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Stepwise substitution reactions of the $(\eta^5\text{-}C_5Me_5)Re(CO)_2I_2$ complex: aryl–iodo and aryl–methyl derivatives *trans*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2(Ar)X$, X = I and Me. X-ray structure of *trans*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2(Ph)I$

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Abstract

The diiodo complex *cis*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2I_2$ undergoes monosubstitution in reaction with arylcopper (ArCu) to produce the corresponding aryl–iodo complexes *trans*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2(Ar)I$, Ar = phenyl and tolyl. These complexes have been fully characterized by using a combination of elemental analyses and IR, ^1H and ^{13}C NMR spectroscopy; additionally *trans*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2(Ph)I$ was studied by X-ray crystallography. This complex crystallizes in the monoclinic space group $P2_1/m$ with $a = 8.091(2)$, $b = 17.471(4)$, $c = 12.995(3)$ Å, $\beta = 93.97(2)°$, $V = 1832.6(7)$ Å^3 and $D_{calc} = 2.107\ g\ cm^{-3}$ for $Z = 4$. The refined structure gave $R = 2.74\%$ and $wR = 2.98\%$ for 2858 observed reflections. Further reaction of the aryl–iodo complexes with MeLi yields the corresponding aryl–methyl derivatives *trans*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2(Ar)Me$. The full spectroscopic characterization of these complexes is also described in this paper.

Keywords: Rhenium; Cyclopentadienyls; Arylation; Crystal structure

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1. Introduction

In recent years there has been an increasing interest in exploring the chemistry of the cyclopentadienyl carbonyl halide rhenium complexes, $CpRe(CO)_2X_2$, Cp = $(\eta^5\text{-}C_5H_5)$; X = Cl, Br and I. Of these dihalides, the dibromide has received much attention. This complex has been shown to be a versatile starting material for either carbonyl or bromide substitution. In the first case, King and Reimann [1] have shown that $CpRe(CO)_2Br_2$ reacts thermally with different phosphites and *tert*-butyl isocyanide, to give the corresponding monocarbonyl dibromide complex. The dibromide complex has also been used as precursor of a series of complexes based on the $CpRe(CO)_2$ fragment, for example the following compounds have been prepared directly or indirectly from this complex: $CpRe(CO)_2H_2$ [2], $CpRe(CO)_2(CH_2(CH_2)_nCH_2)$, $n = 4$ [2] and 5 [3], $CpRe(CO)_2(Me)Br$ [4], $CpRe(CO)_2Me_2$ [5], $CpRe(CO)_2(Me)(COMe)$ [6] and $CpRe(CO)_2(SnPh_3)_2$ [7].

Reactions of the pentamethylcyclopentadienyl analogues are by far much less explored. Since 1986 when reliable and stereoselective syntheses of these dihalides were reported [8], very little work has been done on the reactivity of these derivatives. In this regard, Richmond and coworkers [9] reported the reactions of the dibromide complex $Cp^*Re(CO)_2Br_2$, $Cp^* = (\eta^5\text{-}C_5Me_5)$, with different Grignard and organolithium reagents leading to the formation of the monoanion $[Cp^*Re(CO)_2Br]^-$ which could be isolated and studied by X-ray crystallography. Based on in situ IR analyses, the same authors found that the anion reacts with trifluoroacetic acid, methyl triflate and magic ethyl to yield the corresponding dicarbonyl monobromo derivative *trans*-$Cp^*Re(CO)_2(Br)(R)$, R = H, Me and Et respectively. More recently, and with the aim of preparing the monocarbonyl phosphite derivatives $Cp^*Re(CO)\{P(OMe)_3\}X_2$, X = Cl, Br and I, we studied the thermal reactions of the corresponding $Cp^*Re(CO)_2X_2$ with $P(OMe)_3$, but only for the dibro-

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mide complex was the substitution of CO successfully achieved [10]. Very recently, we have reported the first examples of the dicarbonyl dialkyl rhenium(III) complexes, $Cp^*Re(CO)_2R_2$. These compounds were obtained by alkylation of the dichloride $Cp^*Re(CO)_2Cl_2$ by using the corresponding organocopper reagent (RCu, R = Me and Et). The diethyl complex was studied by X-ray crystallography [11].

