

Half-sandwich rhenium(III) acyl complexes: synthesis, structure and conversion to rhenium(I) and rhenium(III) isonitrile complexes ¹

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Abstract

The synthesis, structure and reactions of rhenium(III) η^1 -acyl complexes bearing a cyclopentadienyl (Cp) or a pentamethylcyclopentadienyl (Cp⁺) ligand are described. Oxidation of the rhenium(I) acyl complex $\text{Li}[\text{CpRe}(\text{CO})_2(\eta^1\text{-PhCO})]$ (**1**) with one equivalent of PhICl_2 affords the rhenium(III) acyl complex *trans*- $\text{CpRe}(\text{CO})_2(\eta^1\text{-PhCO})\text{Cl}$ (*trans*-**2a**). The diphenylcarbene complex $\text{Cp}(\text{CO})_2\text{Re}=\text{CPh}_2$ (**3**) is also formed in this reaction. Similarly, oxidation of **1** with Br_2 gives *cis*/*trans*- $\text{CpRe}(\text{CO})_2(\eta^1\text{-PhCO})\text{Br}$ (*cis*/*trans*-**2b**), which can also be obtained from the alkoxycarbene complex $\text{Cp}(\text{CO})_2\text{Re}=\text{C}(\text{OEt})\text{Ph}$ (**4**) with one equivalent of Br_2 . Oxidation of $\text{Li}[\text{Cp}^+\text{Re}(\text{CO})_2(\eta^1\text{-PhCO})]$ (**5**) with one equivalent of PhICl_2 , Br_2 or I_2 affords selectively the rhenium(III) acyl complexes *cis*/*trans*- $\text{Cp}^+\text{Re}(\text{CO})_2(\eta^1\text{-PhCO})\text{X}$ (X = Cl–I) [*cis*/*trans*-(**6a**–**6c**)]. Cleavage of the $\text{Re}-\text{C}_{\text{acyl}}$ bond of *trans*-**2a** with PhICl_2 and of *cis*/*trans*-**2b** with Br_2 offers a convenient way to the rhenium(III) dihalo complexes *cis*/*trans*- $\text{CpRe}(\text{CO})_2\text{Cl}_2$ (*cis*/*trans*-**7a**) and *cis*/*trans*- $\text{CpRe}(\text{CO})_2\text{Br}_2$ (*cis*/*trans*-**7b**) respectively. Reduction of *cis*/*trans*-**7a** with sodium/amalgam gives in the presence of RNC, the rhenium(I) isonitrile complexes $\text{CpRe}(\text{CO})_2(\text{CNR})$ (**8**: R = Et; **9**: R = ⁱPr; **10**: R = ^tBu). Oxidation of **8**–**10** with one equivalent of bromine leads selectively to the rhenium(III) isonitrile complexes [*trans*- $\text{CpRe}(\text{CO})_2(\text{CNR})\text{Br}]\text{Br}$ (**11**: R = Et; **12**: R = ⁱPr; **13**: R = ^tBu). The crystal structure of the acyl complex *trans*-**2b** and the carbonyl complex $[\text{Cp}_2\text{Re}_2(\text{CO})_4(\mu\text{-Br})][\text{Re}_2(\mu\text{-Br})_3(\text{CO})_6]$ (**14**) are described, complex **14** being formed by the thermal decomposition of *cis*/*trans*-**6b**.

Keywords: Isonitrile complexes; Rhenium; Alkyl complexes

1. Introduction

Transition metal acyl complexes are a ubiquitous class of compounds, which have been studied extensively due to their involvement in many catalytic and stoichiometric reactions [1]. In this context several rhenium(I) acyl complexes have been prepared using three main methods. The first involves acylation of a suitable rhenate complex, as shown by the reactions of $\text{Na}[\text{Re}(\text{CO})_5]$ with various acid halides [2]. The second involves addition of a nucleophile at the carbon atom of coordinated carbon monoxide. Illustrative examples of this approach are the reactions of the cationic carbonyl complexes $[\text{Re}(\text{CO})_4\text{L}_2]^+$ (L = CO, PEt_3 , PPh_3 ; L_2 = 2,2'-bipy, ophen) with alkoxides [3] and alkylamines [4],

or the reactions of the neutral carbonyl complexes $\text{Re}(\text{CO})_{5-n}\text{L}_n\text{X}$ ($n = 0, 2$; L = PR_3 , $\text{P}(\text{OR})_3$; X = Cl, Br, I, Me, $\text{C}(\text{O})\text{Me}$, SnPh_3) [5], $\text{CpRe}(\text{CO})_3$ [6] and $\text{Re}_2(\text{CO})_{10}$ [7] with amines and alkyllithium reagents. The third is based on the well-known CO migratory insertion reaction of alkyl complexes [8]. In comparison, mononuclear rhenium(III) acyl complexes are rare [9]. Seeking for an efficient synthetic approach to this class of compounds, we have recently prepared the technetium(I) and rhenium(I) acyl complexes $\text{Li}[\text{Cp}^+\text{M}(\text{CO})_2(\eta^1\text{-PhCO})]$ ($\text{Cp}^+ = \eta^5\text{-C}_5\text{Me}_5$) and have shown these compounds to be useful starting materials for the synthesis of carbene, carbyne and ylide complexes [10]. In continuation of this work on Group VII transition metal complexes bearing metal–carbon multiple bonds, we describe below the oxidation reactions of the rhenium(I) acyl complexes $\text{Li}[(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{CO})_2(\eta^1\text{-PhCO})]$ (**1**: R = H; **5**: R = Me) with halogens and the stepwise transformation of the resulting rhenium(III) acyl complexes to rhenium(I) and rhenium(III) isonitrile complexes.

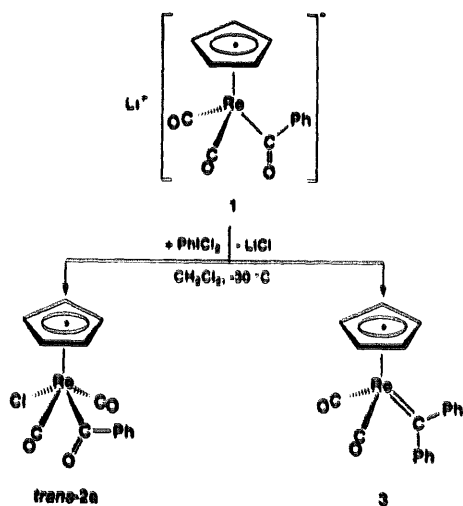
^{*} Corresponding author.

¹ Dedicated to Professor Dr. M.L.H. Green on the occasion of his 60th birthday.

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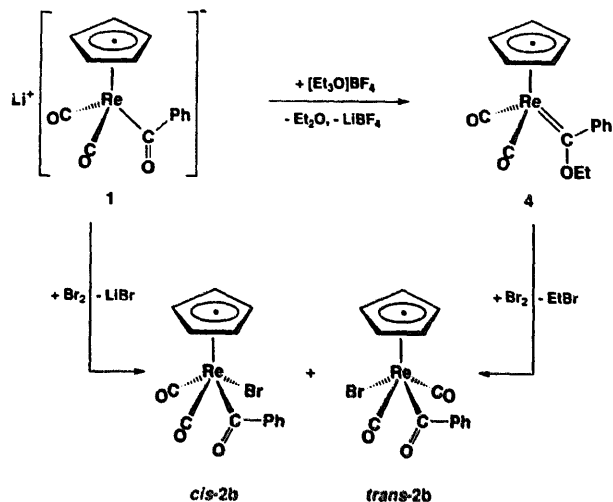
2. Results and discussion

Oxidation of $\text{Li}[\text{CpRe}(\text{CO})_2(\eta^1\text{-PhCO})]$ (**1**) with one equivalent of PhICl_2 in CH_2Cl_2 at -30°C gives the Re^{III} acyl complex *trans*- $\text{CpRe}(\text{CO})_2(\eta^1\text{-PhCO})\text{Cl}$ (*trans*-**2a**) (Eq. (1)). Formation of a minor product in this reaction is indicated by the IR spectra of the reaction solutions, which show besides the two $\nu(\text{CO})$ absorptions of the acyl complex *trans*-**2a** at 2046 and 1975 cm^{-1} , two other $\nu(\text{CO})$ absorptions of much lower intensity at 1970 and 1888 cm^{-1} . The minor product was easily separated from the acyl complex *trans*-**2a** by column chromatography on silica at -20°C and was isolated in 15% yield as a light red, thermally stable microcrystalline solid, which is soluble in all common organic solvents. It was identified by IR and NMR spectroscopy, mass spectrometry and elemental analysis to be the diphenylcarbene complex **3** (Eq. (1)). The acyl complex *trans*-**2a** was isolated as an orange solid in 62% yield. It is soluble in CH_2Cl_2 and Et_2O , but sparingly soluble in pentane and decomposes in solution at room temperature.



(1)

The unprecedented "oxide-aryl" replacement reaction leading from **1** to **3** offers a direct route from an acyl complex to a diarylcarbene complex [11]. Two other routes are known to give compounds analogous to **3**. The first involves the addition of a nucleophile to the carbyne carbon of a cationic carbyne complex. This is exemplified by the reactions of the rhenium complex $[\text{Cp}(\text{CO})_2\text{Re}\equiv\text{CPh}]\text{BCl}_4$ with LiMe and Et_3AlH to afford the carbene complexes $\text{Cp}(\text{CO})_2\text{Re}=\text{C(R)Ph}$ ($\text{R} = \text{Me}, \text{H}$) [12], and by the reaction of the manganese carbyne complex $[\text{Cp}(\text{CO})_2\text{Mn}\equiv\text{CMe}]\text{BCl}_4$ with LiMe to give the carbene complex $\text{Cp}(\text{CO})_2\text{Mn}=\text{CMe}_2$ [13]. The second includes the carbene transfer reaction of $\text{CpMn}(\text{CO})_2\text{THF}$ with Ph_2CN_2 [14].

