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Ethyltriphenylphosphonium perrhenate and (iodomethyl)triphenylphosphonium perrhenate

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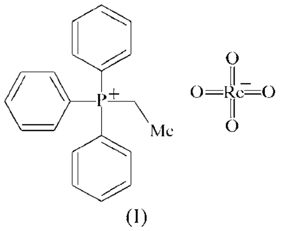
Ethyltriphenylphosphonium perrhenate, $(C_{20}H_{20}P)[ReO_4]$, and (iodomethyl)triphenylphosphonium perrhenate, $(C_{19}H_{17}IP)[ReO_4]$, have been crystallized from 2-propanol. Both crystal structures consist of phosphonium cations and perrhenate anions. The cations show the typical propeller-like geometry. In both crystals, the positions of the nearly tetrahedral anions are stabilized by weak C—H$\cdots$O hydrogen bonds, and for the latter compound, I$\cdots\pi$ interactions also occur.

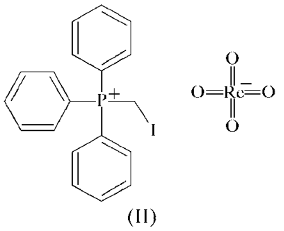
Comment

In studies of the interaction of gaseous HCl with $[ReO_4]^-$ ions, Yatirajam & Harjinder (1975) and Lis & Jeżowska-Trzebiatowska (1977) used tetraphenylphosphonium and tetraphenylarsonium perrhenates suspended in various solvents. The highly symmetric cations possessing $\overline{4}$ symmetry which are present in these perrhenates seem to be one of the reasons for the disorder observed in the oxochlororhenate(VI) (Lis & Jeżowska-Trzebiatowska, 1977).

Our current focus on perrhenates uses less-symmetrical cations containing the triphenylphosphonium moiety as starting materials for the synthesis of rhenium(VI) compounds. We report here the preparation and crystallization of two such salts, (I) and (II), with ethyltriphenylphosphonium and (iodomethyl)triphenylphosphonium cations, respectively.



(I)



(II)

Both crystal structures consist of phosphonium cations and nearly tetrahedral perrhenate anions (Fig. 1). Apart from the three planar phenyl rings, the P atoms are bonded to methylene groups, which are further bonded to a methyl group in the case of (I) and to an I atom in case of (II). The triphenylphosphonium moieties show similar propeller-like geometries. However, the positions of the methyl group in (I) and the I atom in (II) with respect to the phenyl rings are different.

The crystal structure of (I) contains ethyltriphenylphosphonium cations and perrhenate anions, both lying in general positions. The P atom is bonded to one ethyl group and three phenyl groups to form the cation, with the usual propeller-like symmetry (Table 1). The methyl group is in a *trans* position with respect to one of the phenyl groups. As expected (Broder *et al.*, 2002), the environment of the P atom is nearly tetrahedral. The P atom deviates from the planes of the phenyl rings, with a maximum distance of 0.138 (3) Å from the plane of the C11–C61 ring.