Continuing with our interest in studying the chemical and photochemical [12] reactions of the pentamethylcyclopentadienyl dicarbonyl dihalide rhenium complexes, in the present work we would like to report the reactions of the diiodo derivative $Cp^*Re(CO)_2I_2$ with arylcopper (ArCu, Ar = Ph and Tol) leading to the monoaryl complexes $Cp^*Re(CO)_2(Ar)I$. The X-ray structure of the phenyl complex is also included. Additionally, the reactions of these monoiodo derivatives with MeLi leading to the aryl–methyl complexes *trans*-$Cp^*Re(CO)_2(Ar)(Me)$ are also described.

2. Experimental

All reactions were carried out under nitrogen in Schlenk apparatus connected to a double manifold providing low vacuum or nitrogen. Solvents were dried by conventional methods, distilled under nitrogen and used immediately. Infrared spectra were measured by using a Perkin-Elmer Model FT 1605 intrument, in KBr solution cell. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 instrument at 200 and 50 MHz respectively. Mass spectra were obtained on a Hewlett-Packard Model 5985 mass spectrometer with electron impact. Masses are based on the ^{187}Re isotope. Microanalyses were performed by M.K. Yang of the S.F.U. Microanalytical Laboratory. $Cp^*Re(CO)_2I_2$ [8] was prepared according to a modified procedure, by Me_3NO induced decarbonylation of the cation $[Cp^*Re(CO)_3I]^+$ [13]. The arylcopper reagents were prepared in situ according to literature procedures [14].

2.1. Syntheses of trans-$Cp^*Re(CO)_2(Ar)I$, Ar = phenyl and p-tolyl

To a brown solution of the arylcopper reagent (prepared from 150 mg (0.73 mmol) of $CuBr \cdot SMe_2$ (Aldrich) and 0.69 mmol of phenyllithium (1.8 M in cyclohexane/ether, Aldrich) or p-tolylmagnesium bromide (1.0 M in diethyl ether, Aldrich), in 15 ml of THF at 0 °C), 200 mg (0.32 mmol) of solid *cis*-$Cp^*Re(CO)_2I_2$ was added. The resulting mixture was stirred at 0 °C for 40 min and then warmed to room temperature and stirred for an additional 30 min. The reaction mixture was then concentrated under vacuum to about 5 ml and 0.5 ml of water was added to destroy the excess of ArCu. Filtration through Celite and evaporation of the solvent yielded an orange-red solid, which was dissolved in about 1 ml of CH_2Cl_2 and chromatographed on a neutral alumina column (prepared in hexane). Elution with CH_2Cl_2/hexane (1:3) moved an orange band which gave 110 mg (60% yield) of the phenyl complex *trans*-$Cp^*Re(CO)_2(Ph)I$, and 81 mg (43% yield) of *trans*-$Cp^*Re(CO)_2(p\text{-}Tol)I$ respectively.

2.1.1. trans-$Cp^*Re(CO)_2(Ph)I$

Obtained as orange–red crystals after crystallization from CH_2Cl_2/hexane (1:2) at −23 °C. M.p. start decomposition at 168 °C. IR (CH_2Cl_2): 2015 s and 1942 vs cm^{-1}, ν(CO). ^1H NMR ($CDCl_3$) δ: 1.75 (s, 15H, Cp*) and 7.20 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 10.70 ($C_5\mathit{Me}_5$), 102.06 (C_5Me_5), 125.02, 127.17, 128.78 and 145.10 (phenyl) and 194.46 (*C*O). Mass spectrum (EI, based on ^{187}Re) *m/z*: M^+ (582), $M^+ - CO$ (554), $M^+ - 2CO$ (526), $M^+ - Ph$ (505) and $M^+ - PhI$ (378). Anal. Found: C, 37.37; H, 3.44. $C_{18}H_{20}O_2IRe$ Calc.: C, 37.18; H, 3.44%.

