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trans-Bromodicarbonyl(η^5-cyclopentadienyl)(2,3,5,6-tetrafluorophenyl)rhenium(III)

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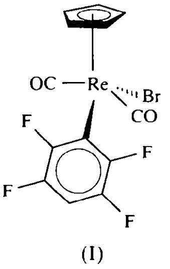
Abstract

The complex *trans*-[ReBr(η^5-C_5H_5)(C_6HF_4)$(CO)_2$] was prepared by reacting the hydride complex *trans*-[Re(η^5-C_5H_5)(C_6HF_4)H$(CO)_2$] with bromoform. The structure consists of discrete monomers of the rhenium complex, the coordination polyhedron being defined by a bromide [Re—Br 2.611 (1) Å], two carbonyls [Re—C 1.949 (9) and 1.960 (9) Å], a tetrafluorophenyl group (TFP) [Re—C 2.172 (8) Å] and a cyclopentadienyl group [Re—C 2.229 (9)–2.318 (8) Å].

Comment

As part of our study on the photochemical reactions of cyclopentadienyl rhenium tricarbonyl complexes with fluorinated aromatic molecules (Klahn *et al.*, 1992; Higgitt *et al.*, 1997), we describe here the structure of the title complex, (I), resulting from substitution of the hydride ligand by bromide in the complex *trans*-[Re(η^5-C_5H_5)(C_6HF_4)H$(CO)_2$].



(I)

The crystal structure of (I) consists of discrete monomers of the rhenium complex. The structure may be described as a five-coordinate square pyramid with the η^5-cyclopentadienyl ring occupying the unique apical site and the CO groups mutually *trans* in the square base. The cyclopentadienyl ligand (Cp) is bonded to the rhenium in a typical η^5-coordination mode. The whole arrangement displays a non-crystallographic quasi-mirror plane containing the rhenium and bromine ions, and bisecting the two planar cycles. An analysis of the Re—C(Cp) distances [2.229 (9)–2.318 (8) Å] shows a slight slippage [0.11 (1) Å] of the Re atom towards the C12—C13 bond.

The Re—C(CO) bond lengths and the interbond angle relating the carbonyls (OC—Re—CO), which clearly establish the *trans* orientation of these ligands, are quite similar to those observed in several other dicarbonyl rhenium complexes possessing the same stereochemistry (Lee *et al.*, 1995).

The Re—C(TFP) distance is shorter than the one estimated for an Re—Csp^2 single bond (2.22 Å; Carrol & Bau, 1978). The presence of the electron-withdrawing F atoms in the TFP ring can account for the shortening of the Re—C(TFP) bond by increasing the contribution of Re—C σ bonding. The above assumption may also explain the lengthening of the Re—Br bond [2.6113 (11) Å] *trans* to the TFP ligand, when compared with the Re—Br distance [2.579 (2) Å] observed in *trans*-[ReBr$_2$(η^5-C_5Me_5)$(CO)_2$] (Einstein *et al.*, 1986).

The only intermolecular interaction is provided by a C13—H13···Br1(1 + *x*, *y*, *z*) hydrogen bond [H13···Br1 2.87 (1) Å and C13—H13···Br1 147.2 (5)°], leading to the formation of linear chains parallel to the *a* crystallographic direction. Interactions among chains are provided by van der Waals forces.

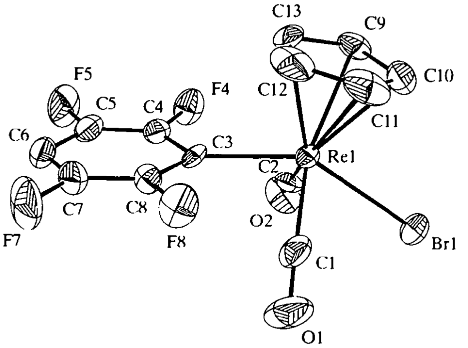


Fig. 1. View of the title molecule showing the labelling scheme used. Displacement ellipsoids are shown at the 50% probability level.

