

# Dialkyldicarbonyl rhenium complexes ( $\eta^5\text{-C}_5\text{Me}_5$ )Re(CO)<sub>2</sub>R<sub>2</sub>, R = Me and Et. X-ray structure of *trans*-( $\eta^5\text{-C}_5\text{Me}_5$ )Re(CO)<sub>2</sub>Et<sub>2</sub>

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## Abstract

The compounds *cis*-( $\eta^5\text{-C}_5\text{Me}_5$ )Re(CO)<sub>2</sub>Me<sub>2</sub> and *trans*-( $\eta^5\text{-C}_5\text{Me}_5$ )Re(CO)<sub>2</sub>Et<sub>2</sub> were prepared by alkylation of *cis*-( $\eta^5\text{-C}_5\text{Me}_5$ )Re(CO)<sub>2</sub>Cl<sub>2</sub> using the corresponding organocopper (RCu). Photolysis of *cis*-( $\eta^5\text{-C}_5\text{Me}_5$ )Re(CO)<sub>2</sub>Me<sub>2</sub> in frozen toluene-*d*<sub>8</sub> readily produces the *trans*-( $\eta^5\text{-C}_5\text{Me}_5$ )Re(CO)<sub>2</sub>Me<sub>2</sub>. All the compounds were characterized by spectroscopy and analyses, and the stereochemistry assigned from examination of  $\nu(\text{CO})$  IR intensities; additionally *trans*-( $\eta^5\text{-C}_5\text{Me}_5$ )Re(CO)<sub>2</sub>Et<sub>2</sub> was studied by X-ray crystallography. Crystal data: monoclinic *P*2<sub>1</sub>/*m*, *a* = 8.034(8) Å, *b* = 11.991(8) Å, *c* = 8.69(2) Å,  $\beta$  = 91.38°, *V* = 837(2) Å<sup>3</sup>, *Z* = 4,  $\lambda(\text{Mo K}\alpha)$  = 0.7107 Å, *R<sub>F</sub>* = 0.0285 and *wR<sub>I</sub>* = 0.071 for 1670 measured reflections with  $5 < 2\theta < 50^\circ$ .

**Keywords:** Rhenium; Cyclopentadienyls; Alkyls; Crystal structure

## 1. Introduction

Substitution reactions of rhenium dicarbonyldihalide complexes were first reported by Nesmeyanov et al. for the reaction of CpRe(CO)<sub>2</sub>Br<sub>2</sub> (Cp =  $\eta^5\text{-C}_5\text{H}_5$ ) with Grignard reagents, to yield the CpRe(CO)<sub>2</sub>Me<sub>2</sub> complex [1]. However, this synthetic method could not be reproduced [2]. The same compound could be prepared either from the dianion [CpRe(CO)<sub>2</sub>]<sup>2-</sup> and MeI [3], or by stepwise hydride substitution of CpRe(CO)<sub>2</sub>H<sub>2</sub> [4]. In the pentamethylcyclopentadienyl rhenium dicarbonyl series, Richmond and co-workers [2] reported the reactions of the dibromo complex Cp\*Re(CO)<sub>2</sub>Br<sub>2</sub> (Cp\* =  $\eta^5\text{-C}_5\text{Me}_5$ ) with different Grignard and organolithium reagents but none of the cases resulted in the incorporation of the organo ligand; instead, only the formation of the monoanion [Cp\*Re(CO)<sub>2</sub>Br]<sup>-</sup> was observed. In this work we report, for the first time, the syntheses and characterization of dialkylrhenium(III) complexes possessing a 'four-legged piano-stool' type of structure containing the Cp\* ligand. The dimethyl derivative *cis*-( $\eta^5\text{-C}_5\text{Me}_5$ )Re(CO)<sub>2</sub>Me<sub>2</sub> was provided by us to Hill and Palmer, who studied the mechanism of the

photochemical isomerization of the complex prior to this publication. However, neither details of its preparation nor its characterization (other than IR) were reported [5]<sup>1</sup>. Even more scarce are structural parameters for the Cp or Cp\* rhenium dialkyldicarbonyl derivatives. To our knowledge only the closely related complexes *trans*-( $\eta^5\text{-C}_5\text{H}_5$ )Re(CO)<sub>2</sub>(H)(CH<sub>2</sub>Ph) [7] and *trans*-( $\eta^5\text{-C}_5\text{H}_5$ )Re(CO)<sub>2</sub>(Me)(COMe) [4] have been studied by X-ray crystallography.

## 2. Experimental

All reactions were carried out under nitrogen using Schlenk apparatus connected to a double manifold providing low vacuum or nitrogen. Infrared spectra were measured in solution (KBr cells) on Perkin-Elmer model FT-1605 and Bruker IFS 85 spectrophotometers. <sup>1</sup>H and <sup>13</sup>C spectra were measured at 400 and 100 MHz respectively, on a Bruker WM-400 instrument. Mass spectra were recorded on a Hewlett-Packard 5985 spectrometer,

<sup>1</sup>We have been informed that both isomers of the dimethyl complex have been prepared from the dianion [Cp\*Re(CO)<sub>2</sub>]<sup>2-</sup> and MeI [6].