2.1.2. trans-$Cp^*Re(CO)_2(p\text{-}Me\text{–}C_6H_4)I$

Red–orange microcrystals obtained as for the previous compound, melt with decomposition at 183 °C. IR (CH_2Cl_2): 2015 and 1942 cm^{-1}, ν(CO). ^1H NMR ($CDCl_3$) δ: 1.94 (s, 15H, Cp*), 2.29 (s, 3H, *Me*–C_6H_4), 6.07 (d, 2H) and 7.45 (d, 2H) p-tolyl. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 10.76 ($C_5\mathit{Me}_5$), 20.78 (*Me*–C_6H_4), 101.98 (C_5Me_5), 119.04, 130.21, 134.67 and 144.89 (Me–C_6H_4) and 194.47 (CO). Mass spectrum (EI, based on ^{187}Re) *m/z*: M^+ (596), $M^+ - CO$ (568) and $M^+ - 2CO$ (538). Anal. Found: C, 38.50; H, 3.77. $C_{19}H_{22}O_2IRe$ Calc.: C, 38.30; H, 3.69%.

2.2. Syntheses of trans-$Cp^*Re(CO)_2(Ar)Me$, Ar = phenyl and tolyl

To a stirred solution of 150 mg of *trans*-$Cp^*Re(CO)_2(Ar)I$, dissolved in 10 ml of THF, was added dropwise an excess of MeLi (0.5 ml, 1.6 M ether solution, Aldrich) at room temperature. The mixture slowly changed from orange to colourless, and the IR spectrum showed the complete disappearance of the precursor iodo complex, and intense absorptions at 1995 and 1914 cm^{-1} and weak bands at 1845 and 1724 cm^{-1} were observed. The latter bands disappeared after the addition of 0.05 ml of MeI. A small amount of water (1 drop) was added to destroy the excess of MeLi, and the solvent was evaporated under vacuum to dryness. The residue was then dissolved in CH_2Cl_2 and chromatographed on a neutral alumina column (prepared in hexane). Elution with hexane/CH_2Cl_2 moved the product, which was obtained as a white solid after solvent evaporation under vacuum.

Table 1
Crystal data and structure refinement for *trans*-Cp* Re(CO)$_2$(Ph)I

Empirical formula	$C_{18}H_{20}IO_2Re$
Formula weight	581.4
Temperature	298 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions	$a = 8.091(2)$ Å $b = 17.471(4)$ Å $c = 12.995(3)$ Å $\beta = 93.97(2)°$
Volume	1832.6(7) Å^3
Z	4
Density (calc.)	2.107 g cm^{-3}
Absorption coefficient	8.319 mm^{-1}
F(000)	1088
2θ range for data collection	3.0 to 50.0°
Index range	$0 \le h \le 9$, $-8 \le k \le 20$, $-15 \le l \le 15$
Reflections collected	3540
Independent reflections	3227 ($R_{int} = 0.53\%$)
Observed reflections	2858($F > 2.0\sigma(F)$)
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma w(F_o - F_c)^2$
Weights	$w^{-1} = \sigma^2(F) + 0.0010F^2$
Number of parameters refined	200
Final R indices (obs. data)	$R = 2.74\%$, $wR = 2.98\%$
R indices (all data)	$R = 3.22\%$, $wR = 3.03\%$
Goodness-of-fit	1.13
Largest and mean Δ/σ	0.001, 0.000
Data-to-parameter ratio	14.3:1
Largest diff. peak and hole	1.21 and -0.73 e Å^{-3}

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å $\times 10^3$) for the non-hydrogen atoms of *trans*-Cp* Re(CO)$_2$(Ph)I

