

fac-Bromotricarbonyl[2-(2-pyridylmethyl)-2,3-dihydro-1H-isoindol-1-one]rhenium(I) methanol solvate

Lihui Wei* and Jon Zubieta

1-014 CST, Department of Chemistry, 111 College Place, Syracuse University, NY 13244, USA

Correspondence e-mail: lwei@syr.edu

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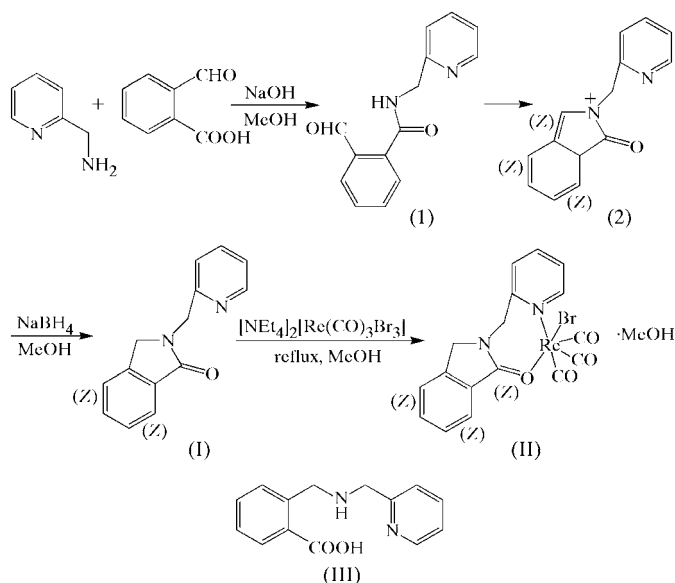
The structure of the title compound, *fac*-[ReBr(C₁₄H₁₂N₂O)(CO)₃]·CH₄O, consists of neutral mononuclear molecular units of distorted octahedral geometry, with the three carbonyl donors in a facial orientation. The remaining coordination sites are occupied by the Br atom, the pyridine N atom and the ketone O-atom donor of the ligand. The molecules pack in stacks of antiparallel tapes, with a network of classical (O—H···Br) and non-classical (C—H···O) hydrogen bonds between the methanol solvent molecule and the complex molecule.

Comment

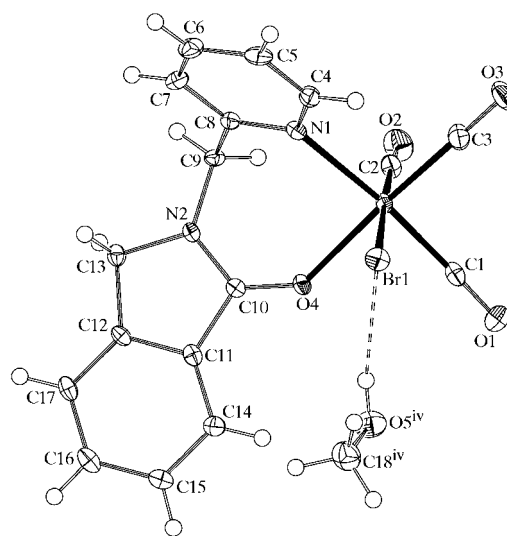
The ligand 2-(2-pyridylmethyl)-2,3-dihydro-1H-isoindol-1-one, (I), was an unexpected product from the reaction of 2-(aminomethyl)pyridine with 2-carboxybenzaldehyde, NaOH

attempted to prepare 2-[N-(2-pyridylmethyl)aminomethyl]-benzoic acid, (III). Although one equivalent of NaOH was added to protect the carboxylic acid group, a coupling reaction between the carboxylic acid group and the primary amine group occurred, forming intermediate (1). Condensation of the carboxyaldehyde and the amine group of (1) provided Schiff base (2), which upon reduction using sodium borohydride in methanol gave the ligand (I). Complex (II) was synthesized upon refluxing a methanol solution of the common tricarbonylrhenium(I) starting material [NEt₄]₂[Re(CO)₃Br₃] (Alberto *et al.*, 1994) with (I). The structure of complex (II) is shown in Fig. 1, and selected bond lengths and angles are given in Table 1.