Experimental

The title complex, (I), was synthesized by UV irradiation (300 nm) of a quartz tube containing [Re(η^5-C_5H_5)$(CO)_3$] (300 mg, 0.894 mmol) in neat 1,2,4,5-tetrafluorobenzene (12 ml) for 1 h. The dark-orange solution was evaporated under vacuum and the resulting brown solid was dissolved in dry tetrahydrofuran (15 ml). $CHBr_3$ (0.3 ml) was added, and the mixture, which contained mainly *trans*-[Re(η^5-C_5H_5)(C_6HF_4)H$(CO)_2$] and unreacted [Re(η^5-C_5H_5)$(CO)_3$], was stirred under nitrogen at room temperature for 4 h. The residue obtained after evaporation of the solvent was chromatographed on neutral alumina. Elution with hexanes/CH_2Cl_2 (5:1) afforded (I) (153 mg, 0.455 mmol). Crystals suitable for

X-ray analysis were obtained by slow diffusion of hexanes into a CH_2Cl_2 solution of (I).

Crystal data

[$ReBr(C_5H_5)(C_6HF_4)(CO)_2$]
$M_r = 536.29$
Monoclinic
$P2_1/n$
$a = 7.864\,(2)$ Å
$b = 6.964\,(2)$ Å
$c = 24.361\,(6)$ Å
$\beta = 97.74\,(2)°$
$V = 1321.9\,(5)$ Å^3
$Z = 4$
$D_x = 2.695$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5–12.5°$
$\mu = 12.262$ mm^{-1}
$T = 293\,(2)$ K
Needle
$0.48 \times 0.16 \times 0.12$ mm
Intense orange

Data collection

Siemens $R3$ diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XPREP* in *SHELXTL/PC*; Sheldrick, 1991)
$T_{\min} = 0.04$, $T_{\max} = 0.23$
2385 measured reflections
2234 independent reflections

1802 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 8$
$l = -28 \rightarrow 20$
2 standard reflections every 98 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.088$
$S = 1.011$
2234 reflections
191 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.06P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.01$

$\Delta\rho_{\max} = 1.31$ e Å^{-3}
$\Delta\rho_{\min} = -1.23$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0029 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

Re1—C1	1.949 (9)	Re1—C11	2.297 (9)
Re1—C2	1.960 (9)	Re1—C10	2.310 (9)
Re1—C3	2.172 (8)	Re1—C9	2.318 (8)
Re1—C12	2.229 (9)	Re1—Br1	2.6113 (11)
Re1—C13	2.241 (9)		

The title structure was difficult to solve with the uncorrected raw data, and only when a careful absorption correction was performed was it possible to solve it through direct methods and refine it properly by least squares on F^2. A measure of the importance of the correction can be seen in some final parameters calculated with corrected and uncorrected data, *viz* the R indexes (0.034 and 0.107), the residual electron density around the Re atom (+1.31/−1.23 and +8.45/−9.52 e Å^{-3}) *etc.* Non-H atoms were refined anisotropically, whereas H atoms were idealized (C—H 0.93 Å) and allowed to ride with isotropic displacement factors 1.2 times larger than those of their hosts. The final residual electron density, though rather large in relative terms, is not unusual in structural studies of organometallic rhenium complexes.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1143). Services for accessing these data are described at the back of the journal.

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A cylindrical macrocycle with two caesium cations sandwiched between two diaza-18-crown-6 macrocycles

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Abstract

Colorless crystals of [51,52-difluoro-12,15,29,32,37,40,45,48-octaoxa-1,9,18,26-tetraazapentacyclo[26.8.8.8^{9,18}.1^{3,7}.1^{20,24}]dopentaconta-3,5,7(51),20,22,24(52)-hexaene-1$\kappa^6 N^1,N^{26},O^{29},O^{32},O^{37},O^{40}$;2$\kappa^6 N^9,N^{18},O^{12},O^{15},O^{45},O^{48}$]-