Atom	x	y	z	U_{eq} [a]
Re	1093(1)	8435(1)	7981(1)	30(1)
I	1854(1)	7114(1)	9142(1)	60(1)
O(1)	−328(8)	8769(3)	10059(4)	89(2)
O(2)	−1214(7)	7221(3)	6962(5)	92(2)
C(1)	191(8)	8623(3)	9280(5)	47(2)
C(2)	−391(8)	7679(4)	7377(5)	49(2)
C(3)	3847(7)	8717(4)	8153(5)	45(2)
C(4)	3015(7)	9403(3)	7949(4)	42(2)
C(5)	2227(7)	9371(3)	6948(5)	44(2)
C(6)	2558(8)	8632(4)	6526(4)	49(2)
C(7)	3551(8)	8233(3)	7259(5)	46(2)
C(8)	5041(9)	8555(5)	9063(6)	78(3)
C(9)	3129(10)	10117(4)	8621(6)	75(3)
C(10)	1448(10)	10022(5)	6346(7)	80(3)
C(11)	2072(11)	8388(5)	5438(5)	83(3)
C(12)	4388(10)	7483(4)	7076(7)	81(3)
C(13)	−997(7)	9191(3)	7537(4)	38(2)
C(14)	−1250(8)	9864(3)	8081(5)	53(2)
C(15)	−2499(10)	10382(4)	7762(7)	72(3)
C(16)	−3538(10)	10242(5)	6904(7)	75(3)
C(17)	−3314(5)	9586(6)	6365(6)	65(3)
C(18)	−2076(7)	9067(4)	6667(5)	49(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

2.2.1. *trans-Cp* Re(CO)$_2$(C$_6$H$_5$)Me*

Crystallization from hexane at −23 °C, yield 87 mg (72%) of white microcrystal, which decomposed above 150 °C. Anal. Found: C, 48.51; H, 5.05. $C_{19}H_{23}O_2Re$ Calc.: C, 48.61; H, 4.90%. IR (hexane): 2003 s and 1928 vs cm^{-1}, ν(CO). ^{1}H NMR (CDCl$_3$) δ: 0.73 (s, 3H, Me), 1.65 (s, 15H, Cp*), 7.03 (m, 3H, Ph) and 7.65 (m, 2H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$) δ: −21.24 (*Me*), 9.19 (C$_5$*Me*$_5$), 99.48 (*C*$_5$Me$_5$), 124.01, 128.34, 131.26 and 146.54 (*Ph*) and 201.23 (*C*O). Mass spectrum (EI, based on ^{187}Re) m/z: M$^+$ (470), M$^+$ − CO (442).

2.2.2. *trans-Cp* Re(CO)$_2$(p-MeC$_6$H$_4$)Me*

This complex was obtained as colourless microcrystals in 42% yield, which decomposed over 134 °C. Anal. Found: C, 50.36; H, 5.28. $C_{20}H_{25}O_2Re$ Calc.: C, 49.61; H, 5.17%. IR (hexane): 2002 s and 1928 vs cm^{-1}, ν(CO). ^{1}H NMR (CDCl$_3$) δ: 0.60 (s, 3H, Me), 1.55 (s, 15H, Cp*), 2.60 (s, 3H, MeC$_6$H$_4$), 6.89 (d, 2H, tolyl) and 7.55 (d, 2H, tolyl). ^{13}C{^{1}H} NMR (CDCl$_3$) δ: −6.12 (*Me*), 9.20 (C$_5$*Me*$_5$), 20.78 (MeC$_6$H$_4$), 99.47 (*C*$_5$Me$_5$), 126.00, 129.54, 133.45 and 145.34 (*tolyl*) and 201.18 (*C*O). Mass spectrum (EI, based on ^{187}Re) m/z: M$^+$ (484), M$^+$ − CO (456).

2.3. *Crystal structure determination*

A red prismatic shaped crystal of *trans*-Cp* Re(CO)$_2$(Ph)I, ca. 0.44 × 0.20 × 0.20 mm^3 mounted on a glass fibre was used for crystallographic measurements. The intensity data were collected at 298 K on a Siemens R3/V diffractometer using graphite monochromated Mo Kα radiation in the $2\theta/\theta$ scan mode with two standard reflections monitored every 100 reflections. Lattice parameters and their e.s.d.s were derived from the setting angles of 25 reflections with $5° \le 2\theta \le 40°$. The structure was solved by direct phase determination. The positional and anisotropic thermal parameters for all non-hydrogen atoms were refined by full-matrix least-square cycles. The hydrogen atom positions were calculated geometrically and they were let to ride on their parent carbon atoms with fixed isotropic U. The atomic scattering factors were taken from the SHELXTL PLUS program. Table 1 summarizes the crystal data and data collection conditions. The final positional and equivalent isotropic thermal parameters of all non-hydrogen atoms are listed in Table 2. Selected interatomic distances and bond angles are included in Table 3.