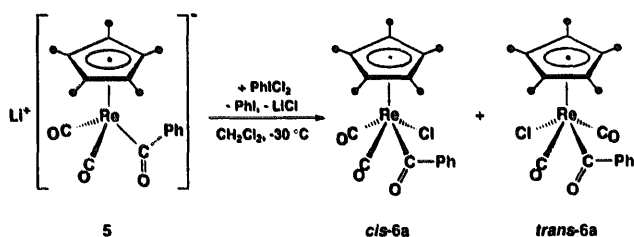


Scheme 1.

Oxidation of **1** with one equivalent of bromine in CH_2Cl_2 at -30°C leads to the rhenium(III) acyl complex $\text{CpRe}(\text{CO})_2(\eta^1\text{-PhCO})\text{Br}$ (**2b**), which was obtained as a mixture of the *cis* and the *trans* isomer and isolated after purification by column chromatography on silica at -20°C as a yellow solid in 75% yield (Scheme 1). It is soluble in CH_2Cl_2 and Et_2O , but sparingly soluble in pentane, and decomposes in solution at room temperature. IR spectra of the reaction solutions and of the isolated yellow solid indicate that the *trans* stereoisomer (*trans*-**2b**) is predominantly formed in this reaction. The ratio *trans*-**2b**/*cis*-**2b** was determined from the relative intensity of the cyclopentadienyl proton resonances in the ^1H NMR spectrum of the isolated solid, and was found to be 9:1. Alternatively, the rhenium(III) acyl complexes *cis*-**2b** and *trans*-**2b** can be obtained by oxidation of the Fischer-type ethoxycarbene complex $\text{Cp}(\text{CO})_2\text{Re}=\text{C(OEt)Ph}$ (**4**) with one equivalent of bromine (Scheme 1). Again the *trans* stereoisomer (*trans*-**2b**) is the main product of this unprecedented oxidative carbene-acyl transformation reaction. Most oxidation reactions of Fischer-type carbene complexes proceed with a cleavage of the metal-carbon double bond [15].

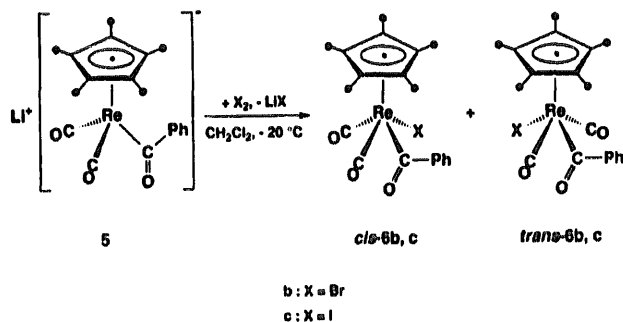
Treatment of $\text{Li}[\text{Cp}^*\text{Re}(\text{CO})_2(\eta^1\text{-PhCO})]$ (**5**) with one equivalent of PhICl_2 in CH_2Cl_2 at -30°C affords a mixture of the rhenium(III) acyl complexes *cis*- and *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^1\text{-PhCO})\text{Cl}$ (*cis*/*trans*-**6a**) (Eq. (2)). Formation of a rhenium diphenylcarbene byproduct was not observed in this reaction, in contrast to the oxidation reaction of **1** with PhICl_2 (Eq. (1)). The mixture of stereoisomers *cis*-**6a** and *trans*-**6a** was isolated as an orange-yellow solid in 77% yield after evaporation of the solvent and extraction of the residue with $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (1:5). Integration of the pentamethylcyclopentadienyl proton signals in the ^1H NMR spectrum of the isolated solid gave a *trans*-**6a**/*cis*-**6a**

ratio of 2.1:1. Alternatively, the reaction mixture can be purified by column chromatography on neutral alumina at -20°C . Using an Et_2O /pentane (1:1) mixture as eluent, the two stereoisomers can be separated, the less adsorbed and more soluble *trans* isomer being eluted first. Thereby the pure stereoisomers were isolated as orange–yellow, microcrystalline solids, which are soluble in CH_2Cl_2 and Et_2O , but sparingly soluble in pentane, and decompose slowly in CH_2Cl_2 at room temperature without any sign of thermal isomerization.

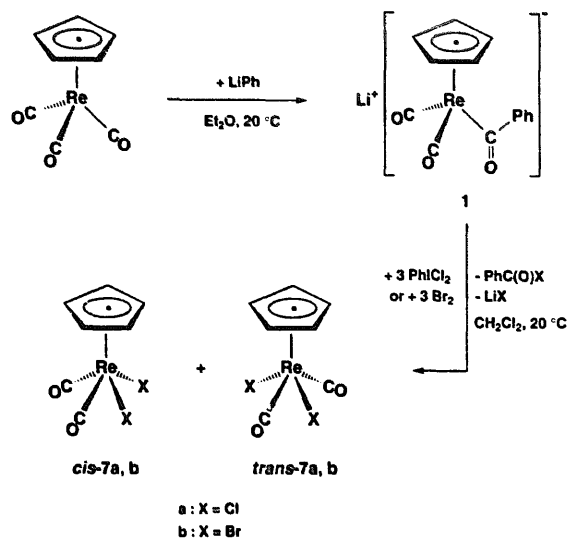


(2)

In a similar reaction to that giving *cis*/*trans*-**6a**, oxidation of **5** with one equivalent of bromine or iodine affords selectively the rhenium(III) acyl complexes *cis*/*trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^1\text{-PhCO})\text{Br}$ (*cis*/*trans*-**6b**) and *cis*/*trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^1\text{-PhCO})\text{I}$ (*cis*/*trans*-**6c**) respectively (Eq. (3)). Again IR spectra of the reaction solutions and the isolated solids indicate that the *trans* stereoisomers *trans*-**6b** and *trans*-**6c** are predominantly formed in these reactions. Purification of the reaction solution by low-temperature column chromatography on silica gives the mixture of isomers *cis*/*trans*-**6b** and *cis*/*trans*-**6c** as orange–yellow, microcrystalline solids in 79 and 74% yields respectively. Integration of the pentamethylcyclopentadienyl proton resonances in the ^1H NMR spectrum of the obtained iodo isomers in C_6D_6 at room temperature [*trans*-**6c**: $\delta(\text{Cp}^*) = 1.72$; *cis*-**6c**: $\delta(\text{Cp}^*) = 1.69$] gave a *trans*-**6c**/*cis*-**6c** ratio of 2.8:1. The iodo complexes *cis*-**6c** and *trans*-**6c** were found to be stable in CH_2Cl_2 at room temperature over at least 12 h. However, they decompose when heated in a sealed capillary *in vacuo* at 82°C .



(3)



Scheme 2.

In an attempt to determine the structure of the thermal decomposition products of the rhenium(III) acyl complexes **2a**, **2b** and **6a–6c**, a saturated orange–yellow solution of the isomers *cis*-**6b** and *trans*-**6b** in Et_2O was allowed to crystallize at room temperature by slow evaporation of the solvent. Suitable green crystals for a single-crystal X-ray diffraction study separated from the resulting green solution and were shown to be the salt **14** of the homodinuclear complex cation $[\text{Cp}_2^*\text{Re}_2(\text{CO})_4(\mu\text{-Br})]^+$ and the homodinuclear complex anion $[\text{Re}_2(\mu\text{-Br})_3(\text{CO})_6]^-$ (see crystal structure of **14**).

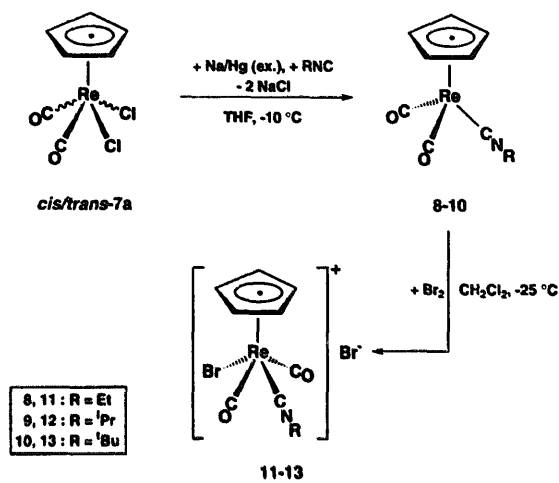
Treatment of **1** with three equivalents of PhICl_2 in CH_2Cl_2 at -78°C and subsequent warming of the reaction mixture to room temperature gives, after oxidative cleavage of the $\text{Re}-\text{C}_{\text{acyl}}$ bond, the rhenium(III) dichloro complexes *cis*- and *trans*- $\text{CpRe}(\text{CO})_2\text{Cl}_2$ (*cis*/*trans*-**7a**) (Scheme 2). IR monitoring of this reaction reveals the intermediate formation of the rhenium(III) acyl complex *trans*-**2a** according to Eq. (1). This reacts subsequently with additional PhICl_2 to give *cis*/*trans*-**7a**. In the latter reaction benzoyl chloride is liberated, as evidenced by its two characteristic IR absorptions in CH_2Cl_2 at 1775 and 1732 cm^{-1} [16]. The stereoisomers *cis*-**7a** and *trans*-**7a** were separated by column chromatography on silica at -15°C and isolated as red (*trans*-**7a**) and red–brown (*cis*-**7a**) microcrystalline solids in 30 and 35% yields respectively.

The oxidation of **1** with PhICl_2 to give *cis*/*trans*- $\text{CpRe}(\text{CO})_2\text{Cl}_2$ (*cis*/*trans*-**7a**), combined with the quantitative transformation of $\text{CpRe}(\text{CO})_3$ with LiPh to **1**, provides an efficient two-step synthesis of the dichloro complexes starting from $\text{CpRe}(\text{CO})_3$ (Scheme 2). This synthetic procedure is more convenient than the previously reported three-step synthesis of *cis*/*trans*- $\text{CpRe}(\text{CO})_2\text{Cl}_2$ from $\text{CpRe}(\text{CO})_3$, involving in the key

step the oxidation of $\text{CpRe}(\text{CO})_2\text{N}_2$ by HCl [17]. A direct oxidation of $\text{CpRe}(\text{CO})_3$ to *cis*/*trans*- $\text{CpRe}(\text{CO})_2\text{Cl}_2$ has not succeeded so far, the reactions of $\text{CpRe}(\text{CO})_3$ with Cl_2 and SbCl_5 affording only the salts $[\text{CpRe}(\text{CO})_3\text{Cl}]\text{Cl}$ and $[\text{CpRe}(\text{CO})_3\text{Cl}]\text{SbCl}_6$ respectively [18].

