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Key indicators

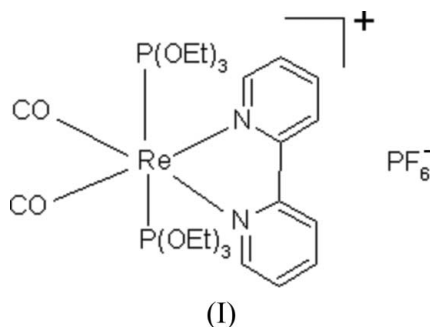
Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(\text{C}-\text{C}) = 0.012$ Å
Disorder in main residue
 R factor = 0.033
 wR factor = 0.073
Data-to-parameter ratio = 15.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**(2,2'-Bipyridyl)dicarbonylbis(triethoxyphosphine- κP)-rhenium(I) hexafluorophosphate**

In the title compound, $[\text{Re}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{C}_6\text{H}_{15}\text{O}_3\text{P})_2(\text{CO})_2]\text{PF}_6$, the carbonyl ligands are mutually *cis* and lie *trans* to the N donors of the 2,2'-bipyridyl ligand, while the triethoxyphosphine ligands are mutually *trans*. The Re^{I} centres exhibit approximate octahedral coordination, the major distortions from which arise from the narrow bite angle of the 2,2'-bipyridyl ligand which is expressed in the $\text{N}-\text{Re}-\text{N}$ angles of 74.0 (3) and 74.3 (3)°. There are two cations and two anions in the asymmetric unit. The title compound is of interest because it has been shown to be a photocatalyst for CO_2 reduction [Ishitani, George, Ibusuki, Johnson, Koike, Nozaki, Pac, Turner & Westwell (1994). *Inorg. Chem.* **33**, 4712–4717].

Received 21 September 2005
Accepted 26 September 2005
Online 5 October 2005

Comment

The title compound, (I), is of interest because it has been shown to be a photocatalyst for CO_2 reduction (Ishitani *et al.*, 1994). A structure determination showed that the carbonyl ligands are mutually *cis*, while the triethoxyphosphine ligands are mutually *trans*. The carbonyl groups are *trans* to the N-atom donors of the 2,2'-bipyridyl (2,2'-bipy) ligand. The Re^{I} centres occupy approximately octahedral coordination environments. The major distortions from ideal octahedral geometry arise from the narrow chelate angle of the 2,2'-bipyridyl ligand; the $\text{N}-\text{Re}-\text{N}$ angles are 74.0 (3) and 74.3 (3)°.



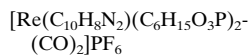
Rhenium complexes containing similar arrays of ligands are unusual; the only previous example of the $(2,2'\text{-bipy})\text{Re}(\text{CO})_2\text{P}_2$ fragment which has been structurally characterized is the less symmetrical *cis,trans*-dicarbonyl(4,4'-dimethyl-2,2'-bipyridyl)(triethoxyphosphine)(triphenylphosphine)rhenium(I) hexafluorophosphate (Koike *et al.*, 2000).

Experimental

The title compound was prepared using the method reported previously by Ishitani *et al.* (1994) by photolysis (> 360 nm long-pass

filter) of (2,2'-bipyridyl)tricarbonylrhenium trifluoromethanesulfonate in MeCN in the presence of P(OEt)₃. Reaction with NH₄PF₆ in MeOH yielded the title salt which was subjected to column chromatography on silica with MeCN/CH₂Cl₂ (1:5 v/v) as eluant. Crystals were obtained by slow diffusion of diethyl ether into a solution of the product in MeCN.