3. Results and discussion

3.1. *Aryl–iodo complexes trans-Cp* Re(CO)$_2$(Ar)I, Ar = phenyl and tolyl*

The syntheses of the aryl–iodo derivatives were carried out following the recommended methodology for

Table 3
Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for *trans*-Cp*Re(CO)$_2$(Ph)I

Re–I	2.803(1)
Re–C(1)	1.913(6)
Re–C(2)	1.916(6)
Re–C(3)	2.278(6)
Re–C(4)	2.299(6)
Re–C(5)	2.342(6)
Re–C(6)	2.325(6)
Re–C(7)	2.285(7)
Re–C(13)	2.191(5)
O(1)–C(1)	1.152(9)
O(2)–C(2)	1.152(9)
C(3)–C(4)	1.391(8)
C(3)–C(7)	1.444(9)
C(3)–C(8)	1.500(10)
C(4)–C(5)	1.410(8)
C(4)–C(9)	1.522(10)
C(5)–C(6)	1.435(9)
C(5)–C(10)	1.495(10)
C(6)–C(7)	1.390(9)
C(6)–C(11)	1.503(9)
C(7)–C(12)	1.500(10)
C(13)–C(14)	1.395(9)
C(13)–C(18)	1.397(8)
C(14)–C(15)	1.397(10)
C(15)–C(16)	1.371(12)
C(16)–C(17)	1.361(12)
C(17)–C(18)	1.388(10)
I–Re–C(1)	75.5(2)
I–Re–C(2)	76.2(2)
C(1)–Re–C(2)	102.3(3)
C(4)–Re–C(5)	35.4(2)
C(3)–Re–C(6)	59.9(2).
C(4)–Re–C(6)	59.6(2)
C(5)–Re–C(6)	35.8(2)
C(3)–Re–C(7)	36.9(2)
C(4)–Re–C(7)	59.8(2)
C(5)–Re–C(7)	59.1(2)
C(6)–Re–C(7)	35.1(2)
I–Re–C(13)	140.8(2)
C(1)–Re–C(13)	78.1(2)
C(2)–Re–C(13)	81.8(2)
Re–C(1)–O(1)	177.0(6)
Re–C(2)–O(2)	175.5(6)
C(4)–C(3)–C(7)	107.5(5)
C(4)–C(3)–C(8)	126.1(6)
C(7)–C(3)–C(8)	125.8(6)
C(3)–C(4)–C(5)	108.9(5)
C(3)–C(4)–C(9)	125.9(6)
C(5)–C(4)–C(9)	124.6(6)
C(4)–C(5)–C(6)	107.7(5)
C(4)–C(5)–C(10)	126.8(6)
C(6)–C(5)–C(10)	124.6(6)
C(5)–C(6)–C(7)	107.7(5)
C(5)–C(6)–C(11)	124.8(6)
C(7)–C(6)–C(11)	127.1(6)
C(3)–C(7)–C(6)	108.2(5)
C(3)–C(7)–C(12)	126.0(6)
C(6)–C(7)–C(12)	125.1(6)
Re–C(13)–C(14)	120.8(4)
Re–C(13)–C(18)	123.2(4)
C(14)–C(13)–C(18)	115.9(5)
C(13)–C(14)–C(15)	121.6(6)
C(14)–C(15)–C(16)	121.1(7)
C(15)–C(16)–C(17)	118.2(7)
C(16)–C(17)–C(18)	121.6(7)
C(13)–C(18)–C(17)	121.7(6)