In a similar reaction to that yielding *cis*/*trans*-**7a**, treatment of **1** in CH_2Cl_2 with slightly more than three equivalents of bromine gives a mixture of the rhenium(III) dibromo complexes *cis*- and *trans*- $\text{CpRe}(\text{CO})_2\text{Br}_2$ (*cis*/*trans*-**7b**) (Scheme 2). This was isolated after purification by column chromatography as a brown solid in 76% yield. Again IR monitoring of this reaction revealed the intermediate formation of the rhenium(III) acyl complexes *cis*-**2b** and *trans*-**2b** according to Scheme 1. These then react with additional bromine to give *cis*/*trans*-**7b**. In the latter reaction benzoyl bromide is liberated, as evidenced by its characteristic IR $\nu(\text{CO})$ absorption in CH_2Cl_2 at 1774 cm^{-1} [16]. An alternative method for the synthesis of *cis*/*trans*- $\text{CpRe}(\text{CO})_2\text{Br}_2$ involves the direct bromination of $\text{CpRe}(\text{CO})_3$ with Br_2 in trifluoroacetic acid [19].

The dihalo complexes were found to be very useful starting materials for the synthesis of rhenium(I) and rhenium(III) isonitrile complexes bearing a cyclopentadienyl ligand (Scheme 3). Thus, reductive dehalogena-



Scheme 3.

tion of *cis*/*trans*-**7a** with excess Na/Hg in the presence of an alkyl isonitrile gives the rhenium(I) isonitrile complexes $\text{CpRe}(\text{CO})_2(\text{CNR})$ (**8**: $\text{R} = \text{Et}$; **9**: $\text{R} = i\text{Pr}$; **10**: $\text{R} = t\text{Bu}$) (Scheme 3). These were isolated in good yields as white, slightly air-sensitive solids, which are soluble in common organic solvents including paraffin hydrocarbons. The isonitrile complexes **9** and **10** have been obtained previously from the reaction of the

Table 1

$\nu(\text{C}\equiv\text{NR})$, $\nu(\text{CO})$ and $\nu(\text{C}=\text{O})_{\text{acyl}}$ absorptions (cm^{-1}) of **1–13**; solvents: (a) CH_2Cl_2 , (b) Et_2O , (c) *n*-pentane

Complex	$\nu(\text{C}\equiv\text{NR})$	$\nu(\text{CO})$	$\nu(\text{C}=\text{O})_{\text{acyl}}$	Solvent
$\text{Li}[\text{CpRe}(\text{CO})_2(\eta^1\text{-PhCO})]$ (1)	—	1918 s, 1908 s, 1800 s, 1787 s	—	b
<i>trans</i> - $\text{CpRe}(\text{CO})_2[\eta^1\text{-PhCO}]\text{Cl}$ (<i>trans</i> - 2a)	—	2046 s, 1975 vs	1617 m	a
<i>cis</i> - $\text{CpRe}(\text{CO})_2[\eta^1\text{-PhCO}]\text{Br}$ (<i>cis</i> - 2b)	—	2027 vs, 1955 s	— ^a	a
<i>trans</i> - $\text{CpRe}(\text{CO})_2[\eta^1\text{-PhCO}]\text{Br}$ (<i>trans</i> - 2b)	—	2041 s, 1972 vs	1618 m	a
$\text{Cp}(\text{CO})_2\text{Re}=\text{CPh}_2$ (3)	—	1970 vs, 1888 vs	—	a
$\text{Cp}(\text{CO})_2\text{Re}=\text{C}(\text{OEt})\text{Ph}$ (4)	—	1978 vs, 1907 vs	—	c
—	—	1951 vs, 1872 vs	—	a
—	—	1963 vs, 1891 vs	—	c
$\text{Li}[\text{Cp}^*\text{Re}(\text{CO})_2(\eta^1\text{-PhCO})]$ (5)	—	1898 s, 1890 s, 1784 vs	—	b
<i>cis</i> - $\text{Cp}^*\text{Re}(\text{CO})_2[\eta^1\text{-PhCO}]\text{Cl}$ (<i>cis</i> - 6a)	—	2010 vs, 1935 s	1617 m	a
<i>trans</i> - $\text{Cp}^*\text{Re}(\text{CO})_2[\eta^1\text{-PhCO}]\text{Cl}$ (<i>trans</i> - 6a)	—	2033 s, 1955 vs	1606 m	a
<i>cis</i> - $\text{Cp}^*\text{Re}(\text{CO})_2[\eta^1\text{-PhCO}]\text{Br}$ (<i>cis</i> - 6b)	—	2007 vs, 1935 s	1617 m	a
<i>trans</i> - $\text{Cp}^*\text{Re}(\text{CO})_2[\eta^1\text{-PhCO}]\text{Br}$ (<i>trans</i> - 6b)	—	2030 s, 1954 vs	1609 m	a
<i>cis</i> - $\text{Cp}^*\text{Re}(\text{CO})_2[\eta^1\text{-PhCO}]\text{I}$ (<i>cis</i> - 6c)	—	2004 s, 1933 s	1617 m	a
<i>trans</i> - $\text{Cp}^*\text{Re}(\text{CO})_2[\eta^1\text{-PhCO}]\text{I}$ (<i>trans</i> - 6c)	—	2017 s, 1946 vs	1611 m	a
<i>cis</i> - $\text{CpRe}(\text{CO})_2\text{Cl}_2$ (<i>cis</i> - 7a)	—	2059 vs, 1984 s	—	a
<i>trans</i> - $\text{CpRe}(\text{CO})_2\text{Cl}_2$ (<i>trans</i> - 7a)	—	2076 s, 2011 vs	—	a
<i>cis</i> - $\text{CpRe}(\text{CO})_2\text{Br}_2$ (<i>cis</i> - 7b)	—	2054 vs, 1892 s	—	a
<i>trans</i> - $\text{CpRe}(\text{CO})_2\text{Br}_2$ (<i>trans</i> - 7b)	—	2067 s, 2003 vs	—	a
$\text{CpRe}(\text{CO})_2(\text{CNEt})$ (8)	2130 m, 2106 m	1945 vs, 1891 vs	—	b
—	2128 w, 2099 m	1952 vs, 1903 vs	—	c
$\text{CpRe}(\text{CO})_2(\text{CN}^i\text{Pr})$ (9)	2108 m, 2096 sh	1943 vs, 1892 vs	—	b
—	2106 sh, 2092 m	1950 vs, 1904 vs	—	c
$\text{CpRe}(\text{CO})_2(\text{CN}^t\text{Bu})$ (10)	2111 m, 2069 w, br	1932 vs, 1874 vs	—	a
—	2104 m, 2061 m	1940 vs, 1891 vs	—	b
<i>trans</i> - $[\text{CpRe}(\text{CO})_2(\text{CNEt})\text{Br}]\text{Br}$ (11)	2242 s	2090 s, 2035 vs	—	a
<i>trans</i> - $[\text{CpRe}(\text{CO})_2(\text{CN}^i\text{Pr})\text{Br}]\text{Br}$ (12)	2235 s	2089 s, 2035 vs	—	a
<i>trans</i> - $[\text{CpRe}(\text{CO})_2(\text{CN}^t\text{Bu})\text{Br}]\text{Br}$ (13)	2220 s	2088 s, 2034 vs	—	a

^a The $\nu(\text{C}=\text{O})_{\text{acyl}}$ absorption of *cis*-**2b** was not detected because of the low concentration of this isomer.

vinylidene complex $\text{Cp}(\text{CO})_2\text{Re}=\text{C}=\text{CH}_2$ with the carbodiimides $\text{RN}=\text{C}=\text{NR}$ ($\text{R} = ^i\text{Pr}, ^t\text{Bu}$) [20].

Oxidation of the complexes **8–10** with one equivalent of bromine in CH_2Cl_2 at -25°C yields selectively the rhenium(III) isonitrile complexes [*trans*- $\text{CpRe}(\text{CO})_2(\text{CNR})\text{Br}] \text{Br}$ (**11**: $\text{R} = \text{Et}$; **12**: $\text{R} = ^i\text{Pr}$; **13**: $\text{R} = ^t\text{Bu}$), which were isolated as yellow solids in 95–99% yields (Scheme 3). These are soluble in CH_2Cl_2 , but insoluble in Et_2O and pentane, and decompose in solution at room temperature.

Analogous oxidation reactions to those of **8–10** have been reported previously for the pentamethylcyclopentadienyl Re^I complexes $\text{Cp}^*\text{Re}(\text{CO})_2\text{L}$ [$\text{L} = \text{PMe}_3$, P(OR)_3 ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$)] [21].