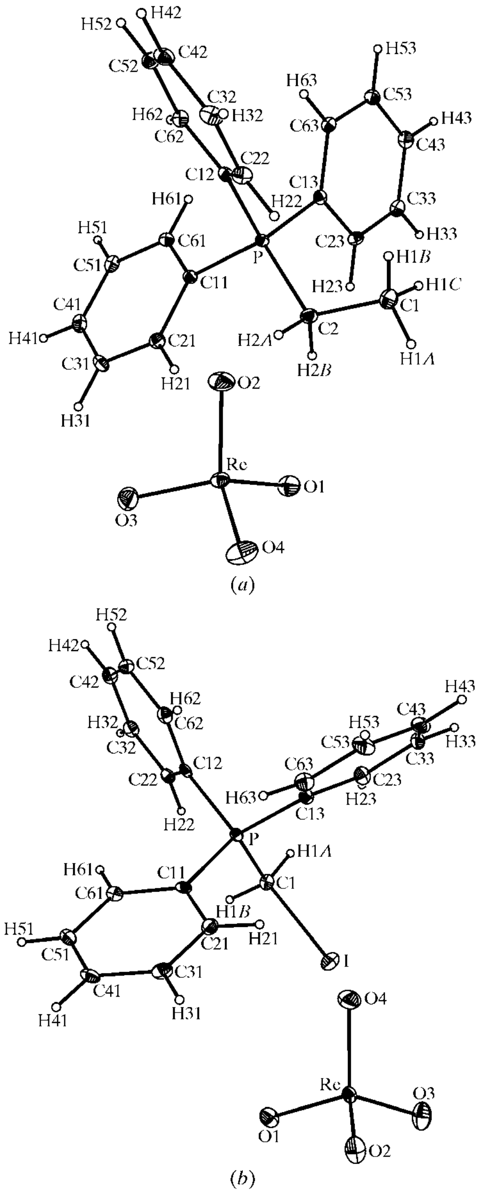


Figure 1
A perspective view of the asymmetric units of (*a*) (I) and (*b*) (II), showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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In published structures containing ethyltriphenylphosphonium cations (Broder *et al.*, 2002; Caira *et al.*, 1978; Bélanger & Beauchamp, 1993; Fedin *et al.*, 1990; Janickis *et al.*, 2002; Ansari *et al.*, 1990), two possible cation geometries have been observed. The criterion is the deviation of the ethyl group from the plane defined by the phenyl ring *trans* to the methyl group. In (I), this deviation is significant, at −0.879 (6) and −0.551 (5) Å for the methyl and the methylene groups, respectively.

In the crystal structure of (I), the cations form tapes along [001]. This pattern is stabilized by weak C—H···O hydrogen bonds involving H atoms from the phenyl rings and the methylene moiety (Table 2). The positions of the interacting perrhenate anions are stabilized in channels between the tapes. For each perrhenate anion, atoms O1 and O2 participate in one hydrogen bond, and atom O4 in two hydrogen bonds. In each cation tape, there are no stacking interactions between the phenyl rings.

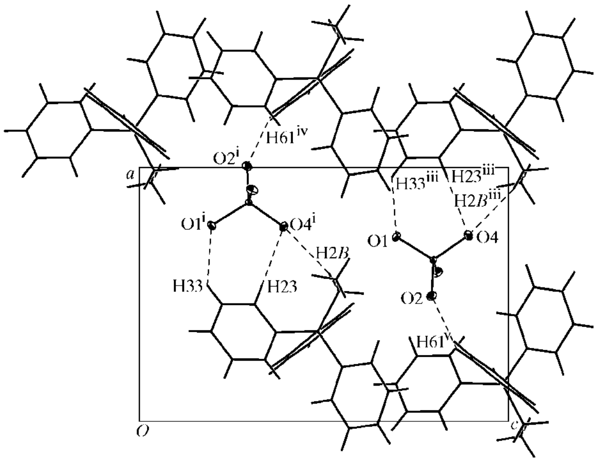

Figure 2
A view of the cation tapes formed along [001] in the structure of (I). [Symmetry codes: (i) $\frac{3}{2} - x, 1 - y, z - \frac{1}{2}$; (iii) $\frac{3}{2} - x, 1 - y, \frac{1}{2} + z$; (iv) $1 + x, y, z$; (v) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$.]

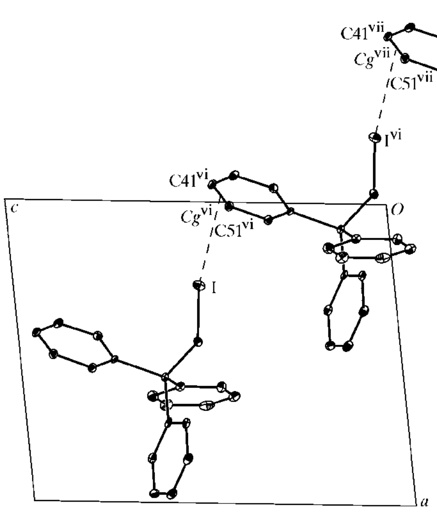

Figure 3
A view of one of the cation chains formed in the crystal structure of (II). H atoms have been omitted for clarity. *Cg* denotes the centroid of the C41—C51 bond. [Symmetry codes: (vi) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (vii) $x - 1, y, z - 1$.]

The crystal structure of (II) consists of (iodomethyl)triphenylphosphonium cations and perrhenate anions lying in general positions. The P atom is bonded to one iodomethyl group and three phenyl groups, forming a cation with the usual (Jin *et al.*, 1995) propeller-like symmetry (Table 3). The I atom is in a *trans* position with respect to one of the phenyl rings and nearly *gauche* with respect to the other two.