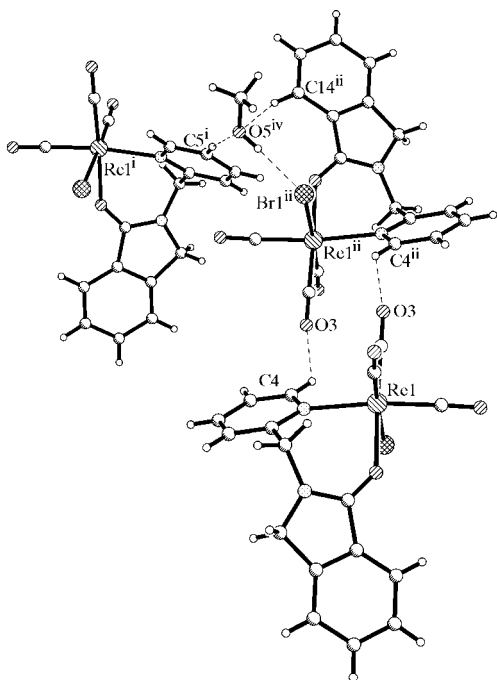
The ligand adopts a bidentate coordination mode through the pyridine (py) N atom and the ketone O atom to form an unusual seven-membered chelate ring. The formation of the seven-membered ring illustrates the flexibility of the ligand. The ligand folds at the methylene group adjacent to the pyridine ring (C9), thus providing appropriate chelate bite distances and angles. The Re—C_{CO} bond distances [1.898 (3)–1.910 (4) Å] are consistent with those found in other tricarbonylrhenium(I) complexes (Banerjee *et al.*, 2002; Wei *et al.*, 2004; Moya *et al.*, 1994). The Re—Br [2.6409 (4) Å] and Re—N_{py} [2.239 (3) Å] bond lengths are comparable to those of six-coordinated rhenium compounds with ligands *trans* to carbonyl groups (Banerjee *et al.*, 2002; Wei *et al.*, 2004). For example, in [Re(CO)₃Br{(2-pyridylmethyl)NH₂}] and [Re(CO)₃Br{(2-pyridylmethyl)NH(2-thienylmethyl)}], the average Re—Br and Re—N_{py} bond distances are 2.636 (6) and 2.190 (4) Å, respectively (Banerjee *et al.*, 2002). The C10=O4 bond length in (II) [1.248 (3) Å] is as expected for a C=O double bond. The Re—O bond distance [2.182 (2) Å] lies within the range of the bond lengths between Re and ketone O atoms reported previously (Creber *et al.*, 2000; Wang *et al.*,



and sodium borohydride in methanol (see scheme). Following literature procedures (Li *et al.*, 2003; Musie *et al.*, 2003), we

**Figure 1**

A view of the structure of complex (II), showing the atom-labeling scheme and 50% probability displacement ellipsoids. [Symmetry code: (iv) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$]


Figure 2

A view showing the classical and non-classical hydrogen bonds in (II). [Symmetry codes: (i) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (ii) $-1 - x, 2 - y, -z$; (iv) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$.]

2003; Jiménez-Pulido *et al.*, 2001). The *cis* and *trans* angles fall in the ranges 82.85 (6)–98.41 (12) and 172.06 (12)–177.57 (10)°, respectively, showing minor deviations from the idealized octahedral limits. The steric requirements of the CO ligands are manifested in the mean C–Re–N and C–Re–O *cis* angle of 94.0 (4)°, and in the mean C–Re–N and C–Re–O *trans* angle of 174.2 (1)°.

The crystal packing consists of antiparallel stacks of (II), with a network of hydrogen bonds between the methanol solvent molecule and adjacent *fac*-[ReBr(C₁₄H₁₂N₂O)(CO)₃] molecules (Table 2). This arrangement leads to the formation of a classical intramolecular O–H···Br hydrogen bond and intermolecular non-classical C–H···O hydrogen bonds (Fig. 2). The bond distances and angles of the hydrogen bonds are of the same order as those reported in other compounds containing such bonds (Bakir, 2001, 2002; Correia *et al.*, 2001). For example, in *fac*-[ReCl(C₁₇H₁₃N₅O₂)(CO)₃]-C₂H₆OS (Bakir, 2001), hydrogen bonds with O–H and O–C distances of 2.47–2.55 and 3.183 (7)–3.436 (7) Å, respectively, and C–H···O angles of 142–174° are observed.