3. Spectroscopic investigations

3.1. IR, ^1H NMR and ^{13}C NMR spectra

The IR spectra of the complexes **1–13** show, in the region $2300\text{--}1500\text{ cm}^{-1}$, characteristic $\nu(\text{C}\equiv\text{NR})$,

$\nu(\text{CO})$, and $\nu(\text{CO})_{\text{acyl}}$ absorptions of the coordinated isonitrile, carbonyl and acyl ligands respectively (Table 1). The number and relative intensity of the $\nu(\text{CO})$ absorptions of the “four-legged piano-stool” complexes **2a**, **2b**, **6a–7b** and **11–13** indicate the number of isomers and the relative position of the carbonyl ligands in the coordination sphere. Thus, only two absorption bands are observed in the IR spectra of the complexes **2a** and **11–13**, the higher energy absorption of the symmetric $\nu(\text{CO})$ vibration being less intense than the lower energy absorption of the antisymmetric $\nu(\text{CO})$ vibration [19b, c]. This indicates the presence of only the *trans* isomer. In comparison, four $\nu(\text{CO})$ absorptions are found in the IR spectra of the complexes **2b** and **6a–7b**, indicating the presence of a mixture of *cis/trans* isomers. As expected, the higher energy absorption of all *cis* isomers (*cis-2b*, *cis-6a–cis-7b*) is more intense than the lower energy $\nu(\text{CO})$ absorption [19b, c]. The angle 2θ between the two CO ligands has been calculated for the complex *trans-2b*, using the relationship $I_a/I_s = \tan^2 \theta$, where I_a and I_s are the

Table 2
 ^1H NMR data of the complexes *trans-2a–13*; relative intensities and multiplicities in parentheses, coupling constants in hertz

Complex	$\text{CH}_3\text{CH}_2\text{NC}$ Me_2CHNC Me_3CNC	C_5Me_5	$\text{CH}_3\text{CH}_2\text{NC}$ Me_2CHNC	C_5H_5	C_6H_5	Solvent T ($^\circ\text{C}$)
<i>trans-2a</i>	—	—	—	5.67 (5, s)	7.44 (2, m) ^a , 7.51 (1, m) ^b 7.71 (2, m) ^c	CD_2Cl_2 – 30
<i>cis-2b</i>	—	—	—	5.98 (5, s)	— ^d	CD_2Cl_2 – 20
<i>trans-2b</i>	—	—	—	5.67 (5, s)	7.44 (2, m) ^a , 7.51 (1, m) ^b 7.69 (2, m) ^c	CD_2Cl_2 – 20
3	—	—	—	5.42 (5, s)	7.49 (4, m) ^a , 7.61 (2, m) ^b , 7.76 (4, m) ^c	CD_2Cl_2 – 20
<i>cis-6a</i>	—	1.99 (15, s)	—	—	7.39–7.60 (5, m) ^d	CD_2Cl_2 – 20
<i>trans-6a</i>	—	1.94 (15, s)	—	—	7.39–7.60 (5, m) ^d	CD_2Cl_2 – 20
<i>cis-6b</i>	—	2.03 (15, s)	—	—	7.36–7.61 (5, m) ^d	CD_2Cl_2 – 20
<i>trans-6b</i>	—	2.00 (15, s)	—	—	7.36–7.61 (5, m) ^d	CD_2Cl_2 – 20
<i>cis-6c</i>	—	2.15 (15, s) ^e	—	—	7.34–7.61 (5, m) ^d	CD_2Cl_2 + 20
<i>trans-6c</i>	—	2.15 (15, s) ^e	—	—	7.34–7.61 (5, m) ^d	CD_2Cl_2 + 20
8	0.61 (3, t) $^3J(\text{HH}) = 7.2$	—	2.77 (2, q) $^3J(\text{HH}) = 7.2$	4.68 (5, s)	—	C_6D_6 + 20
9	0.78 (6, d) $^3J(\text{HH}) = 6.5$	—	3.32 (1, sept) $^3J(\text{HH}) = 6.5$	4.69 (5, s)	—	C_6D_6 + 20
10	0.97 (9, s)	—	—	4.68 (5, s)	—	C_6D_6 + 20
11	1.50 (3, t) $^3J(\text{HH}) = 7.2$	—	4.52 (2, q) $^3J(\text{HH}) = 7.2$	6.42 (5, s)	—	CD_2Cl_2 – 50
12	1.55 (6, d) $^3J(\text{HH}) = 6.6$	—	5.13 (1, sept) $^3J(\text{HH}) = 6.6$	6.49 (5, s)	—	CD_2Cl_2 – 30
13	1.67 (9, s)	—	—	6.44 (5, s)	—	CD_2Cl_2 – 40

^{a,b,c} Resonances of *meta*-, *para*- and *ortho*-protons of the phenyl group respectively; ^d the phenyl proton resonances of the *cis* and *trans* isomer are superimposed; ^e the methyl protons of the Cp^* ligand of the *cis* and *trans* isomer have, by accident, the same chemical shift.

intensities of the asymmetric and symmetric $\nu(\text{CO})$ bands respectively [19b, c]. The obtained value of 109° is very close to that found in the crystal structure of *trans*-**2b** [$\text{OC-Re-CO} = 110.1(5)^\circ$] (see crystal structure of *trans*-**2b**).

The $\nu(\text{CO})$ absorptions of the acyl complexes *trans*-**2a** and *trans*-**2b** appear at lower wavenumbers than those of the dihalo complexes *trans*-**7a** and *trans*-**7b** respectively. This can be attributed to an enhancement of the electron density at the metal centre (stronger metal–carbonyl back-bonding), when the chloro or bromo ligand is replaced by the less electronegative benzoyl ligand (Table 1). For the same reason, the $\nu(\text{CO})$ absorptions of the Cp^* -substituted acyl complexes decrease in the series *cis*-**6a** > *cis*-**6b** > *cis*-**6c** and *trans*-**6a** > *trans*-**6b** > *trans*-**6c** and appear at lower wavenumbers than those of the corresponding Cp -substituted acyl complexes (stronger electron releasing ability of the Cp^* ligand). The $\nu(\text{C}\equiv\text{NR})$ absorptions of the $\text{Re}(\text{III})$ isonitrile complexes **11**–**13** appear at considerably higher frequency than those of the uncoordinated alkyl isonitriles [$\nu(\text{C}\equiv\text{NEt}) = 2160\text{ cm}^{-1}$, $\nu(\text{C}\equiv\text{N}^i\text{Pr}) = 2149\text{ cm}^{-1}$, $\nu(\text{C}\equiv\text{N}^t\text{Bu}) = 2140\text{ cm}^{-1}$ in CH_2Cl_2]. This indicates that the alkyl isonitrile acts only as a

σ -donor ligand towards the electron-poor rhenium centre in these compounds. In comparison, two $\nu(\text{C}\equiv\text{NR})$ absorptions are observed in the IR spectra of the $\text{Re}(\text{I})$ isonitrile complexes **8**–**10** at lower frequency than those of the uncoordinated alkyl isonitriles, suggesting extensive metal–isonitrile back-donation in these compounds.

All acyl complexes are distinguished by an absorption of medium intensity between 1600 and 1620 cm^{-1} , which can be assigned to the $\nu(\text{C}=\text{O})$ absorption of the acyl ligand. This absorption appears in the same range as that of other neutral rhenium η^1 -acyl complexes [**2a**, **2d**–**f**].

Finally, two $\nu(\text{CO})$ absorptions of almost equal intensity are observed in the IR spectra of the pseudo-octahedral complexes **3**, **4** and **8**–**10**. These absorptions decrease in the series **3** > **4** > **8**–**10**, indicating the decreasing σ -donor/ π -acceptor ability of the ligand in the series diphenylcarbene > alkoxy(phenyl)carbene > alkyl isonitrile.

Further support for the structures assigned to the complexes is given by the ^1H NMR spectra (Table 2). Thus, one singlet resonance is observed for the cyclopentadienyl protons of the complexes **2a** and **11**–**13**, indicating the presence of only one isomer (*trans* iso-

Table 3
 ^{13}C NMR data of the complexes *trans*-**2a**–**13**; coupling constants in hertz

Complex	C_3Me_3	$\text{CH}_3\text{CH}_2\text{NC}$ Me_2CHNC Me_3CNC	$\text{CH}_3\text{CH}_2\text{NC}$ Me_2CHNC Me_3CNC	C_3H_5 C_3Me_3	C_6H_5	$\text{CH}_3\text{CH}_2\text{NC}$ Me_2CHNC Me_3CNC	CO	PhCO Re = C	Solvent T (°C)
<i>trans</i> - 2a	—	—	—	96.7	128.5 ^a , 128.6 ^b , 132.0 ^c , 152.7 ^d	—	197.9	214.7	CD_2Cl_2 – 30
<i>trans</i> - 2b	—	—	—	96.1	128.5 ^a , 128.6 ^b , 132.0 ^c , 152.3 ^d	—	195.7	213.0	CD_2Cl_2 – 30
3	—	—	—	93.1	128.3 ^a , 130.1 ^b , 132.5 ^c , 164.5 ^d	—	205.3	296.0	CD_2Cl_2 – 20
<i>cis</i> - 6a	9.9	—	—	108.1	128.0 ^a , 129.1 ^b , 131.4 ^c , 147.7 ^d	—	206.7, 208.2	227.8	CD_2Cl_2 – 20
<i>trans</i> - 6a	9.7	—	—	105.6	126.5 ^a , 128.0 ^b , 130.8 ^c , 155.0 ^d	—	200.0	223.7	CD_2Cl_2 – 20
<i>cis</i> - 6b	10.2	—	—	107.7	128.1 ^a , 129.3 ^b , 131.5 ^c , 149.1 ^d	—	205.3, 207.2	224.6	CD_2Cl_2 – 10
<i>trans</i> - 6b	10.0	—	—	105.2	126.6 ^a , 128.0 ^b , 130.7 ^c , 154.7 ^d	—	198.3	222.1	CD_2Cl_2 – 10
<i>cis</i> - 6c	10.8	—	—	107.3	128.1 ^a , 130.0 ^b , 131.6 ^c , 153.3 ^d	—	203.0, 207.0	221.4	CD_2Cl_2 20
<i>trans</i> - 6c	11.0	—	—	105.0	126.9 ^a , 128.3 ^b , 130.8 ^c , 156.2 ^d	—	196.7	220.3	CD_2Cl_2 20
8	—	15.6	39.2	83.0	—	145.7	199.2	—	C_6D_6 + 20
9	—	23.8	48.6	83.1	—	146.6	199.2	—	C_6D_6 + 20
10	—	30.9	57.0	83.1	—	148.7	199.1	—	C_6D_6 + 20
11	—	14.5	44.2	95.4	—	102.6	179.9	—	CD_2Cl_2 – 50
12	—	22.5	54.3	95.7	—	102.3	180.2	—	CD_2Cl_2 – 30
13	—	30.1	63.5	96.5	—	103.7	180.2	—	CD_2Cl_2 – 40

^{a,b,c,d} C_m , C_o , C_p and C_{ipso} resonances of the phenyl group respectively.

mer). In comparison, the ^1H NMR spectra of **2b** and **6a–7b** display two cyclopentadienyl or pentamethylcyclopentadienyl proton resonances, indicating the presence of a mixture of *cis/trans* isomers.

