-hydrogen atoms of the complex cation of **2** are listed in Table 5 and those of **3** in Table 6.

3.5. Structure determination for **2**

In the case of **2** the systematic conditions led us to attempt solution in the space group $P2_1/c$, although there were 17 weak but observed ($I_0 \geq 2.5\sigma(I_0)$) reflections which violated the condition for the c glide. The structure was solved routinely from the Patterson map by the heavy-atom method. All non-hydrogen atoms of the molecular ions were located from electron density difference maps.

The entire structure displays rather high thermal parameters. Anisotropic thermal parameters were refined for Re which none the less remained relatively isotropic. Refined anisotropic thermal parameters for the methyl carbon atoms of the Cp* group were extreme (although not unreasonable in terms of the over-

TABLE 4. Crystallographic data for the structure determinations of $[\text{Cp}^*\text{Re}(\text{CO})(\text{NCMe})(\eta^3\text{-C}_3\text{H}_5)][\text{BF}_4] \cdot \frac{1}{2}\text{toluene}$ (**2**) and $[\text{Cp}^*\text{Re}(\text{NCMe})_2(\eta^3\text{-C}_3\text{H}_5)][\text{BF}_4]$ (**3**)

	2	3
Formula	$\text{ReF}_4\text{ONC}_{19.5}\text{BH}_{27}$	$\text{ReF}_4\text{N}_2\text{C}_{17}\text{BH}_{26}$
Formula weight	564.44	531.42
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a (Å)	8.381(2)	11.296(2)
b (Å)	15.389(2)	12.012(2)
c (Å)	17.161(3)	14.760(2)
β (°)	91.71(2)	
V (Å ³)	2212.4	2002.7
Z	4	4
ρ_c (g cm ⁻³)	1.695	1.762
$\lambda(\text{Mo K}\alpha_1)$ (Å)	0.70930	0.70930
$\mu(\text{Mo K}\alpha)$ (cm ⁻¹)	56.1	61.9
Minimum 2θ (°); maximum 2θ (°)	4; 44	4; 50
Transmission ^b	0.579–0.753	0.231–0.329
Crystal dimensions (mm × mm × mm)	0.11 × 0.27 × 0.30	0.30 × 0.35 × 0.38
R_F ^c	0.060	0.027
R_{wF} ^d	0.081	0.034

^a Cell dimensions were determined from 25 reflections (**2**, $30^\circ \leq 2\theta \leq 34^\circ$; **3**, $36^\circ \leq 2\theta \leq 44^\circ$).

^b The data were corrected for the effects of absorption by the gaussian integration method.

^c $R_F = \sum(|F_o| - |F_c|) / \sum|F_o|$ (**2**, 1950; **3**, 1815 data ($I_0 \geq 2.5\sigma(I_0)$)).

^d $R_{wF} = [\sum(w(|F_o| - |F_c|)^2) / \sum(wF_o^2)]^{1/2}$ for data ($I_0 \geq 2.5\sigma(I_0)$) (**2**, $w = [\sigma(F_o)^2 + 0.0005F_o^2]^{-1}$; **3**, $w = [\sigma(F_o)^2 + 0.0004F_o^2]^{-1}$).

all thermal motion of the complex) and this entire group was finally modelled, instead, with two half-occupancy sites for each atom and two isotropic thermal parameters, one for the methyl groups and another for the ring carbon atoms. Chemically equivalent C–C bond lengths and C–C–C bond angles within this group were restrained toward their respective mean values during refinement. Hydrogen atoms for the Cp* and allyl groups were included in calculated positions (C–H, 0.95 Å) with appropriate occupancies and their coordinate shifts were linked during refinement with those for the carbon atoms to which they were bound. A single parameter was refined for the isotropic thermal motion of the hydrogen atoms of the Cp* group and another for those of the allyl group.