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and elemental analyses were obtained at the Microanalyses Department of Simon Fraser University, Canada. The complex  $cis\text{-Cp}^*\text{Re}(\text{CO})_2\text{Cl}_2$  was obtained in 70% yield, by decarbonylation of  $[\text{Cp}^*\text{Re}(\text{CO})_3\text{Cl}]\text{SbCl}_5$  with  $\text{Me}_3\text{NO}$ . This is similar to the published procedure used to prepare the  $cis\text{-Cp}^*\text{Re}(\text{CO})_2\text{I}_2$  [8]. The organo copper RCu, R = Me and Et [9], were prepared according to literature procedures. Solvents were purified by conventional methods and distilled under nitrogen prior to use. Low temperature photolyses were carried out in a 5 mm NMR tube placed in a transparent Dewar containing liquid nitrogen and irradiated with a 100 W mercury lamp, through a Corning filter No. 5970,  $\lambda = 320\text{--}400$  nm.

### 2.1. Preparation of $cis\text{-}(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2\text{Me}_2$

To a suspension of yellow MeCu in 15 ml of THF (prepared from 150 mg (0.73 mmol) of  $\text{CuBr}\cdot\text{SMe}_2$  (Aldrich) and 0.5 ml (0.69 mmol) of MeLi (Aldrich, 1.4 M in diethyl ether) at  $-23$  °C), 100 mg (0.22 mmol) of solid  $cis\text{-Cp}^*\text{Re}(\text{CO})_2\text{Cl}_2$  was added. The resulting mixture was stirred at  $-23$  °C for 30 min and then warmed up to room temperature and stirred for additional 45 min. The reaction mixture was then concentrated under vacuum to about one-third of its initial volume and 0.5 ml of water was added to destroy the excess MeCu. Filtration through Celite and evaporation of the solvent, yielded a light-yellow solid which was shown to be a mixture of the dimethyl complex and  $\text{Cp}^*\text{Re}(\text{CO})_3$  (about 7:1, by IR). Column chromatography on silica gel 60 (70–230 mesh, prepared in hexane) with hexane as the eluent, moved first  $\text{Cp}^*\text{Re}(\text{CO})_3$  and then the product as a light-yellow band from which a light-yellow solid was obtained, 45 mg, 49% yield. M.p.  $160$  °C with decomposition; IR (hexane): 1987 vs and 1909 vs,  $\text{cm}^{-1}$ ,  $\nu(\text{CO})$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.07 (s, 6H, Me) and 1.84 (s, 15H, Cp\*); (toluene- $d_8$ )  $\delta$ : 0.31 (s, 6H, Me) and 1.43 (s, 15H, Cp\*).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$ :  $-11.84$  (Me), 9.39 ( $\text{C}_5\text{Me}_5$ ), 99.50 ( $\text{C}_5\text{Me}_5$ ) and 213.82 (CO). Mass spectrum (MS) (EI, based on  $^{187}\text{Re}$ )  $m/z$ :  $\text{M}^+$  (408),  $\text{M}^+ - \text{CO}$  (380), and  $\text{M}^+ - 2\text{Me}$  (378). Anal. Found: C, 41.47; H, 5.20.  $\text{C}_{14}\text{H}_{21}\text{O}_2\text{Re}$ . Calc.: C, 41.37; H, 5.17%.

### 2.2. Preparation of $trans\text{-}(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2\text{Me}_2$

To an NMR tube was added  $cis\text{-Cp}^*\text{Re}(\text{CO})_2\text{Me}_2$  (6.3 mg) and toluene- $d_8$  (0.6 ml). This sample was degassed three times under high vacuum and sealed. The spectrum was recorded before irradiation (Fig. 1(a)). The sample was then frozen in liquid nitrogen and irradiated for 60 min under this condition. The spectrum (b) was obtained immediately following photolysis, after the sample reached room temperature. The same procedure was repeated after two additional periods of

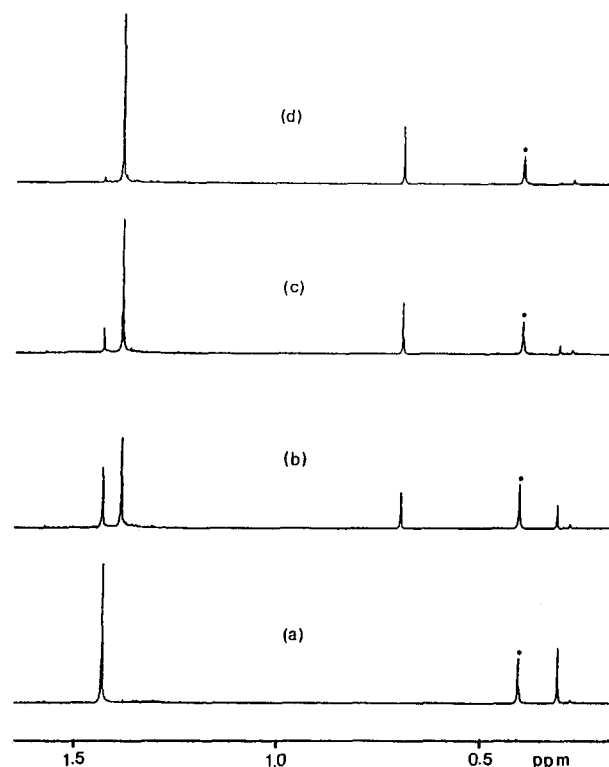


Fig. 1.  $^1\text{H}$  NMR spectral changes accompanying UV photolysis of  $cis\text{-Cp}^*\text{Re}(\text{CO})_2\text{Me}_2$  in toluene- $d_8$ . The resonance at 0.40 ppm is due to an impurity and does not change with UV irradiation. (a)  $cis\text{-Cp}^*\text{Re}(\text{CO})_2\text{Me}_2$  before irradiation. Photolysis times: (b) 60 min, (c) 120 min and (d) 180 min.