The ^{13}C NMR spectra are also consistent with the proposed structures of the new compounds (Table 3). Thus, only one carbonyl carbon resonance is observed in the ^{13}C NMR spectra of the complexes **2a** and **11–13** indicating, in agreement with the IR spectra, a *trans* arrangement of the two carbonyl ligands in these compounds. In comparison, the ^{13}C NMR spectra of the complexes **6a–6c** display three carbonyl carbon resonances, giving evidence of a mixture of *cis/trans* isomers. Both carbonyl carbon resonances of the *cis* isomer appear at lower field than the carbonyl carbon resonance of the corresponding *trans* isomer (Table 3). This trend is the same as that observed for Group VI transition metal carbonyl complexes, where a stronger metal–carbonyl back-bonding causes a deshielding of the carbonyl carbon nucleus [22]. For the same reason, the carbonyl carbon resonances of the Re^{I} isonitrile complexes **8–10** appear at lower field (δ 199.1–199.2) than those of the Re^{III} isonitrile complexes **11–13** (δ 179.9–180.2). Also, the metal-bound isonitrile carbon resonances of the Re^{I} complexes **8–10** (δ 145.7–148.7) appear at lower field than those of the Re^{III} complexes **11–13** (δ 102.3–103.7), because of the stronger metal–isonitrile back-bonding in the former compounds. All rhenium(III) η^1 -acyl complexes are distinguished by an acyl carbon resonance at δ 213.0–227.8, which appears at higher field than those of pentacarbonylrhenium(I) η^1 -acyl complexes [2f, 23].

4. Crystal structures of *trans*-**2b** and **14**

The structure of the acyl complex *trans*-**2b** was determined by a single-crystal X-ray diffraction study. A PLATON plot of the structure of *trans*-**2b** is given in Fig. 1. Selected bond lengths and angles are listed in Table 4. The coordination geometry around the rhenium

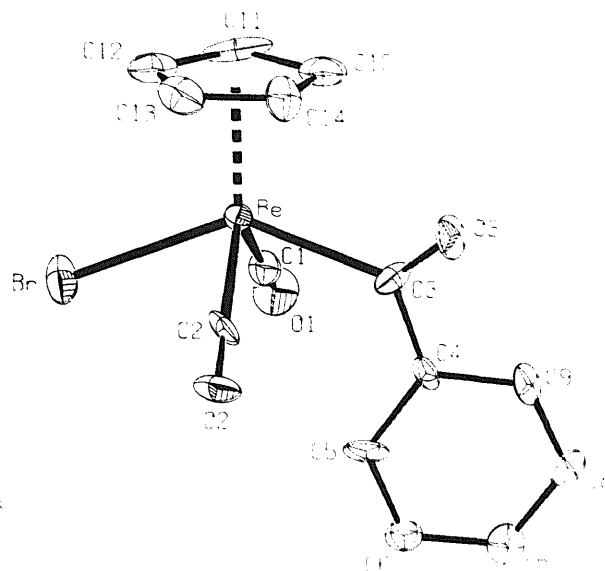


Fig. 1. Crystal structure of the acyl complex *trans*-**2b** (PLATON plot). Hydrogen atoms are omitted for clarity.

atom is typical for four-legged piano-stool complexes of the type CpML_4 [24], and can be described as square pyramidal with the cyclopentadienyl ligand at the apex. A *trans*-arrangement of the acyl and the bromo ligand is observed. The basal plane of the pyramid, defined by the atoms Br, C1, C2 and C3, is essentially parallel to the cyclopentadienyl ring plane, the dihedral angles between the best planes being 4.7° . The $\text{Re}-\text{Cp}_{\text{center}}$ distance (1.916 Å) is slightly shorter than that of *trans*- $\text{CpRe}(\text{CO})_2(\eta^1\text{-MeCO})\text{Me}$ [$d(\text{Re}-\text{Cp}_{\text{center}}) = 1.948$ Å] [9b]. The $\text{Re}-\text{C}_{\text{carbonyl}}$ bond lengths [$\text{Re}-\text{C1} = 1.94(2)$ Å; $\text{Re}-\text{C2} = 1.944(12)$ Å] are close to those of other rhenium(III) carbonyl complexes [9b, 17b], and the $\text{Re}-\text{C}_{\text{acyl}}$ bond length [$\text{Re}-\text{C3} = 2.212(11)$ Å] similar to that of the rhenium(III) acyl complex *trans*- $\text{CpRe}(\text{CO})_2(\eta^1\text{-MeCO})\text{Me}$ [$d(\text{Re}-\text{C}_{\text{acyl}}) = 2.192(4)$ Å] [9b]. A comparison of the angles around the sp^2 -hybridized acyl carbon atom excludes any interaction of the acyl oxygen atom with the rhenium centre, as predicted on the basis of electron counting formalisms.

Table 4

Selected bond lengths (Å) and bond angles ($^\circ$) with estimated standard deviations for *trans*-**2b**^a

Re–C(1)	1.94(2)	C(1)–Re–Br	77.9(3)
Re–C(2)	1.944(12)	C(2)–Re–Br	81.2(3)
Re–C(3)	2.212(11)	C(3)–Re–Br	138.6(3)
Re–Br	2.6019(14)	C(1)–Re–C(2)	110.1(5)
Re–C(10)	2.238(11)	C(1)–Re–C(3)	79.5(5)
Re–C(11)	2.315(11)	C(2)–Re–C(3)	74.6(5)
Re–C(12)	2.273(13)	Re–C(3)–O(3)	120.5(9)
Re–C(13)	2.252(13)	Re–C(3)–C(4)	121.9(8)
Re–C(14)	2.212(12)	O(3)–C(3)–C(4)	117.6(10)
Re–cp	1.916	cp–Re–Br	111.6
C(3)–O(3)	1.22(2)	cp–Re–C(3)	109.8

^a cp denotes the centre of the cyclopentadienyl ring.

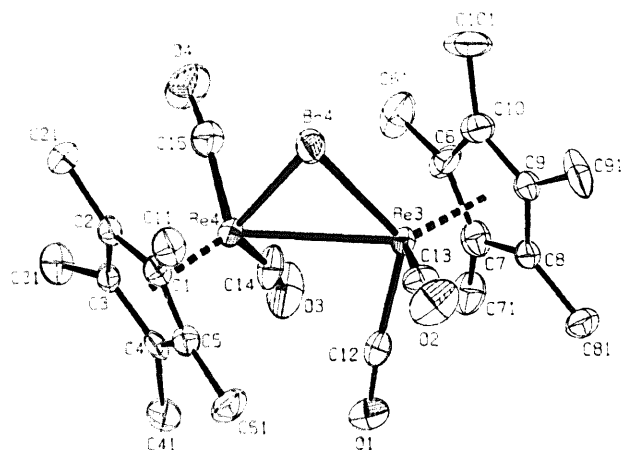


Fig. 2. Crystal structure of the cation $[\text{Cp}^*_2\text{Re}_2(\text{CO})_4(\mu\text{-Br})]^+$ in **14** (PLATON plot). Hydrogen atoms are omitted for clarity.

The structure of **14** was also determined by a single-crystal X-ray diffraction study. A PLATON plot of the cation in **14** is given in Fig. 2, that of the anion in Fig. 3. Selected bond lengths and angles are listed in Table 5. The cation in **14** consists of two $\text{Cp}^*\text{Re}(\text{CO})_2$ fragments, which are linked together by an Re–Re single bond and a bromo ligand forming a symmetric bridge between the two formally divalent rhenium centres. The two $\text{Cp}^*\text{Re}(\text{CO})_2$ fragments are *trans* arranged with respect to the plane defined by the bromo and the two rhenium atoms. The Re–Re distance of the cation in **14** [2.9927(14) Å] is similar to those observed for other dinuclear rhenium carbonyl complexes bearing an Re–

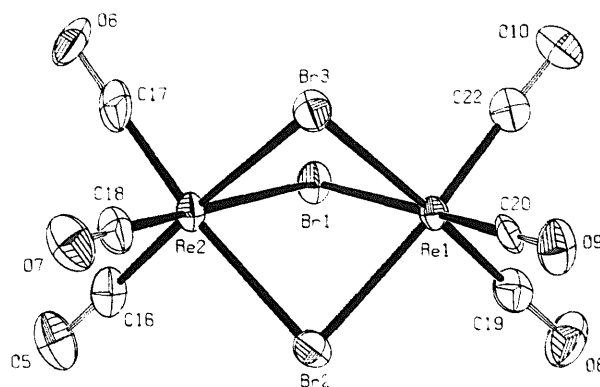


Fig. 3. Crystal structure of the anion $[\text{Re}_2(\mu\text{-Br})_3(\text{CO})_6]^-$ in **14** (PLATON plot).