direct aryl/halide exchange in cyclopentadienyl rhenium halide complexes, reported by Sweet and Graham [15], that is, by using an excess of arylcopper (ArCu) as arylating agent. Treatment of *cis*-Cp*Re(CO)$_2$I$_2$ with excess of ArCu (Ar = Ph and tolyl) in THF affords the corresponding monosubstituted products *trans*-Cp*Re(CO)$_2$(Ar)I. These orange–red crystalline products are air stable as a solid or in organic solvents such as CH$_2$Cl$_2$, THF and toluene, in which they are highly soluble. They are also very stable with respect to thermal isomerization. No isomerization was observed even in boiling THF or toluene, though the complexes do not survive for long at these temperatures. Both compounds exhibit only two ν(CO) absorptions in the IR spectra at 2015 and 1942 cm^{-1} (in CH$_2$Cl$_2$ solution), and the lower wavenumber one is much more intense. On this criterion, as well as the correspondence between our IR values and those reported for *trans*-Cp*Re(CO)$_2$I$_2$ [8], *trans*-Cp*Re(CO)$_2$[PO(OMe)$_2$]I [16], and *trans*-Cp*Re(CO)$_2$(Et)Br [9], we consider that our products are also the *trans* isomers. The ^{1}H NMR spectra, in addition to the Cp*, show the expected resonances for the aryl ligands. The appearance of a single resonance for the CO in the ^{13}C{^{1}H} NMR spectra is further evidence for the *trans* orientation of the carbonyl ligands in this type of molecule. Furthermore, the X-ray structure of *trans*-Cp*Re(CO)$_2$(Ph)I (see below and Fig. 1) confirms the above assumption.

The use of an excess of ArCu in reaction with the diiodo complex should produce the disubstituted complex Cp*Re(CO)$_2$Ar$_2$ in a similar manner to the reaction of Cp*Re(CO)$_2$Cl$_2$ with alkylcopper (RCu, R = Me

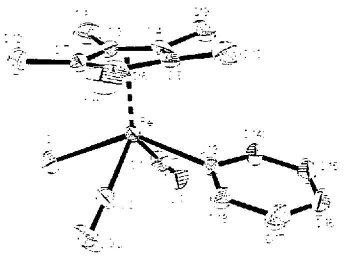

Fig. 1. Perspective view (ORTEP plot) of a molecule of *trans*-Cp*Re(CO)$_2$(Ph)I showing the atom labelling (hydrogen atoms are omitted for clarity).

and Et) from which $Cp^*Re(CO)_2R_2$ could be isolated and fully characterized [11]. It is now clear that the formation of the dialkyl (or diaryl) products occurs stepwise, and the reactivity of the alkyl–halide (or aryl–halide) intermediate $Cp^*Re(CO)_2(R)X$, toward substitution of the remaining halide ligand, depends on the nature of X, the chloro being more reactive compared to the iodo analogue. This result suggests that the reaction of $Cp^*Re(CO)_2(R)X$ is facilitated by increased polarity of the $Re^{\delta+}-X^{\delta-}$ bond. Similar arguments were used by Sweet and Graham [15] to explain the low yield of CpRe(CO)(NO)(Ar) by using CpRe(CO)(NO)I instead of the chloro analogue, in reaction with excess of ArCu.

Steric factors, which can also affect the halide substitution of $Cp^*Re(CO)_2(R)X$, R = alkyl or aryl, can be ruled out since preliminary results on methylation of $Cp^*Re(CO)_2I_2$ and phenylation of $Cp^*Re(CO)_2Cl_2$ (using an excess of the corresponding organocopper) yield $Cp^*Re(CO)_2(Me)I$ and $Cp^*Re(CO)_2(Ph)_2$ respectively [17].