60 min (spectra (c) and (d) in Fig. 1). The  $trans\text{-Cp}^*\text{Re}(\text{CO})_2\text{Me}_2$  complex was recovered after chromatography through a short neutral alumina column and solvent evaporation under vacuum (4.6 mg, 73%). This compound was characterized only by IR,  $^1\text{H}$  NMR and MS. IR (hexane): 1996 s, and 1923 vs,  $\text{cm}^{-1}$ ,  $\nu(\text{CO})$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.5 (s, 6H, Me) and 1.75 (s, 15H, Cp\*); (toluene- $d_8$ )  $\delta$ : 0.69 (s, 6H, Me) and 1.38 (s, 15H, Cp\*). MS (EI, based on  $^{187}\text{Re}$ )  $m/z$ :  $\text{M}^+$  (408),  $\text{M}^+ - \text{CO}$  (380), and  $\text{M}^+ - 2\text{Me}$  (378).

### 2.3. Preparation of $trans\text{-Cp}^*\text{Re}(\text{CO})_2\text{Et}_2$

This compound was prepared in a similar manner to that described for  $cis\text{-Cp}^*\text{Re}(\text{CO})_2\text{Me}_2$ , except that the preparation of EtCu and its reaction with the dichloro complex was carried out at  $-78$  °C. Hexane elution of the silica gel column yielded a light-yellow solution from which the diethyl complex was obtained in 58% yield, as a pale yellow solid, after solvent evaporation under vacuum. A second light-yellow band was further eluted with a mixture of 5:1 hexane- $\text{CH}_2\text{Cl}_2$ , which yielded a small amount (about 5%) of the ethylene complex  $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-CH}_2\text{CH}_2)$ . This was identified by IR and  $^1\text{H}$  NMR; both spectra are identical to those reported for this compound [10].

Colourless crystals of *trans*-Cp\*Re(CO)<sub>2</sub>Et<sub>2</sub>, suitable for X-ray crystallography, were obtained from hexane solution at –20 °C. The compound decomposed over 145 °C. IR (hexane): 1984 s, and 1908 vs, cm<sup>-1</sup>  $\nu$ (CO). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 1.28 (s, 15H, Cp\*), 1.37 (q (*J* = 7.5 Hz), 4H, CH<sub>2</sub>) and 2.10 (t (*J* = 7.5 Hz), 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$ : –9.58 (CH<sub>2</sub>), 9.13 (C<sub>5</sub>Me<sub>5</sub>), 23.18 (CH<sub>3</sub>), 98.16 (C<sub>5</sub>Me<sub>5</sub>) and 208.58 (CO). MS (EI, based on <sup>187</sup>Re) *m/z*: M<sup>+</sup> (436), M<sup>+</sup>–CO (408), M<sup>+</sup>–2Et (378). Anal. Found: C, 52.10; H, 5.62. C<sub>16</sub>H<sub>25</sub>O<sub>2</sub>Re. Calc.: C, 52.24; H, 5.75%.

#### 2.4. Crystal structure determination

A colourless block-shaped crystal of *trans*-Cp\*Re(CO)<sub>2</sub>Et<sub>2</sub>, ca.0.1 × 0.2 × 0.3 mm<sup>3</sup> mounted on a glass fibre was used for crystallographic measurements. Intensity data were collected at 293 K on a Rigaku AFC6S four-circle diffractometer with graphite-monochromated Mo K $\alpha$  X-radiation,  $\lambda$  = 0.7107 Å. Accurate unit cell dimensions were obtained by a least squares refinement of the values of 25 centred reflections in the range 12 < 2 $\theta$  < 30°. Intensities of 1670 reflections were measured for 5 < 2 $\theta$  < 50° in an  $\omega$ –2 $\theta$  scan mode. An empirical absorption correction based on azimuthal scans of three reflections was applied, resulting in transmission factors ranging from 0.75 to 1. Equivalent reflections were merged and Lorentz and polarization corrections were also applied in the usual way. The rhenium atom was located from Patterson synthesis [11]. A difference Fourier map then revealed the positions of all the other nonhydrogen atoms. Initially the structure was refined in the acentric space group *P*2<sub>1</sub>. Since the two space groups could not be distinguished on the basis of *E*-statistics, we refined