Re single bond, such as $\text{Re}_2(\text{CO})_{10}$ [$d(\text{Re}-\text{Re}) = 3.0413(11)$ Å] [25] and $\text{Cp}_2\text{Re}_2(\text{CO})_5$ [$d(\text{Re}-\text{Re}) = 2.957(1)$ Å] [26]. As expected this distance is considerably shorter than the Re–Re distance in the anion of **14** [$\text{Re}(1) \dots \text{Re}(2) = 3.475(2)$ Å], where any bonding interaction between the two rhenium centres can be excluded on the basis of electron counting formalisms. The Re–Br bond lengths of the cation [2.515(2) and 2.517(2) Å] are shorter than those of bromo-bridged rhenium(I) carbonyl complexes, such as $\text{Re}_2\text{Br}_2(\text{CO})_6(\text{THF})_2$ [$d(\text{Re}-\text{Br})_{\text{av.}} = 2.643$ Å] [27], $\text{Re}_2\text{Br}_2(\text{CO})_6(\text{P}_2\text{Ph}_4)$ [$d(\text{Re}-\text{Br}) = 2.649$ Å] [28], or $\text{Re}_2\text{Br}_2(\text{CO})_6(\text{Se}_2\text{Ph}_2)$ [$d(\text{Re}-\text{Br}) = 2.656$ Å] [29]. This may be ascribed to the difference in the covalence radii of a rhenium(II) and a rhenium(I) atom. The structure of the

Table 5

Selected bond lengths (Å) and bond angles (°) with estimated standard deviations for **14**^a

Cation in 14			
Re(3)–Re(4)	2.9927(14)	Re(3)–Re(4)–Br(4)	53.48(4)
Re(3)–Br(4)	2.515(2)	Re(4)–Re(3)–Br(4)	53.53(4)
Re(4)–Br(4)	2.517(2)	Br(4)–Re(3)–C(12)	123.8(3)
Re(3)–C(12)	1.923(10)	Br(4)–Re(3)–C(13)	86.5(3)
Re(3)–C(13)	1.912(11)	Re(4)–Re(3)–C(12)	77.7(3)
Re(4)–C(14)	1.916(11)	Re(4)–Re(3)–C(13)	108.7(3)
Re(4)–C(15)	1.925(12)	Br(4)–Re(4)–C(14)	122.5(3)
Re(3)–cp*(1)	1.958	Br(4)–Re(4)–C(15)	86.8(4)
Re(4)–cp*(2)	1.963	Re(3)–Re(4)–C(14)	77.6(3)
Re(3)–Br(4)–Re(4)	72.99(5)	Re(4)–Re(3)–C(15)	109.5(3)
Anion in 14			
Re(1)–Br(1)	2.648(2)	Br(1)–Re(1)–Br(2)	80.19(6)
Re(1)–Br(2)	2.650(2)	Br(1)–Re(1)–Br(3)	82.01(5)
Re(1)–Br(3)	2.643(2)	Br(2)–Re(1)–Br(3)	82.69(5)
Re(2)–Br(1)	2.656(2)	Br(1)–Re(1)–C(20)	174.4(3)
Re(2)–Br(2)	2.645(2)	Br(2)–Re(1)–C(22)	174.2(3)
Re(2)–Br(3)	2.645(2)	Br(3)–Re(1)–C(19)	176.2(3)
Re(1)–C(19)	1.864(10)	Re(1)–Br(1)–Re(2)	81.87(5)
Re(1)–C(20)	1.896(10)	Re(1)–Br(2)–Re(2)	82.03(5)
Re(1)–C(22)	1.883(10)	Re(1)–Br(3)–Re(2)	82.16(5)
Re(2)–C(16)	1.896(10)	Br(1)–Re(2)–C(18)	173.3(3)
Re(2)–C(17)	1.912(12)	Br(2)–Re(2)–C(17)	173.6(3)
Re(2)–C(18)	1.876(10)	Br(3)–Re(2)–C(16)	176.5(3)

^a cp*(1) and cp*(2) denote the centres of the pentamethylcyclopentadienyl rings.

anion in **14** has been determined previously as its $[(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{Re}(\text{CO})_3]$ salt [30] and is therefore not discussed here.

5. Experimental

Standard Schlenk procedures were used for all syntheses and sample manipulations. The solvents were dried by standard methods (n-pentane over CaH_2 , Et_2O , THF and toluene over Na/benzophenone; CH_2Cl_2 over P_2O_5 and Na/Pb alloy), distilled under nitrogen and stored over 4 Å molecular sieves prior to use. All column chromatography was carried out in a thermostatted column of 20 cm length and 2.0 cm diameter. The stationary phase was silica (Merck, 0.063–0.2 mm) which was degassed, dried in vacuo at room temperature and saturated with nitrogen.

Elemental analyses were performed by the Microanalytical Laboratory of the Humboldt-Universität zu Berlin. IR spectra were recorded on a Bruker IFS-55 spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AM-300 spectrometer in dry deoxygenated methylene- d_2 -chloride or benzene- d_6 . Chemical shifts were referenced to residual solvent signals (methylene- d_2 -chloride, δ_{H} 5.32 and δ_{C} 53.8 ppm; benzene- d_6 , δ_{H} 7.15 and δ_{C} 128.0). Mass spectra were obtained with a HP 5995A spectrometer; m/z values are given relative to the ^{187}Re , ^{35}Cl and ^{79}Br isotopes.

The acyl complexes **1** and **5** were prepared from $\text{CpRe}(\text{CO})_3$ and $\text{Cp}^*\text{Re}(\text{CO})_3$ respectively, following the procedures described previously [6,10]. $\text{CpRe}(\text{CO})_2\text{C}(\text{OEt})\text{Ph}$ was obtained from **1** by reaction with $[\text{Et}_3\text{O}]\text{BF}_4$ in CH_2Cl_2 . PhICl_2 , ethyl isonitrile, isopropyl isonitrile, and *tert*-butyl isonitrile were prepared according to published procedures [31,32]. Elementary bromine was distilled and stored under nitrogen.

5.1. *trans*- $\text{CpRe}(\text{CO})_2[\eta^1\text{-PhCO}]\text{Cl}$ (*trans*-**2a**) and $\text{Cp}(\text{CO})_2\text{Re}=\text{CPh}_2$ (**3**)

210 mg (0.76 mmol) of freshly prepared PhICl_2 was added at -40°C to a suspension of 320 mg (0.76 mmol) of **1** in 30 ml of CH_2Cl_2 . The mixture was then allowed to warm to -30°C and stirred for 2 h at this temperature. The resulting brown suspension was evaporated to dryness at -20°C and the residue was purified by column chromatography on silica at -20°C . Elution with Et_2O /pentane (1:2) afforded first an orange band, from which complex **3** was obtained as a light red, microcrystalline solid after removal of the solvent *in vacuo* and crystallization of the residue from pentane. Yield: 55 mg (15%). Anal. Found: C, 50.30; H, 3.00. $\text{C}_{20}\text{H}_{15}\text{O}_2\text{Re}$ (473.55) Calc.: C, 50.73; H, 3.19%. EI-MS (70 eV): m/z 474 ($[\text{M}]^+$), 446 ($[\text{M}-\text{CO}]^+$), 418 ($[\text{M}-2\text{CO}]^+$).

Further elution with Et_2O /n-pentane (2:1) gave a yellow fraction, which was concentrated *in vacuo* at -20°C and treated with cold pentane (-70°C) to bring about complete precipitation of the complex *trans*-**2a**. Orange solid. Yield: 210 mg (62%). Anal. Found: C, 37.23; H, 2.10; Cl, 7.66. $\text{C}_{14}\text{H}_{10}\text{ClO}_3\text{Re}$ (447.89) Calc.: C, 37.54; H, 2.25; Cl, 7.92%. EI-MS (70 eV): m/z 412 ($[\text{M}-\text{HCl}]^+$), 384 ($[\text{M}-\text{HCl}-\text{CO}]^+$), 356 ($[\text{M}-\text{HCl}-2\text{CO}]^+$), 336 ($[\text{M}-\text{C}_6\text{H}_5\text{Cl}]^+$), 328 ($[\text{M}-\text{HCl}-3\text{CO}]^+$), 308 ($[\text{M}-\text{C}_6\text{H}_5\text{Cl}-\text{CO}]^+$), 280 ($[\text{M}-\text{C}_6\text{H}_5\text{Cl}-2\text{CO}]^+$), 252 ($[\text{M}-\text{C}_6\text{H}_5\text{Cl}-3\text{CO}]^+$).

5.2. *cis* / *trans*- $\text{CpRe}(\text{CO})_2[\eta^1\text{-PhCO}]\text{Br}$ (*cis* / *trans*-**2b**) from **1** and Br_2

A suspension of 820 mg (1.96 mmol) of **1** in 50 ml of CH_2Cl_2 was treated at -78°C with a solution of 0.1 ml (1.94 mmol) of Br_2 in 10 ml of CH_2Cl_2 . The mixture was allowed to warm to -30°C and stirred for 2 h. The solvent was then removed *in vacuo* at -30°C and the residue purified by column chromatography on silica at -20°C . Elution with Et_2O afforded a yellow fraction, which was concentrated *in vacuo* and treated with cold pentane (-78°C) to bring about precipitation of *cis* / *trans*-**2b** as a yellow solid. Yield: 720 mg (75%). Anal. Found: C, 33.90; H, 2.10. $\text{C}_{14}\text{H}_{10}\text{BrO}_3\text{Re}$ (492.34) Calc.: C, 34.15; H, 2.05%. EI-MS (70 eV): m/z 412 ($[\text{M}-\text{HBr}]^+$), 384 ($[\text{M}-\text{HBr}-\text{CO}]^+$), 356 ($[\text{M}-\text{HBr}-2\text{CO}]^+$), 328 ($[\text{M}-\text{HBr}-3\text{CO}]^+$).

5.3. *cis* / *trans*- $\text{CpRe}(\text{CO})_2[\eta^1\text{-PhCO}]\text{Br}$ (*cis* / *trans*-**2b**) from $\text{Cp}(\text{CO})_2\text{Re}=\text{C}(\text{OEt})\text{Ph}$ (**4**) and Br_2

A solution of 220 mg (0.50 mmol) of **4** in 30 ml of CH_2Cl_2 was treated at -78°C with a solution of 0.026 ml (0.50 mmol) of Br_2 in 5 ml of CH_2Cl_2 and stirred for 2 h at 0°C . After removal of the solvent at -10°C , the residue was purified by column chromatography on silica at -20°C . Some unreacted starting material was first washed away with pentane. The mixture of isomers *cis* / *trans*-**2b** was then eluted with Et_2O and isolated as a yellow solid. Yield: 150 mg (61%). The product was characterized by IR and ^1H NMR spectroscopy.