An electron density difference map also suggested disorder of the BF₄-ion and it was finally modelled as two half-occupancy rigid groups, with a single isotropic thermal parameter for the fluorine atoms and another for boron. A region of electron density in a plane in the vicinity of the inversion centre at 0, $\frac{1}{2}$, 0 was ultimately modelled as two rigid toluene groups (including the H atoms on the rings) with refined partial occupancies. A single isotropic thermal parameter was

refined for the ring carbon atoms and another for the H atoms and the methyl carbon atoms. The methyl H atoms of the toluene, as well as of the acetonitrile ligand, were omitted as no clear evidence as to their locations could be obtained from electron density difference maps.

The possibility of lower symmetry (in particular, the space group $P2_1$) was investigated at some length, but an improved model was not obtained. A complete spherical shell of data ($22^\circ \leq 2\theta \leq 27^\circ$) was measured as a test of the assumed Laue symmetry. $R_{\text{merge}} = 0.039$ for 179 sets (166 of which were observed) of 'equivalent' data, after absorption correction, assuming Laue symmetry $2/m$, $R_{\text{merge}} = 0.032$ for 359 sets (321 of which were observed), assuming Laue symmetry m , and $R_{\text{merge}} = 0.041$ for 356 sets (314 of which were observed), assuming Laue symmetry 2. In no case did a reflection differ by as much as $10\sigma(I_o)$ from the mean value for the set of symmetry equated data.

TABLE 5. Atomic coordinates and isotropic or equivalent isotropic temperature factors for the non-hydrogen atoms of the complex cation of $[\text{Cp}^*\text{Re}(\text{CO})(\text{NCMe})(\eta^3\text{-C}_3\text{H}_5)][\text{BF}_4] \cdot \frac{1}{2}\text{toluene}$ (2)

Atom	x	y	z	U_{iso} (\AA^2)
Re	0.38476(8)	0.11060(4)	0.23038(4)	0.0639 ^a
C(1) ^b	0.165(2)	0.159(1)	0.2902(9)	0.067(2)
C(2) ^b	0.129(2)	0.083(1)	0.2457(9)	0.067(2)
C(3) ^b	0.218(2)	0.014(1)	0.2786(9)	0.067(2)
C(4) ^b	0.308(2)	0.047(1)	0.3418(9)	0.067(2)
C(5) ^b	0.273(2)	0.137(1)	0.3483(9)	0.067(2)
C(11) ^b	0.080(2)	0.246(2)	0.283(1)	0.111(5)
C(12) ^b	-0.002(2)	0.075(2)	0.182(1)	0.111(5)
C(13) ^b	0.203(2)	-0.082(1)	0.257(1)	0.111(5)
C(14) ^b	0.404(2)	-0.006(2)	0.401(1)	0.111(5)
C(15) ^b	0.325(2)	0.197(2)	0.416(1)	0.111(5)
C(101) ^b	0.132(2)	0.145(1)	0.2651(9)	0.067(2)
C(102) ^b	0.135(2)	0.056(1)	0.2468(9)	0.067(2)
C(103) ^b	0.244(2)	0.015(1)	0.2982(9)	0.067(2)
C(104) ^b	0.309(2)	0.078(1)	0.3482(8)	0.067(2)
C(105) ^b	0.238(2)	0.159(1)	0.3274(9)	0.067(2)
C(111) ^b	0.015(2)	0.213(2)	0.231(1)	0.111(5)
C(112) ^b	0.027(2)	0.010(2)	0.186(1)	0.111(5)
C(113) ^b	0.277(2)	-0.083(1)	0.303(1)	0.111(5)
C(114) ^b	0.416(2)	0.060(2)	0.419(1)	0.111(5)
C(115) ^b	0.253(3)	0.242(2)	0.374(1)	0.111(5)
C(6)	0.593(2)	0.186(1)	0.279(1)	0.098(6)
C(7)	0.559(2)	0.213(1)	0.204(1)	0.102(6)
C(8)	0.417(2)	0.246(1)	0.180(1)	0.099(6)
O	0.638(2)	-0.034(1)	0.2190(9)	0.132(5)
C(9)	0.548(2)	0.027(1)	0.218(1)	0.095(6)
N	0.333(2)	0.0870(9)	0.1143(9)	0.079(4)
C(10)	0.299(2)	0.076(1)	0.053(1)	0.088(5)
C(16)	0.248(3)	0.060(2)	-0.034(1)	0.130(8)

^a U_{eq} value, where U_{eq} is the cube root of the product of the principal components of the thermal ellipsoid.