3.2. *Aryl–methyl complexes trans-Cp*Re(CO)₂(Ar)Me, Ar = phenyl and tolyl*

These complexes were prepared from the reaction of the corresponding aryl–iodo complex with methyllithium in THF at room temperature. IR monitoring of the reaction mixture showed, in addition to the $\nu(CO)$ of the product, small bands at about 1845 and 1742 cm^{-1} (THF solution). These bands disappeared after addition of MeI. Taking into account reports on the reaction of $Cp'Re(CO)_2Br_2$, Cp′ = Cp [4] and Cp^* [9], and $Cp^*Re(CO)_2Cl_2$ with MeLi [11], we tentatively assigned these IR absorptions to the anionic complex $[Cp^*Re(CO)_2(Ar)]^-$, which then reacts with MeI to yield the observed product. The less plausible formation of the anion $[Cp^*Re(CO)_2I]^-$ which could form in the reaction can be ruled out since we do not observe any of the methyl–iodo complex $Cp^*Re(CO)_2(Me)(I)$ (expected product from the reaction of the anion and MeI).

The aryl–methyl derivatives $Cp^*Re(CO)_2(Ar)(Me)$ are white crystalline materials, very soluble in most organic solvents, in which they are fairly stable. Like their predecessors, the IR spectra of these compounds also show two bands, the highest wavenumber $\nu_s(CO)$ (at about 2002 cm^{-1}, in hexane) being less intense than the $\nu_{as}(CO)$ observed at lower wavenumber. From the intensity pattern of these bands we conclude that the carbonyl groups are oriented in a diagonal or *trans* position. The OC–Re–CO interbond angles, estimated from the $\nu(CO)$ intensities, are in both cases ca. 115°. The *trans* stereochemistry is confirmed by $^{13}C\{^1H\}$ NMR spectra, where the COs appear as a single resonance at 201 ppm. The ^1H and ^{13}C NMR spectra clearly show the presence of the methyl ligand in the high field region, following the same trend observed for other analogous complexes containing an sp^3 carbon bound to the metal [11].

3.3. *X-ray structure of trans-Cp*Re(CO)₂(Ph)I*

The structure of the phenyl–iodo complex has been confirmed by single-crystal X-ray diffraction analysis. Orange–red crystals of *trans*-$Cp^*Re(CO)_2(Ph)I$ were grown from a mixture CH_2Cl_2/hexane (1:1) at −30°C. The complex exists as discrete molecules in the unit cell with no unusually short inter- or intramolecular contacts. An ORTEP diagram with the atom labelling scheme is shown in Fig. 1. Table 1 summarizes the crystal data and data collection conditions. Atom coordinates are in Table 2, and selected bond distances and angles in Table 3.

The rhenium atom is formally in the III oxidation state and seven coordinated if the Cp^* group is considered as a three-coordinate monoanion, and the overall geometry is of four-legged piano-stool type Cp^*ML_4 [18]. The Re–C(CO) bond lengths are in the expected range of 1.9–2.0 Å observed previously in $Cp^*Re(CO)_2X_2$, X = I (*cis* isomer) and X = Br (*trans* isomer) [8], *trans*-$Cp^*Re(CO)_2Et_2$ [11] and *trans*-$Cp^*Re(CO)_2[PO(OMe)_2]I$ [19]. The Re–I bond length is unremarkable and almost identical to that found in *trans*-$Cp^*Re(CO)_2[PO(OMe)_2]I$ [19]. The Cp^* ring is closely planar with the C atom of the methyl groups, displaced an average of 0.244 Å away from the mean plane. The distance Re–Cp^* (centroid) of 1.965 Å and the C–O bond lengths are unexceptional in comparison to those found in other cyclopentadienyl rhenium complexes. The interbond angle relating the carbonyls OC–Re–CO, 102.2(3)°, which clearly establishes the *trans* orientation of these ligands, is quite similar to that observed in several other dicarbonyl rhenium complexes possessing the same stereochemistry (*trans*-$Cp^*Re(CO)_2Et_2$ 103.1(4)° [11], *trans*-$CpRe(CO)_2(COMe)(Me)$ 101.24(17)° [6], *trans*-$Cp^*Re(CO)_2Br_2$ 104.3(6)° [8] and *trans*-$CpRe(CO)_2(SnPh_3)_2$ 100.4(5)° [7]). As expected, the Re–C(Ph) bond length of 2.191(6) Å is shorter than those in the corresponding alkyl complexes *trans*-$CpRe(CO)_2(COMe)(Me)$ (2.245(4) Å) [6], *trans*-$CpRe(CO)_2(H)(CH_2Ph)$ (2.29(1) Å) [20] and *trans*-$Cp^*Re(CO)_2Et_2$ (2.262(10) Å) [11]. These differences can largely be attributed to the bond contraction commonly observed upon replacing an sp^3 carbon by an sp^2 carbon [21]. On the other hand, the Re–C(Ph) distance found for this complex is slightly larger than that observed for $CpRe(NO)(PPh_3)(Ph)$ (2.139(6) Å) [22]. The smaller contribution Re–C π-bonding from the Re atom in a formal oxidation state of III, compared to the Re(I) in $CpRe(NO)(PPh_3)(Ph)$, can account for the lengthening of the Re–Ph bond. This argument is in good agreement with the length of 2.22 Å estimated for an Re–C(sp^2) single bond [23].