5.4. *cis* / *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2[\eta^1\text{-PhCO}]\text{Cl}$ (*cis* / *trans*-**6a**)

A suspension of 380 mg (0.78 mmol) of **5** in 30 ml of CH_2Cl_2 was treated at -78°C with 215 mg (0.78 mmol) of freshly prepared PhICl_2 . The mixture was then allowed to warm to -30°C and stirred for 2 h. The orange-brown suspension was evaporated to dryness and the residue was taken up at -30°C in a CH_2Cl_2 / Et_2O mixture (1:5). The solution was filtered with a filter canula and the yellow filtrate evaporated to dryness at -30°C . The residue was washed with cold

pentane (-78°C) to give *cis/trans*-**6a** as an intense yellow, microcrystalline solid. Yield: 310 mg (77%). Anal. Found: C, 43.80; H, 3.59. $\text{C}_{19}\text{H}_{20}\text{ClO}_3\text{Re}$ (518.02) Calc.: C, 44.05; H, 3.89%. EI-MS (70 eV): m/z 468 ($[\text{M}-\text{MeCl}]^+$), 440 ($[\text{M}-\text{MeCl}-\text{CO}]^+$), 406 ($[\text{M}-\text{C}_6\text{H}_5\text{Cl}]^+$), 378 ($[\text{M}-\text{C}_6\text{H}_5\text{Cl}-\text{CO}]^+$), 350 ($[\text{M}-\text{C}_6\text{H}_5\text{Cl}-2\text{CO}]^+$).

5.5. *cis/trans*- $\text{Cp}^*\text{Re}(\text{CO})_2[\eta^1\text{-PhCO}]\text{Br}$ (*cis/trans*-**6b**)

A solution of 660 mg (1.35 mmol) of **5** in 30 ml of CH_2Cl_2 was treated at -78°C with a solution of 0.069 ml (1.34 mmol) of Br_2 in 5 ml of CH_2Cl_2 . The mixture was allowed to warm to -20°C and stirred for 1 h. The solvent was then removed *in vacuo* at -20°C and the residue chromatographed on silica at -20°C . Elution with Et_2O /pentane (3:1) afforded an orange fraction, which was evaporated to dryness to afford the mixture of isomers *cis/trans*-**6b** as an orange–yellow, micro-

crystalline solid. Yield: 600 mg (79%). Anal. Found: C, 40.00; H, 3.37. $\text{C}_{19}\text{H}_{20}\text{BrO}_3\text{Re}$ (562.48) Calc.: C, 40.57; H, 3.58%. EI-MS (70 eV): m/z 534 ($[\text{M}-\text{CO}]^+$), 506 ($[\text{M}-2\text{CO}]^+$), 478 ($[\text{M}-3\text{CO}]^+$), 468 ($[\text{M}-\text{MeBr}]^+$), 440 ($[\text{M}-\text{MeBr}-\text{CO}]^+$), 406 ($[\text{M}-\text{C}_6\text{H}_5\text{Br}]^+$), 378 ($[\text{M}-\text{C}_6\text{H}_5\text{Br}-\text{CO}]^+$), 350 ($[\text{M}-\text{C}_6\text{H}_5\text{Br}-2\text{CO}]^+$).

5.6 *cis/trans*- $\text{Cp}^*\text{Re}(\text{CO})_2[\eta^1\text{-PhCO}]\text{I}$ (*cis/trans*-**6c**)

A suspension of 365 mg (0.75 mmol) of **5** in 30 ml of CH_2Cl_2 was treated at -30°C with a solution of 190 mg (0.75 mmol) of I_2 in 10 ml of CH_2Cl_2 . The mixture was then allowed to warm to room temperature and stirred for 15 min. The resulting red–brown suspension was evaporated to dryness and the residue chromatographed on silica at -10°C . Elution with Et_2O /pentane (3:1) gave an orange fraction, which after removal of the solvent at -10°C afforded the mixture of isomers *cis/trans*-**6c** as an orange–yellow microcrystalline solid. M.p. 82°C (dec.). Yield: 335 mg

Table 6
Crystallographic data for *trans*-**2b** and **14**

	<i>trans</i> - 2b	14
<i>Crystal data</i>		
Molecular formula	$\text{C}_{14}\text{H}_{10}\text{BrO}_3\text{Re}$	$\text{C}_{30}\text{H}_{30}\text{Br}_4\text{O}_{10}\text{Re}_4$
Molecular weight	492.34	1614.98
Crystal size (mm^3)	$0.1 \times 0.2 \times 0.15$	$0.5 \times 0.7 \times 0.9$
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Z	4	2
<i>a</i> (Å)	7.459(2)	9.818(6)
<i>b</i> (Å)	15.207(7)	12.754(6)
<i>c</i> (Å)	11.938(2)	16.518(9)
$\alpha(^{\circ})$		75.09(4)
$\beta(^{\circ})$	94.73(2)	76.73(4)
$\gamma(^{\circ})$		86.92(4)
<i>V</i> (Å ³)	1349.5(8)	1945(2)
ρ_{calc} (g cm^{-3})	2.423	2.757
<i>F</i> (000)	912	1460
$\mu(\text{Mo K}\alpha \text{Xmm}^{-1})$	11.964	16.071
<i>Data collection</i>		
<i>T</i> (K)	165(5)	193(2)
Radiation (Mo K α) (Å)	0.7069	0.71073
2 θ min./max. ($^{\circ}$)	4, 45	3, 48
Total data	2333	6108
Data unique	1712	5347
<i>Refinement</i>		
No. of reflections	1662 ($I > 2\sigma(I)$)	5332 ($I > 4\sigma(I)$)
No. of parameters refined	172	433
Absorption correction	DIABAS	DIABAS
min./max.	0.78/1.347	0.795/1.34
min./max. density (e Å^{-3})	−1.569/1.413	−1.262/1.294
R_1^a	0.0459	0.0311
wR_2^b	0.1215	0.0758
GOF ^c	0.956	1.072

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$; ^c goodness of fit = $[\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$.

(74%). Anal. Found: C, 37.66; H, 3.31. $C_{19}H_{20}IO_3Re$ (609.47) Calc.: C, 37.44; H, 3.31%. EI-MS (70 eV): m/z 505 ($[M-CO-C_6H_5]^+$), 406 ($[M-C_6H_5I]^+$), 378 ($[M-C_6H_5I-CO]^+$).

5.7. *cis/trans-CpRe(CO)₂Cl₂* (*cis/trans-7a*) from **1** and $PhICl_2$

A suspension of 495 mg (1.18 mmol) of **1** in 30 ml of CH_2Cl_2 was treated at $-78^\circ C$ with a solution of 970 mg (3.53 mmol) of freshly prepared $PhICl_2$ in 20 ml of CH_2Cl_2 and the mixture was allowed to warm to room temperature and stirred for 5 h. The resulting brown solution was diluted with 20 ml of Et_2O and filtered with a filter canula from the insoluble lithium salts. The filtrate was evaporated to dryness and the residue purified by column chromatography on silica at $-15^\circ C$. Elution with Et_2O gave an orange fraction, which was evaporated to dryness to give *trans-7a* as a red, microcrystalline solid. Yield: 135 mg (30%). Further elution with acetone/ CH_2Cl_2 (1:1) gave a brown fraction, which was evaporated to dryness. The residue was washed once with a cold ($-78^\circ C$) Et_2O /pentane (1:2) mixture to afford *cis-7a* as a red-brown, microcrystalline solid. Yield: 155 mg (35%). $C_7H_5Cl_2O_2Re$ (378.23). The two isomers were characterized by IR and 1H NMR spectroscopy.

5.8. *cis/trans-CpRe(CO)₂Br₂* (*cis/trans-7b*) from **1** and Br_2

A suspension of 330 mg (0.79 mmol) of **1** in 30 ml of CH_2Cl_2 was treated at $-78^\circ C$ with a solution of

0.041 ml (0.79 mmol) of Br_2 in 5 ml of CH_2Cl_2 and stirred for 2 h at $-10^\circ C$. Selective formation of the benzoyl complexes *cis-2b* and *trans-2b* was confirmed by IR spectroscopy. A solution of 0.09 ml (1.75 mmol) of Br_2 in 10 ml of CH_2Cl_2 was then added to the yellow-brown suspension and the mixture was allowed to warm to room temperature and stirred for 3 h. Completion of the reaction was observed by IR spectroscopy. The resulting brown solution was diluted with 20 ml of Et_2O and filtered with a filter canula from the insoluble lithium salts. The filtrate was evaporated to dryness and the residue washed twice with a cold ($-78^\circ C$) Et_2O /pentane (1:3) mixture and recrystallized from Et_2O to afford *cis/trans-7b* as a brown, microcrystalline solid. Yield: 280 mg (76%). Anal. Found: C, 17.56; H, 0.99. $C_7H_5Br_2O_2Re$ (467.13) Calc.: C, 18.00; H, 1.08%. The product was characterized by IR and 1H NMR spectroscopy.

5.9. $CpRe(CO)_2CNEt$ (**8**)

A solution of 180 mg (0.48 mmol) of *cis/trans-7a* in 30 ml of THF was treated at $-10^\circ C$ with 0.06 ml (0.81 mmol) of $EtNC$ and 0.30 ml (1.50 mmol Na) of 0.85% (w/w) sodium amalgam and the mixture stirred for 5 h. The resulting yellow solution was filtered with a filter canula from the grey precipitate consisting of NaCl and residual sodium amalgam, and the filtrate was evaporated to dryness. The residue was taken up in an Et_2O /pentane (3:1) mixture and the solution was filtered with a filter canula. The solvent was stripped off *in vacuo* and the residue was crystallized from a minimum amount of pentane at $-78^\circ C$ to afford complex **8**.