^b Site occupancy, 0.5.

TABLE 6. Atomic coordinates and equivalent isotropic temperature factors for the non-hydrogen atoms of the complex cation of $[\text{Cp}^*\text{Re}(\text{NCMe})_2(\eta^3\text{-C}_3\text{H}_5)][\text{BF}_4]$ (3)

Atom	x	y	z	U_{eq} ^a (\AA^2)
Re	0.15352(3)	0.09565(3)	0.13110(2)	0.0458
C(1)	0.1492(9)	0.0761(8)	0.2870(6)	0.0580
C(2)	0.2223(9)	-0.0051(9)	0.2514(6)	0.0546
C(3)	0.3150(9)	0.0457(10)	0.2032(7)	0.0592
C(4)	0.3008(9)	0.1641(10)	0.2110(8)	0.0651
C(5)	0.1916(9)	0.1812(9)	0.2635(7)	0.0579
C(21)	0.0382(12)	0.0601(13)	0.3436(7)	0.0857
C(22)	0.2117(15)	-0.1324(10)	0.2637(8)	0.0804
C(23)	0.4212(9)	-0.0152(15)	0.1622(10)	0.0858
C(24)	0.3912(13)	0.2507(13)	0.1862(11)	0.0978
C(25)	0.1408(14)	0.2900(11)	0.2958(9)	0.0864
C(6)	0.2549(12)	0.1329(12)	0.0094(7)	0.0744
C(7)	0.1356(11)	0.1741(10)	0.0029(7)	0.0677
C(8)	0.1120(13)	0.2568(10)	0.0678(8)	0.0721
N(1)	-0.0312(6)	0.0870(6)	0.1337(5)	0.0493
C(9)	-0.1307(7)	0.0842(7)	0.1336(6)	0.0554
C(10)	-0.2607(7)	0.0785(9)	0.1331(8)	0.0687
N(2)	0.1297(8)	-0.0548(8)	0.0630(6)	0.0606
C(11)	0.1166(10)	-0.1335(8)	0.0217(7)	0.0624
C(12)	0.0991(13)	-0.2363(10)	-0.0305(9)	0.0903

^a U_{eq} is the cube root of the product of the principal components of the thermal ellipsoid.

The final full-matrix least-squares refinement involved 136 parameters, using 1950 data ($I_o \geq 2.5\sigma(I_o)$) and 62 restraints. An empirical 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 $(\sin \theta)/\lambda$. The refinement converged at $R_F = 0.060$ and $R_{wF} = 0.081$. Large peaks near Re in the final difference map (maximum, 1.9(2) electrons \AA^{-3} ; 1.1 \AA from Re) are more probably attributable to unmodelled disorder or twinning, or perhaps to errors in the data as a consequence of the considerable sample decay, than to unrecognized lower symmetry and we feel that a better result is probably not obtainable from these data.

3.6. Structure determination for 3

The structure of 3 was solved from the Patterson map by the heavy-atom method. Coordinates and anisotropic thermal parameters were refined initially for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions (C-H, 0.95 \AA). In subsequent cycles of refinement their coordinate shifts were linked with those for the carbon atoms to which they were bound, except those of the acetonitrile ligands for which the CH_3 fragments were refined as rigid groups restrained to axial symmetry about their C-C bonds. A single parameter was refined for the isotropic thermal motion of the hydrogen atoms of the Cp^* group,

another for those of the allyl group and another for those of the acetonitrile ligands.