Experimental

For the preparation of ligand (I), 2-(aminomethyl)pyridine (2.88 g, 25.85 mmol) was added to a stirred solution of 2-carboxybenzaldehyde (4.00 g, 26.64 mmol) and NaOH (1.07 g, 26.64 mmol) in methanol (50 ml). The solution was refluxed at 323 K for 2 h and turned yellow. After cooling in an ice bath, excess NaBH₄ (1.24 g, 32.72 mmol) was added to the solution and the yellow color slowly disappeared. After stirring for 30 min, excess HCl was added until the

pH of the solution reached 5.0. The solution was filtered and the filtrate was evaporated to dryness. The residue was purified by silica-gel column chromatography using CH₃OH/CH₂Cl₂ (5:95) to give (I) (yield 4.4 g, 76%). For the preparation of (II), ligand (I) (0.07 g, 0.33 mmol) was added to a solution of (NEt₄)₂[Re(CO)₃Br₃] (0.25 g, 0.33 mmol) in methanol (30 ml) and the resulting solution refluxed for 2 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The residue was dissolved in a minimum amount of chloroform. Colorless crystals suitable for X-ray analysis were obtained from the solution after 30 min (yield 0.15 g, 80%). Analysis found: C 35.6, H 2.23, N 4.76%; calculated: C 35.5, H 2.11, N 4.88%. IR (KBr, cm⁻¹): ν 2026, 1997, 1868 [ν [*fac*-Re(CO)₃]].

Crystal data

[ReBr(C₁₄H₁₂N₂O)(CO)₃]-CH₄O
M_r = 606.44
 Monoclinic, *P*₂₁/*n*
a = 7.3195 (7) Å
b = 15.5186 (14) Å
c = 16.4240 (15) Å
 β = 94.182 (2)°
V = 1860.6 (3) Å³
Z = 4

D_x = 2.165 Mg m⁻³
 Mo K α radiation
 Cell parameters from 6164 reflections
 θ = 1.8–31.5°
 μ = 8.71 mm⁻¹
T = 90 (2) K
 Block, colorless
 0.24 × 0.14 × 0.10 mm

Data collection

Bruker SMART APEX CCD detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1997)
T_{min} = 0.229, *T_{max}* = 0.421
 21 761 measured reflections

6164 independent reflections
 5404 reflections with *I* > 2 σ (*I*)
R_{int} = 0.035
 θ_{max} = 31.5°
h = -10 → 10
k = -22 → 22
l = -23 → 23

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.028
wR(*F*²) = 0.063
S = 1.04
 6164 reflections
 246 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 0.1451P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.002$
 $\Delta\rho_{max} = 1.64 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.81 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Re1–C3	1.898 (3)	Re1–O4	2.182 (2)
Re1–C1	1.907 (3)	Re1–N1	2.239 (3)
Re1–C2	1.910 (4)	Re1–Br1	2.6409 (4)
C3–Re1–C1	89.90 (14)	C2–Re1–N1	98.41 (12)
C3–Re1–C2	86.44 (14)	O4–Re1–N1	88.56 (9)
C1–Re1–C2	88.95 (14)	C3–Re1–Br1	94.30 (11)
C3–Re1–O4	176.30 (12)	C1–Re1–Br1	88.73 (10)
C1–Re1–O4	87.68 (11)	C2–Re1–Br1	177.57 (10)
C2–Re1–O4	96.31 (11)	O4–Re1–Br1	82.85 (6)
C3–Re1–N1	93.49 (12)	N1–Re1–Br1	83.86 (7)
C1–Re1–N1	172.06 (12)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O5–H5···Br1 ⁱ	0.82	2.54	3.296 (3)	153
C4–H4···O3 ⁱⁱ	0.93	2.57	3.275 (4)	133
C5–H5A···O5 ⁱⁱⁱ	0.93	2.34	3.263 (5)	169
C14–H14···O5 ^{iv}	0.93	2.53	3.351 (4)	147

Symmetry codes: (i) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (ii) $-1 - x, 2 - y, -z$; (iii) $x - 1, y, z - 1$; (iv) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$.

All H atoms were located in difference Fourier maps and refined as riding on their parent atoms ($C-H = 0.93-0.97 \text{ \AA}$), with $U_{iso}(H)$ values of $1.2U_{eq}(\text{parent atom})$. A residual peak of electron density was located in the vicinity of the Re atom. However, the absorption correction could not be adjusted to further minimize this. Such residuals are not uncommon in structures containing atoms with large absorption coefficients.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT-NT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 2000); software used to prepare material for publication: *SHELXTL-NT*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1088). Services for accessing these data are described at the back of the journal.

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