Table 7

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for *trans-2b*

Atom	x	y	z	U_{eq}^a
Re	5037(1)	3537(1)	1709(1)	14(1)
Br	6273(2)	3444(1)	-263(1)	31(1)
C(1)	5293(16)	2282(10)	1511(10)	28(3)
O(1)	5608(13)	1550(6)	1410(8)	32(2)
C(2)	2927(18)	3963(8)	806(9)	22(3)
O(2)	1706(12)	4238(6)	323(7)	30(2)
C(3)	2706(15)	3055(8)	2563(10)	22(3)
O(3)	2232(14)	3434(6)	3386(8)	36(3)
C(4)	1621(15)	2269(8)	2137(9)	20(3)
C(5)	1435(16)	1974(9)	1046(10)	28(3)
C(6)	428(16)	1251(9)	733(10)	23(3)
C(7)	-463(16)	797(8)	1532(10)	23(3)
C(8)	-321(15)	1078(8)	2622(10)	22(3)
C(9)	688(15)	1818(9)	2910(10)	24(3)
C(10)	6074(16)	3794(8)	3492(10)	23(3)
C(11)	7628(19)	3649(9)	2910(15)	39(4)
C(12)	7638(17)	4302(9)	2078(11)	34(3)
C(13)	6207(19)	4870(8)	2152(11)	33(3)
C(14)	5230(17)	4583(8)	3002(10)	26(3)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

as a white, microcrystalline solid. Yield: 100 mg (58%).
Anal. Found: C, 33.01; H, 2.96. $C_{10}H_{10}NO_2Re$ (362.40)
Calc.: C, 33.14; H, 2.78%.

5.10. $CpRe(CO)_2CN^iPr$ (**9**)

A solution of 250 mg (0.66 mmol) of *cis/trans*-**7a** in 40 ml of THF was treated at $-10^\circ C$ with 0.09 ml (0.99 mmol) of iPrNC and 0.50 ml (2.5 mmol Na) of 0.85% (w/w) sodium amalgam and the mixture worked

up as described above for the synthesis of **8** to afford complex **9** as a white, microcrystalline solid. Yield: 130 mg (52%). Anal. Found: C, 34.57; H, 3.04. $C_{11}H_{12}NO_2Re$ (376.43) Calc.: C, 35.10; H, 3.21%.

5.11. $CpRe(CO)_2CN^tBu$ (**10**)

A solution of 200 mg (0.53 mmol) of *cis/trans*-**7a** in 40 ml of THF was treated at $-10^\circ C$ with 0.09 ml (0.80 mmol) of tBuNC and 0.40 ml (2.0 mmol Na) of

Table 8

Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **14**

Atom	x	y	z	U_{eq}^a
Re(1)	2099(1)	3827(1)	1329(1)	21(1)
Re(2)	1183(1)	3894(1)	3476(1)	25(1)
Br(1)	-381(1)	3958(1)	2348(1)	28(1)
Br(2)	2427(1)	2375(1)	2740(1)	30(1)
Br(3)	2791(1)	5200(1)	2126(1)	34(1)
Re(3)	6445(1)	160(1)	2855(1)	22(1)
Re(4)	6515(1)	-2026(1)	2491(1)	24(1)
Br(4)	6817(1)	-1630(1)	3856(1)	39(1)
C(1)	4550(9)	-3094(7)	3343(6)	25(2)
C(11)	3935(10)	-3274(8)	4292(6)	37(2)
C(2)	5634(9)	-3732(7)	2952(6)	23(2)
C(21)	6322(10)	-4704(7)	3440(6)	29(2)
C(3)	5791(9)	-3368(7)	2044(5)	23(2)
C(31)	6666(11)	-3905(8)	1389(6)	37(2)
C(4)	4839(10)	-2478(7)	1875(6)	29(2)
C(41)	4561(13)	-1945(8)	1007(7)	46(3)
C(5)	4069(10)	-2329(7)	2690(6)	27(2)
C(51)	2786(10)	-1629(8)	2832(8)	43(3)
C(6)	8821(10)	630(7)	2242(7)	36(2)
C(61)	9984(11)	-30(8)	1892(9)	53(3)
C(7)	7930(10)	1379(7)	1807(6)	31(2)
C(71)	7992(12)	1702(8)	848(6)	41(3)
C(8)	7074(9)	1917(7)	2409(6)	26(2)
C(81)	6183(10)	2889(7)	2186(7)	36(2)
C(9)	7440(10)	1491(7)	3221(6)	28(2)
C(91)	6903(14)	1903(9)	4007(7)	49(3)
C(10)	8523(10)	709(7)	3121(7)	34(2)
C(101)	9322(12)	153(9)	3779(8)	56(4)
O(1)	4544(8)	561(6)	1567(5)	47(2)
O(12)	5223(10)	353(7)	2069(6)	29(2)
O(2)	3787(9)	372(7)	4187(5)	57(2)
C(13)	4766(11)	269(8)	3686(6)	35(2)
O(3)	7691(10)	-646(6)	677(5)	59(2)
C(14)	7268(11)	-1102(8)	1378(7)	38(2)
O(4)	9487(8)	-2942(7)	2236(6)	64(2)
C(15)	8397(12)	-2574(8)	2365(8)	44(3)
O(5)	-544(8)	2273(7)	5016(5)	52(2)
C(16)	89(9)	2884(9)	4422(6)	33(2)
O(6)	-331(11)	5781(7)	4121(5)	69(3)
C(17)	249(12)	5075(9)	3885(6)	42(3)
O(7)	3297(8)	3884(7)	4571(5)	53(2)
C(18)	2462(11)	3896(9)	4163(6)	39(2)
O(8)	1268(9)	2156(6)	505(5)	54(2)
C(19)	1561(10)	2799(8)	839(6)	33(2)
O(9)	5079(7)	3711(6)	285(4)	44(2)
C(20)	3953(10)	3760(7)	685(5)	30(2)
O(10)	1493(8)	5581(6)	-185(5)	44(2)
C(22)	1724(9)	4923(8)	400(6)	31(2)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

0.85% (w/w) sodium amalgam and the mixture worked up as described above for the synthesis of **8** to afford complex **10** as a white, microcrystalline solid. Yield: 125 mg (61%). Anal. Found: C, 36.71; H, 3.83. $C_{12}H_{14}NO_2Re$ (390.46) Calc.: C, 36.91; H, 3.61%.

5.12. [*trans*-CpRe(CO)₂(CNEt)Br]Br (**11**)

A solution of 160 mg (0.44 mmol) of **8** in 20 ml of CH_2Cl_2 was treated at $-78^\circ C$ with a solution of 0.023 ml (0.44 mmol) of Br_2 in 5 ml of CH_2Cl_2 and stirred for 1 h at $-25^\circ C$. Completion of the reaction was revealed by IR spectroscopy. The resulting yellow solution was concentrated *in vacuo*, and cold Et_2O ($-78^\circ C$) was added to precipitate complex **11**. Yellow solid. Yield: 220 mg (95%). Anal. Found: C, 22.75; H, 1.76. $C_{10}H_{10}Br_2NO_2Re$ (522.21) Calc.: C, 23.00; H, 1.93%.

5.13. [*trans*-CpRe(CO)₂(CN^{*i*}Pr)Br]Br (**12**)

A solution of 60 mg (0.16 mmol) of **9** in 10 ml of CH_2Cl_2 was treated at $-78^\circ C$ with a solution of 8.2 μl (0.16 mmol) of Br_2 in 5 ml of CH_2Cl_2 , stirred for 1 h at $-25^\circ C$ and the resulting yellow solution worked up as described above for the synthesis of **11** to afford complex **12** as a yellow solid. Yield: 85 mg (99%). Anal. Found: C, 24.37; H, 2.15. $C_{11}H_{12}Br_2NO_2Re$ (536.24) Calc.: C, 24.64; H, 2.26%.

5.14. [*trans*-CpRe(CO)₂(CN^{*i*}Bu)Br]Br (**13**)

A solution of 150 mg (0.38 mmol) of **10** in 20 ml of CH_2Cl_2 was treated at $-78^\circ C$ with a solution of 0.02 ml (0.38 mmol) of Br_2 in 5 ml of CH_2Cl_2 , stirred for 1 h at $-25^\circ C$, and the resulting yellow solution worked up as described above for the synthesis of **11** to afford complex **13** as a yellow solid. Yield: 200 mg (95%). Anal. Found: C, 25.58; H, 2.30. $C_{12}H_{14}Br_2NO_2Re$ (550.27) Calc.: C, 26.19; H, 2.56%.

6. Crystal structure determination of *trans*-**2b** and **14**

A summary of the crystal data, data collection and refinement for *trans*-**2b** and **14** is given in Table 6. Crystals suitable for X-ray structure determination were selected using a modified device, similar to that of Veith and Bärnighausen [33]. The crystals were mounted on a glass fibre and transferred to an Enraf-Nonius CAD4 four circle diffractometer (for *trans*-**2b**) and a STOE STADI4 four circle diffractometer (for **14**) equipped with a low temperature device. Lattice parameters derived from the setting angles of 25 reflections in the range $18^\circ \leq 2\theta \leq 30^\circ$ for **2b** and 30 reflections in the range $27^\circ \leq 2\theta \leq 29^\circ$ for **14** were obtained. Data

were collected in the ω - 2θ scan mode. After every 200 reflections for *trans*-**2b** and every 2 h for **14**, three standard reflections were monitored and the crystal reoriented in case of deviation between 0.1° and 0.15° . Intensity data were corrected for Lorentz and polarization effects. Structure solution was performed by Patterson methods (SHELXS-86) [34] and subsequent difference Fourier synthesis (SHELXL-93) [35]. Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included using a riding model with $d(C-H) = 0.96 \text{ \AA}$ and $U_{iso} = 0.08 \text{ \AA}^2$. Neutral atom scattering factors were taken from Cromer and Mann [36]. Geometrical calculations and illustrations were performed with PLATON [37]. Final positional and equivalent isotropic thermal parameters are given in Table 7 for *trans*-**2b** and in Table 8 for **14**.

7. Supplementary material available

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405501 for *trans*-**2b** and CSD-405500 for **14**, the names of the authors, and the journal citation.

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