The BF_4 -ion displayed extremely anisotropic thermal parameters and was ultimately modelled with four regularly tetrahedral rigid groups of refined partial occupancies restrained to a net occupancy for the site of 1. A single isotropic thermal parameter was refined for all fluorine atoms and another for the boron atoms. This gives significantly better agreement, for fewer variables, and a flatter electron density difference map for this region than does an ordered model with anisotropic thermal parameters for all F and B atoms.

The handedness of the structure was confirmed by measurement of all symmetry equivalent plus Friedel non-equivalent data for the 37 reflections for which $|F_c^+ - F_c^-|/\sigma(F_o)$ is largest (ranging from 61.6 down to 8.8). In every case the sign of $|F_o^+ - F_o^-|$ was the same as that of $|F_c^+ - F_c^-|$, for the handedness given here.

The final full-matrix least-squares refinement involved 220 parameters, using 1815 data ($I_o \geq 2.5\sigma(I_o)$) and seven restraints. An empirical weighting scheme based on counting statistics was applied such that $\langle w(|F_o| - |F_c|)^2 \rangle$ was nearly constant as a function of both $|F_o|$ and $(\sin \theta)/\lambda$. The refinement converged at $R_F = 0.027$ and $R_{wF} = 0.034$.

4. Supplementary material

4.1. For 2

Additional crystallographic details (one page), boron, fluorine and hydrogen atom parameters and carbon atom parameters of the solvent of crystallization (two pages), anisotropic thermal parameters (one page), least-squares planes (one page), observed and calculated structure factors (14 pages) and a plot of the complex cation showing both disordered sets of the Cp* ligand are available from the authors.

4.2. For 3

Additional crystallographic details (one page), boron, fluorine and hydrogen atom parameters (two pages), anisotropic thermal parameters (one page), torsion angles (one page), least-squares planes (one page) and observed and calculated structure factors (14 pages) are available from the authors.

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References and notes

- 1 J.M. Zhuang and D. Sutton, *Organometallics*, 10 (1991) 1516.
- 2 R.J. Batchelor, F.W.B. Einstein, J.M. Zhuang and D. Sutton, *J. Organomet. Chem.*, 397 (1990) 69.
- 3 (a) C.P. Casey and C.S. Yi, *Organometallics*, 9 (1990) 2413. (b) For related manganese complexes $[\text{CpMn}(\text{CO})_2(\text{allyl})]^+$, see A.M. Rosan, *J. Chem. Soc., Chem. Commun.*, (1981) 311; A.M. Rosan and D.M. Romano, *Organometallics*, 9 (1990) 1048.
- 4 V.V. Krivykh, O.V. Gusev and M.I. Rybinskaya, *J. Organomet. Chem.*, 362 (1989) 351.
- 5 I.R. Lyatifov, G.I. Gulieva, E.I. Mysov, V.N. Babin and R.B. Materikova, *J. Organomet. Chem.*, 326 (1987) 83, 89.
- 6 J.W. Faller and A.M. Rosan, *J. Am. Chem. Soc.*, 98 (1976) 3388.
- 7 R.J. Batchelor, F.W.B. Einstein, R.H. Jones, J.M. Zhuang and D. Sutton, *J. Am. Chem. Soc.*, 111 (1989) 3468.
- 8 For a recent X-ray structure determination of coordinated MeCN in a piano-stool complex, see G.L. Yoong and T.W. Hambley, *J. Organomet. Chem.*, 395 (1990) 269.
- 9 H. Saltzman and J.G. Sharefkin, *Org. Synth.*, 5 (1973) 658.
- 10 E.J. Gabe, Y. LePage, J.-P. Charland, F.L. Lee and P.S. White, *J. Appl. Crystallogr.*, 22 (1989) 384.
- 11 D.J. Watkin, J.R. Carruthers and P.W. Betteridge, *CRYSTALS*, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1984.
- 12 *International Tables for X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, 1975, p. 99.