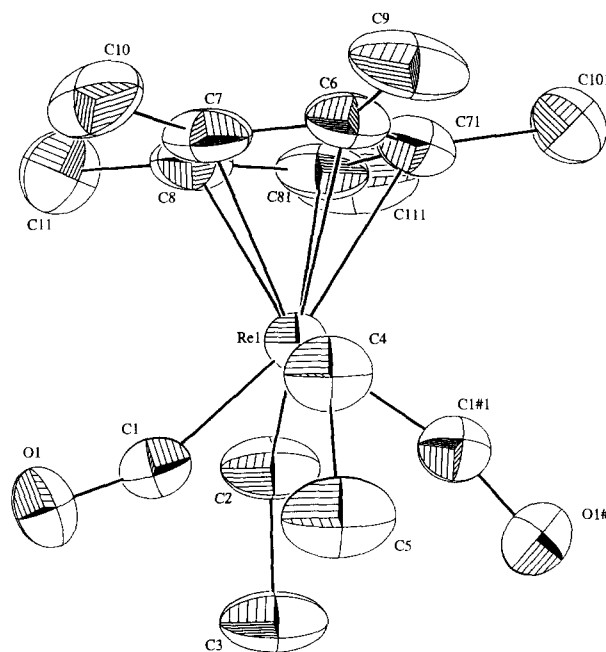


Fig. 2. Perspective view (ORTEP plot) of a molecule of *trans*-Cp\*Re(CO)<sub>2</sub>Et<sub>2</sub> showing the atom labelling (hydrogen atoms are omitted for clarity).

it in the centrosymmetric space group *P*2<sub>1</sub>/*m*. In this space group the rhenium atom and both ethyl group atoms are on the crystallographic mirror plane. All refinement was carried out using *F*<sup>2</sup> in SHELXL [12]. The disorder of the pentamethylcyclopentadienyl group (Cp\*) was best modelled with all atoms having an occupancy of 0.5 and the group refined as a rigid pentagon with ring C–C distances close to 1.4 Å and C–CH<sub>3</sub> distances close to 1.5 Å. All nonhydrogen atoms were refined anisotropically with both rigid-bond

Table 1  
Anisotropic displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) for *trans*-Cp\*Re(CO)<sub>2</sub>Et<sub>2</sub>

	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>
Re(1)	38(1)	47(1)	30(1)	0	1(1)	0
O(1)	112(59)	69(4)	121(6)	–8(4)	–3(4)	–41(4)
C(1)	51(3)	65(4)	55(4)	0(4)	–1(1)	2(4)
C(2)	44(4)	124(9)	40(4)	0	10(4)	0
C(3)	42(5)	143(12)	59(7)	0	10(5)	0
C(4)	64(5)	96(7)	35(4)	0	–1(4)	0
C(5)	76(7)	163(13)	37(5)	0	–12(5)	0
C(6)	37(4)	88(7)	55(5)	9(6)	7(5)	–8(6)
C(7)	34(5)	85(6)	76(6)	–33(8)	4(7)	3(7)
C(8)	38(5)	89(6)	73(6)	26(8)	–6(7)	–5(7)
C(81)	37(5)	97(7)	51(5)	–22(6)	–6(5)	–7(6)
C(71)	45(6)	74(6)	69(6)	–1(8)	–5(7)	–12(7)
C(9)	54(8)	182(15)	61(7)	29(11)	15(7)	–29(10)
C(10)	64(9)	87(8)	139(12)	–65(10)	–18(10)	25(9)
C(11)	88(11)	95(9)	110(10)	68(9)	–31(11)	–1(11)
C(111)	65(9)	184(14)	47(6)	–43(10)	–12(7)	2(12)
C(101)	70(10)	61(7)	227(20)	–15(14)	–41(14)	–14(9)

The anisotropic displacement factor exponent takes the form:  $-2\pi^2(h^2a^*2U_{11} + \dots + 2hka^*b^*U_{12})$ .

and similar anisotropic displacement parameter restraints applied. Hydrogen atoms were placed in calculated positions and refined as 'riding' atoms. Full-matrix least squares refinement of 116 parameters for 1555 independent reflections ( $I \geq \sigma(I)$ ) in the range  $2.34 < \theta < 25.01^\circ$  gave  $R_F = 0.0358$  and  $wR_I = 0.0745$  ( $R_F = 0.0285$  and  $wR_I = 0.0715$  on  $I \geq \sigma(I)$  data). The largest four peaks in the final difference map (corresponding to between 0.65 and 0.83 e  $\text{\AA}^{-3}$ ) are in close proximity to the Cp\* methyl groups; one peak (0.83 e  $\text{\AA}^{-3}$ ) is 0.9  $\text{\AA}$  from the rhenium. The Cp\* methyl carbons shift within the plane of the ring, as illustrated by either  $U$  values in this direction (Fig. 2 and Table 1). Atomic coordinates, bond lengths and angles, and thermal parameters for this compound have been deposited at the Cambridge Crystallographic Data Centre.