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References

[1] R.B. King and R.H. Reimann, *Inorg. Chem.*, *15* (1976) 183.
[2] G.K. Yang and R.G. Bergman, *Organometallics*, *4* (1985) 129.
[3] E. Linder and W. Wassing, *Organometallics*, *10* (1991) 1640.
[4] A.N. Nesmeyanov, N.E. Kolobova, Y.V. Makarov, E.I. Kazimirchurk and K.N. Anisimov, *Bull. Acad. Sci. USSR, Div. Chem.*, (1976) 147.
[5] J.K. Hoyano and W.A.G. Graham, *Organometallics*, *1* (1982) 783.
[6] K.I. Goldberg and R.G. Bergman, *J. Am. Chem. Soc.*, *111* (1989) 1285.
[7] S.W. Lee, K. Yang, J.A. Martin, S.G. Bott and M.G. Richmond, *Inorg. Chim. Acta*, *232* (1995) 57.
[8] F.W.B. Einstein, A.H. Klahn, D. Sutton and K.G. Tyers, *Organometallics*, *5* (1986) 53.
[9] C.M. Nunn, A.H. Cowley, S.W. Lee and M.G. Richmond, *Inorg. Chem.*, *29* (1990) 2105.
[10] A.H. Klahn and S. Arenas, *Bol. Soc. Chil. Quim.*, *38* (1993) 277.
[11] A.H. Klahn, C. Manzur, A. Toro and M. Moore, *J. Organomet. Chem.*, *516* (1996) 51.
[12] W. Xia, R.H. Hill, A.H. Klahn, C. Leiva and G.E. Buono-Core, *Polyhedron*, *18* (1996) 3093.
[13] M. Arenas, S. Silva, A. Toro and A.H. Klahn, *Bol. Soc. Chil. Quim.*, *39* (1994) 285.
[14] G. Costa, A. Camus, L. Gatti and N. Marsich, *J. Organomet. Chem.*, *5* (1966) 568.
[15] J.R. Sweet and W.A.G. Graham, *J. Organomet. Chem.*, *241* (1983) 45.
[16] A.H. Klahn, C. Leiva, K. Mossert and D. Sutton, *J. Organomet. Chem.*, *469* (1994) 69.
[17] A. Toro and A.H. Klahn, unpublished results, 1996.
[18] P. Kubacek, R. Hoffmann and Z. Havlas, *Organometallics*, *1* (1982) 180.
[19] F.W.B. Einstein, C.E.F. Rickard, A.H. Leiva and A.H. Klahn, *Acta Crystallogr.*, *C47* (1991) 862.
[20] E.O. Fischer and A. Frank, *Chem. Ber.*, *111* (1978) 3740.
[21] J.A. March, *Advanced Organic Chemistry*, Wiley, New York, 3rd edn., 1985, p. 19.
[22] S.K. Agbossou, G.S. Bodner, A.J. Patton and J.A. Gladysz, *Organometallics*, 9 (1990) 1184.
[23] W. Carroll and R. Bau, *J. Chem. Soc., Chem. Commun.*, (1978) 825.