Crystal data



$M_r = 875.66$

Orthorhombic, *Pca*2₁

$a = 30.821(6) \text{ \AA}$

$b = 14.136(3) \text{ \AA}$

$c = 15.571(3) \text{ \AA}$

$V = 6784(2) \text{ \AA}^3$

$Z = 8$

$D_x = 1.715 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

Cell parameters from 7686

reflections

$\theta = 2.4\text{--}28.8^\circ$

$\mu = 3.80 \text{ mm}^{-1}$

$T = 150(2) \text{ K}$

Cuboid, yellow

$0.42 \times 0.41 \times 0.37 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector diffractometer

ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 2001)

$T_{\min} = 0.114$, $T_{\max} = 0.245$

42198 measured reflections

12592 independent reflections

11418 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.043$

$\theta_{\text{max}} = 29.0^\circ$

$h = -41 \rightarrow 41$

$k = -19 \rightarrow 19$

$l = -11 \rightarrow 20$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.074$

$S = 1.15$

12592 reflections

790 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.027P)^2 + 11.37P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.003$

$\Delta\rho_{\text{max}} = 1.26 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -1.28 \text{ e \AA}^{-3}$

Absolute structure: Flack (1983),

3084 Friedel pairs

Flack parameter: 0.265 (7)

The asymmetric unit contains two independent cation–anion pairs. In one of the cations there is disorder in the arms of one of the triethoxyphosphine ligands. A disorder model was developed in which all three O atoms, but only one of the methylene C atoms and none of the methyl C atoms, were refined over split sites. Similarity restraints were applied to all C–O and C–C distances involving disordered atoms. The major and minor disorder components refined to occupancies of 0.53 (1) and 0.47 (1), respectively, and these were fixed at 0.50 in the final cycles of least-squares refinement. The wide range of U_{eq} values for the C atoms is a reflection of the approximate nature of the disorder model. H atoms were placed geometrically and refined using a riding model, with C–H distances of 0.95–0.99 Å and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for the other H atoms. The Flack parameter refined to 0.265 (7), indicating the presence of some inversion twinning. The highest peak and deepest trough in the final difference Fourier synthesis are located 0.81 Å from atom Re1A and 1.48 Å from Re1, respectively.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAIN*T (Bruker, 2001); data reduction: *SAIN*T and *SHELXTL* (Bruker, 2001); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994; program(s) used to refine structure: *SHELXL97* (Sheldrick,

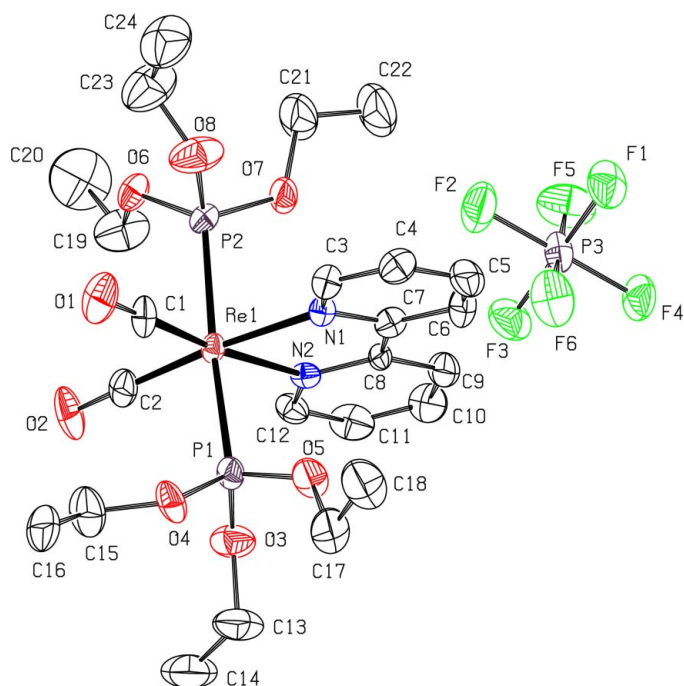


Figure 1

A view of the ordered cation–anion pair with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Except for the orientations of the ethoxy chain, the geometry of the other cation pair is similar.

1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004; *PLATON*).

We thank the Overseas Research Students Awards Scheme for an ORS award to MKK, and EPSRC (UK) for the award of a diffractometer.

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