### 3. Results and discussion

The use of commercially available alkyl Grignard (RMgX) and alkyllithium (RLi) in reactions with the dichloro complex  $\text{cis-Cp}^*\text{Re}(\text{CO})_2\text{Cl}_2$  did not yield the desired dialkyl dicarbonyl product  $\text{Cp}^*\text{Re}(\text{CO})_2\text{R}_2$ . Instead, a compound with absorptions at 1870 and 1790  $\text{cm}^{-1}$  was detected by IR in the reaction with MeLi in THF solution at  $-78^\circ\text{C}$ . Considering the close relation of the dichloro complex with  $\text{Cp}^*\text{Re}(\text{CO})_2\text{Br}_2$  which was shown by Richmond and co-workers, [2] to react with Grignard and organolithium reagents forming the monoanion  $[\text{Cp}^*\text{Re}(\text{CO})_2\text{Br}]^-$  ( $\nu(\text{CO})$ : 1863 and 1789  $\text{cm}^{-1}$  (for RLi) in THF solution at  $-78^\circ\text{C}$ ), we tentatively assigned the absorptions observed in the IR spectrum to the anionic complex  $[\text{Cp}^*\text{Re}(\text{CO})_2\text{Cl}]^-$ . We do not have any evidence for the formation of the monoalkyl-chloro  $\text{Cp}^*\text{Re}(\text{CO})_2(\text{R})\text{Cl}$ , or the dialkyl  $\text{Cp}^*\text{Re}(\text{CO})_2\text{R}_2$  complexes, which could be formed in the reaction. This observation agrees with the results found by Richmond, and is a further confirmation that the use of RLi or RMgX reagents is not reliable for direct alkyl-halide exchange in cyclopentadienyl rhenium dihalide complexes, as was reported by Nesmeyanov et al. [1].

We then turned to organo copper reagents (RCu), which have been shown by Sweet and Graham [13] and Gladysz and co-workers [14] to be efficient alkylating agents for the preparation of alkyllrhenium(I) complexes of the type  $\text{CpRe}(\text{L})(\text{NO})(\text{R})$  L = CO and  $\text{PPh}_3$ . We have, thus, successfully used MeCu and EtCu in reaction with  $\text{cis-Cp}^*\text{Re}(\text{CO})_2\text{Cl}_2$  for the syntheses of the corresponding dialkyllrhenium(III) complexes. The dimethyl complex was obtained as a single isomer after purification on a silica column. The slightly yellow, air-stable, material exhibits only two  $\nu(\text{CO})$  absorptions at 1987 and 1909  $\text{cm}^{-1}$  (hexane solution) of approximately equal intensity, which we and others interpreted

to be typical of a cis-isomer [5,15,16]. Similarly, the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR exhibit just the resonances expected for a single isomer. The  $^1\text{H}$  and  $^{13}\text{C}$  resonances of the Me ligand appear at higher field when compared with  $\text{trans-Cp}^*\text{Re}(\text{CO})_2\text{Me}_2$  (see below) and  $\text{trans-CpRe}(\text{CO})_2\text{Me}_2$  [3,4]. Unfortunately, the Cp analogue remains unreported, which precludes us from comparing the steric and electronic effects of the Cp and Cp\* ligands on the  $\text{cis-Re}(\text{CO})_2\text{Me}_2$  fragment.

The photolyses of  $\text{cis-CpRe}(\text{CO})_2\text{Me}_2$  were carried out with the aim of isolating and characterizing the trans-isomer detected by IR by Hill and Palmer [5] in the photolysis of the former complex at low temperature. In a preliminary experiment, the cis-complex in hexane solution was irradiated at room temperature. The only compound identified from this reaction was  $\text{Cp}^*\text{Re}(\text{CO})_3$ . A similar result was obtained by Hill, when the reaction was carried out in methylcyclohexane and methylcyclohexene. The same authors found that  $\text{cis} \rightarrow \text{trans}$  isomerization occurs in near quantitative yield at temperatures below 100 K. By considering this observation, the cis-complex was photolyzed in frozen toluene- $d_8$  and the reaction monitored by  $^1\text{H}$  NMR (see Experimental section and Fig. 1). After 180 min of irradiation the conversion was almost complete, and  $\text{trans-Cp}^*\text{Re}(\text{CO})_2\text{Me}_2$  was recovered after solvent evaporation. The slightly yellow solid exhibits  $\nu(\text{CO})$  absorption bands at 1996 and 1923  $\text{cm}^{-1}$  (in hexane) in which the higher wavenumber band ( $\nu(\text{CO})$  symmetric) is now the less intense of the pair. On the basis of the relative intensity of these bands, a trans stereochemistry is assigned. A similar pattern was observed in the IR spectrum of the diethyl derivative for which the structure was confirmed by X-ray crystallography (see below). Both bands are also shifted to higher wavenumber when compared with the cis-isomer, following the same trend observed for the cis and trans isomers of  $\text{Cp}^*\text{Re}(\text{CO})_2\text{X}_2$ , X = Cl, Br and I [15].

The reaction of the dichloro complex with ethylcopper, EtCu, produces the diethyldicarbonyl complex  $\text{trans-Cp}^*\text{Re}(\text{CO})_2\text{Et}_2$ , and the ethenedicarbonyl complex  $\text{Cp}^*\text{Re}(\text{CO})_2(\text{CH}_2\text{CH}_2)$ , in 58% and 5% yield respectively. The latter compound was identified by comparing its IR and  $^1\text{H}$  NMR parameters with those reported by Zhuang and Sutton [10]. This product could be formed by dissociation of CO from  $\text{Cp}^*\text{Re}(\text{CO})_2\text{Et}_2$ , followed by the well-known  $\beta$ -hydrogen transfer from one of the ethyl ligands to the metal centre [17]. The hydrido complex intermediate then formed can reductively eliminate ethane and coordinate CO to produce the observed product. We presently have no experimental evidence for the above assertion; however, some effort is currently underway to establish the mechanism of formation of the ethene complex.

The  $\text{trans-Cp}^*\text{Re}(\text{CO})_2\text{Et}_2$  complex was purified by column chromatography and crystallized from hexane.

The colourless crystals are indefinitely stable under N<sub>2</sub> and appear not to deteriorate when exposed to air over periods of hours. It is very soluble in most of the nonpolar organic solvents, and in these solutions it appears not to undergo thermal isomerization. As with the dimethyl derivative, the spectroscopic properties are in agreement with the presence of a single isomer, but in this case only the trans isomer was obtained. The NMR spectra clearly show the presence of the ethyl ligands with no β-C–H agostic interaction, though this is commonly found in these types of complex [18]. Thus, the <sup>1</sup>H NMR spectrum shows a quartet at δ 1.37 (*J*<sub>CH</sub> = 7.5 Hz) and a triplet at δ 2.10 (*J*<sub>CH</sub> = 7.5 Hz) for the methylene and methyl protons respectively. As with the carbon methyl of the dimethyl complex, the methylene carbon resonance is observed to rather high field, at δ –9.58, in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. These features are consistent with a 'normal' ethyl ligand and are in agreement with the structural parameters observed in the solid state (see below).

The assignment of the stereochemistry of the diethyl complex was straightforward from the ν(CO) intensities in the IR spectrum, in which the intensity of the higher wavenumber, symmetric stretching mode (ν<sub>s</sub>) is weaker

Table 2  
Crystal data and structure refinement for *trans*-Cp\*Re(CO)<sub>2</sub>Et<sub>2</sub>

Empirical formula	C <sub>32</sub> H <sub>50</sub> O <sub>4</sub> Re <sub>2</sub>	
Formula weight	871.12	
Temperature	293(2) K	
Wavelength	0.71070 Å	
Crystal system	monoclinic	
Space group	P2 <sub>1</sub> /m	
Unit cell dimensions	<i>a</i> = 8.034(8) Å	α = 90°
	<i>b</i> = 11.991(8) Å	β = 91.38°
	<i>c</i> = 8.69(2) Å	γ = 90°
Volume	837(2) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.727 g cm <sup>-3</sup>	
Absorption coefficient	7.252 mm <sup>-1</sup>	
<i>F</i> (000)	424	
Crystal size	0.1 × 0.2 × 0.3 mm <sup>3</sup>	
θ range for data collection	2.34 to 25.01°	
Index ranges	0 ≤ <i>h</i> ≤ 9, 0 ≤ <i>k</i> ≤ 14, –10 ≤ <i>l</i> ≤ 10	
Reflections collected	1670	
Independent reflections	1555 ( <i>R</i> (int) = 0.0177)	
Refinement method	Full-matrix least squares on <i>F</i> <sup>2</sup>	
Data/restraints/parameters	1555/305/116	
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.113	
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0285, <i>wR</i> <sub>2</sub> = 0.0715	
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0358, <i>wR</i> <sub>2</sub> = 0.0745	
Largest diff. peak and hole	0.830 and –1.172 e Å <sup>-3</sup>	

$$R = \frac{\sum \|F_o - |F_c|\|}{\sum F_o}$$

$$wR_2 = \left\{ \frac{\sum [w(F_o - F_c)^2]}{\sum [w(F_o)^2]} \right\}^{1/2}$$

$$\text{Goodness of fit on } F^2_s = \left\{ \frac{\sum [w(F_o - F_c)^2]}{\text{number of data - number of parameters}} \right\}^{1/2}$$

$$\text{Weight, } w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP], \quad a = 0.0406, \quad b = 2.0511,$$

$$\text{where } P = [\text{Maximum}(F_o^2, 0) + 2F_c^2]/3.$$

Table 3  
Atomic coordinates (×10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) for the nonhydrogen atoms of *trans*-Cp\*Re(CO)<sub>2</sub>Et<sub>2</sub>

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>a</sup>
Re(1)	651(1)	2500	2364(1)	64(1)
O(1)	–1530(9)	463(5)	1762(9)	101(2)
C(1)	–758(8)	1266(7)	1969(9)	57(2)
C(2)	–994(12)	2500	4439(12)	69(3)
C(3)	–2861(13)	2500	4230(14)	81(4)
C(4)	392(13)	2500	–234(11)	65(3)
C(5)	–1318(16)	2500	–989(13)	92(4)
C(7)	3208(8)	1758(6)	2245(8)	65(3)
C(8)	2787(7)	1789(6)	3803(8)	67(3)
C(81)	2628(7)	2913(6)	4218(8)	62(3)
C(71)	2993(8)	3560(6)	2948(8)	63(3)
C(9)	4113(11)	3218(8)	259(10)	99(5)
C(10)	3715(14)	744(7)	1374(11)	97(4)
C(11)	2646(14)	808(8)	4860(11)	98(5)
C(111)	2458(12)	3348(9)	5833(10)	99(5)
C(101)	3209(15)	4817(7)	2948(12)	120(7)

<sup>a</sup> Defined as one third of the trace of the orthogonalized *U*<sub>*ij*</sub> tensor.

than the lower wavenumber antisymmetric stretching mode (ν<sub>as</sub>). Similar patterns of intensity have been observed in other dicarbonyl rhenium complexes possessing a four-legged piano-stool type of structure [15,16,19]. We have used the relative ν(CO) IR intensities to calculate the OC–Re–CO angle (2θ) using the relationship tan<sup>2</sup>θ = *I*<sub>as</sub>/*I*<sub>s</sub> [20]. The angle thus determined by this method is 114°. This value is greater than the one measured from the X-ray structure analysis (103.1(4)°). Similar trends were observed for the complexes *trans*-Cp\*Re(CO)<sub>2</sub>Br<sub>2</sub> [15] and *trans*-CpRe(CO)<sub>2</sub>(SnPh<sub>3</sub>)<sub>2</sub> [21]. Furthermore, the structure determination unequivocally shows that this compound adopts the trans geometry, as shown in Fig. 2.

The substitution of the chloride ligands should occur stepwise. In that case, the formation of either, cis or trans alkyl-chloro intermediate Cp\*Re(CO)<sub>2</sub>(R)(Cl), should control the stereochemistry of the dialkyl product. Since we do not have any experimental evidence for this type of intermediate, we have used steric arguments to explain the observed stereochemistry of the dialkyldicarbonyl complexes of rhenium. In this regard, the more bulky ethyl groups will be placed in the least sterically hindered position, i.e. trans or diagonal. In view to the recent report describing the cyclic voltammetry properties of CpRe(CO)<sub>2</sub>Br<sup>•</sup> and its participation in a free-radical reaction leading to *trans*-CpRe(CO)<sub>2</sub>H<sub>2</sub> [21], a transient radical Cp\*Re(CO)<sub>2</sub>R<sup>•</sup>, formed by chlorine atom abstraction from the intermediate alkyl-chloro complex Cp\*Re(CO)<sub>2</sub>(R)(Cl), is likely to be involved in these reactions. It is evident that more work needs to be done in order to gain more insight into the mechanism of these reactions. In that direction, we are now studying the reactions of the more bulky diiodo

Table 4

Bond lengths (Å) and angles (deg) with e.s.d.s in parentheses for *trans*-Cp\*Re(CO)<sub>2</sub>Et<sub>2</sub>

Re(1)–C(1)	1.889(8)
Re(1)–C(7)	2.244(7)
Re(1)–C(2)	2.262(10)
Re(1)–C(4)	2.263(10)
Re(1)–C(8)	2.266(6)
Re(1)–C(81)	2.290(6)
Re(1)–C(6)	2.312(6)
O(1)–C(1)	1.157(9)
C(2)–C(3)	1.507(14)
C(6)–C(71)	1.368(3)
C(6)–C(7)	1.402(3)
C(6)–C(9)	1.505(4)
C(7)–C(8)	1.404(4)
C(7)–C(10)	1.494(3)
C(8)–C(81)	1.402(3)
C(8)–C(11)	1.498(4)
C(81)–C(71)	1.388(4)
C(81)–C(111)	1.507(4)
C(71)–C(101)	1.517(4)
C(1#1)–Re(1)–C(1)	103.1(4)
C(1#1)–Re(1)–C(7)	147.9(3)
C(1)–Re(1)–C(7)	103.1(3)
C(1)–Re(1)–C(2)	77.6(3)
C(7)–Re(1)–C(2)	126.1(3)
C(1#1)–Re(1)–C(4)	77.2(3)
C(1)–Re(1)–C(4)	77.2(3)
C(7)–Re(1)–C(4)	90.9(3)
C(2)–Re(1)–C(4)	139.0(4)
C(1#1)–Re(1)–C(8)	146.9(3)
C(1)–Re(1)–C(8)	104.4(3)
C(7)–Re(1)–C(8)	36.28(13)
C(2)–Re(1)–C(8)	90.5(3)
C(4)–Re(1)–C(8)	127.0(3)
C(1#1)–Re(1)–C(81)	111.2(3)
C(1)–Re(1)–C(81)	134.4(3)
C(7)–Re(1)–C(81)	59.8(2)
C(2)–Re(1)–C(81)	81.2(3)
C(4)–Re(1)–C(81)	138.4(3)
C(8)–Re(1)–C(81)	35.83(11)
C(1#1)–Re(1)–C(6)	112.2(3)
C(1)–Re(1)–C(6)	132.5(3)
C(7)–Re(1)–C(6)	53.08(11)
C(2)–Re(1)–C(6)	139.2(3)
C(4)–Re(1)–C(6)	80.7(3)
C(8)–Re(1)–C(6)	59.0(2)
C(81)–Re(1)–C(6)	58.1(2)
O(1)–C(1)–Re(1)	175.2(7)
C(3)–C(2)–Re(1)	120.2(7)
C(5)–C(4)–Re(1)	119.7(7)
C(71)–C(6)–C(7)	108.9
C(71)–C(6)–C(9)	125.8
C(7)–C(6)–C(9)	124.8
C(71)–C(6)–Re(1)	73.0(2)
C(7)–C(6)–Re(1)	69.4(3)
C(9)–C(6)–Re(1)	129.9(2)
C(6)–C(7)–C(8)	107.0
C(6)–C(7)–C(10)	126.0
C(8)–C(7)–C(10)	125.8
C(6)–C(7)–Re(1)	74.8(3)
C(8)–C(7)–Re(1)	72.7(2)
C(10)–C(7)–Re(1)	127.4(2)

Table 4 (continued)

C(81)–C(8)–C(7)	107.4
C(81)–C(8)–C(11)	126.0
C(7)–C(8)–C(11)	126.5
C(81)–C(8)–Re(1)	73.0(3)
C(7)–C(8)–Re(1)	71.0(2)
C(11)–C(8)–Re(1)	124.5(2)
C(71)–C(81)–C(7)	108.1
C(71)–C(81)–C(111)	125.0
C(8)–C(81)–C(111)	125.7
C(71)–C(81)–Re(1)	73.5(2)
C(8)–C(81)–Re(1)	71.1(3)
C(111)–C(81)–Re(1)	130.8(2)
C(6)–C(71)–C(81)	108.5
C(6)–C(71)–C(101)	125.2
C(81)–C(71)–C(101)	125.6
C(6)–C(71)–Re(1)	72.6(2)
C(81)–C(71)–Re(1)	71.4(2)
C(101)–C(71)–Re(1)	129.6(2)

Symmetry transformations used to generate equivalent atoms: #1  $x$ ,  $-y + 1/2$ ,  $z$ .

complex Cp\*Re(CO)<sub>2</sub>I<sub>2</sub> with aryl and alkyl copper reagents.

### 3.1. X-ray structure of *trans*-Cp\*Re(CO)<sub>2</sub>Et<sub>2</sub>

Discrete molecules of *trans*-Cp\*Re(CO)<sub>2</sub>Et<sub>2</sub> exist in the crystal, with no unusually short inter- or intramolecular contacts. An ORTEP diagram with the atom labelling scheme is shown in Fig. 2. Table 2 summarizes the crystal data and data collection conditions. Atom coordinates are listed in Table 3, and bond distances and angles in Table 4.

Both the rhenium and ethyl group atoms are located on the crystallographic mirror plane which generates one of the CO groups and enforces a disordered Cp\* ligand. The Re–C(CO) bond lengths are in the range 1.85–2.00 Å that have been reported for *trans*-Cp\*Re(CO)<sub>2</sub>Br<sub>2</sub> [15], *trans*-CpRe(CO)<sub>2</sub>(H)(CH<sub>2</sub>Ph) [7] and *trans*-CpRe(CO)<sub>2</sub>(COMe)(CH<sub>3</sub>) [4]. The C–O bond lengths are also in the expected range of 1.10–1.16 Å found for metal carbonyl groups. The interbond angle relating the carbonyl groups C(1)–Re–C(1#1) of 103.1(4)° is quite similar to that observed for the *trans*-Cp\*Re(CO)<sub>2</sub>Br<sub>2</sub> (104.3(6)°), *trans*-CpRe(CO)<sub>2</sub>(COMe)(CH<sub>3</sub>) (101.24(17)°) and *trans*-CpRe(CO)<sub>2</sub>(SnPh<sub>3</sub>)<sub>2</sub> (100.4(4)°) [21] and indicates the *trans* or diagonal orientation of the two CO ligands. This fact is also confirmed by considering the ethyl groups interbond angle C(2)–Re–C(4) (139.0(4)°), which is almost identical to the Br–Re–Br and Me–Re–COMe angles of their isostructural complexes *trans*-Cp\*Re(CO)<sub>2</sub>Br<sub>2</sub> (138.97(7)°) [15] and *trans*-CpRe(CO)<sub>2</sub>(COMe)(CH<sub>3</sub>) (138.91(17)°) [4] respectively. In spite of the disorder observed for the Cp\*, this ligand is bonded to the

rhodium in a typical  $\eta^5$ -coordination mode. The C–C bond distances within the ring and the average Re–C(ring) bond distances, are comparable with those observed in other transition-metal complexes containing the Cp\* group, with average values of 1.393 Å and 2.279 Å respectively [15].

The most important feature provided by the X-ray structure of the compound is the Re–Et moiety, which can be considered to have a ‘classical’ ethyl ligand, i.e. with nonagostic interaction (Re–H–C). Unfortunately, there is no direct comparison in the literature for the Re–C distance of the CH<sub>2</sub>CH<sub>3</sub> ligand. Formerly, Re–C(sp<sup>3</sup>) bond values of 2.29(1) Å and 2.245(4) Å were found in *trans*-CpRe(CO)<sub>2</sub>(H)(CH<sub>2</sub>Ph) [7] and *trans*-CpRe(CO)<sub>2</sub>(COMe)(CH<sub>3</sub>) [4], the only others *trans*-containing alkyl ligand Re(III) complexes studied by X-ray crystallography. The C–C single bond value of 1.507 Å (slightly shorter than the C(sp<sup>3</sup>)–C(sp<sup>3</sup>) single bond value of 1.54 Å), and the Re–C–C angle of 119.8(7)°, are in very good agreement with similar parameters observed in other ethyl complexes of this type [18]. A further confirmation of the above statement is in the conformation adopted about the C–C bond, i.e. staggered rather than the eclipsed usually found in constrained ethyl groups [22].

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