It is interesting to note that the I atom in (II) is not involved in any hydrogen bonds. However, it participates in I···π interactions with the C41—C51 edge of the C11–C61 phenyl ring of the molecule at ($x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$), with I···C51 and I···C41 distances of 3.509 (4) and 3.553 (4) Å, respectively. Chains of interacting cations are thus formed, running parallel to the [101] direction (Fig. 3). Similar interactions were observed in one of the previously reported structures with (iodomethyl)triphenylphosphonium cations (Scherfize *et al.*, 1985; Vogt *et al.*, 1993; Jin *et al.*, 1995), the relevant I···C distances being approximately 3.7 and 3.4 Å.

The positions of the perrhenate anions between the cation chains in (II) are stabilized by weak C—H···O hydrogen bonds, with parameters within the range proposed by Desiraju & Steiner (1999). There are more such stabilizing interactions than in the structure of (I). The environment of each cation consists of the anions at ($\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$), ($\frac{1}{2} - x, \frac{1}{2} - y, z + \frac{1}{2}$) and ($1 - x, -y, 1 - z$).

Experimental

The title compounds were prepared by reaction of the relevant phosphonium chlorides with ammonium perrhenate in a stoichiometric molar ratio in aqueous solutions at room temperature. In each case, a fine white precipitate was obtained immediately, which was then filtered off on a medium-density filter and washed with small portions of distilled water until no chloride anions were detected in the filtrate. Crystals of (I) and (II) were obtained by recrystallization of the crude product from solutions in 2-propanol at room temperature.

Compound (I)

Crystal data

$(C_{20}H_{20}P)[ReO_4]$
$M_r = 541.53$
Orthorhombic, $P2_12_12_1$
$a = 9.924$ (2) Å
$b = 13.345$ (3) Å
$c = 14.467$ (3) Å
$V = 1915.9$ (7) Å^3
$Z = 4$
$D_x = 1.877$ Mg m^{-3}
$D_m = 1.85$ Mg m^{-3}
D_m measured by flotation at 298 K in ethyl bromide/toluene
Mo $K\alpha$ radiation
Cell parameters from 20 452 reflections
$\theta = 3.5$–$35.0°$
$\mu = 6.45$ mm^{-1}
$T = 100$ (2) K
Block, colourless
0.30 × 0.12 × 0.12 mm

Data collection

Kuma KM-4 CCD area-detector diffractometer
ω scans
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2003)
$T_{min} = 0.274$, $T_{max} = 0.512$
31 016 measured reflections
8115 independent reflections
7569 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 35.0°$
$h = -15 \rightarrow 9$
$k = -21 \rightarrow 21$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.040$
$S = 1.02$
8115 reflections
236 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.017P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 1.88$ e Å^{-3}
$\Delta\rho_{\min} = -1.44$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00407 (12)
Absolute structure: Flack (1983), with 3521 Friedel pairs
Flack parameter = −0.019 (5)

Table 1
Selected geometric parameters (Å, °) for (I).

P—C11	1.799 (3)	P—C13	1.796 (3)
P—C12	1.791 (3)	P—C2	1.807 (2)
C11—P—C2—C1	163.9 (2)	C13—P—C2—C1	45.5 (2)
C12—P—C2—C1	−76.8 (2)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*B*···O4^{i}	0.99	2.55	3.409 (3)	145
C23—H23···O4^{i}	0.95	2.49	3.369 (3)	154
C33—H33···O1^{i}	0.95	2.58	3.341 (3)	137
C61—H61···O2^{ii}	0.95	2.45	3.301 (3)	149

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

Compound (II)

Crystal data

$(C_{19}H_{17}IP)[ReO_4]$
$M_r = 653.40$
Monoclinic, $P2_1/n$
$a = 10.116$ (3) Å
$b = 15.478$ (3) Å
$c = 12.748$ (3) Å
$\beta = 96.62$ (3)°
$V = 1982.7$ (9) Å^3
$Z = 4$
$D_x = 2.189$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5124 reflections
$\theta = 3.5$–28.0°
$\mu = 7.79$ mm^{-1}
$T = 100$ (2) K
Prism, colourless
0.25 × 0.25 × 0.10 mm

Data collection

Kuma KM-4 CCD area-detector diffractometer
ω scans
Absorption correction: empirical (Walker & Stuart, 1983)
$T_{\min} = 0.202$, $T_{\max} = 0.457$
11 836 measured reflections
4653 independent reflections
3930 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 28.0°$
$h = -13 \rightarrow 13$
$k = -20 \rightarrow 20$
$l = -16 \rightarrow 9$

Table 3
Selected geometric parameters (Å, °) for (II).

I—C1	2.137 (3)	P—C13	1.788 (4)
P—C11	1.790 (3)	P—C1	1.800 (3)
P—C12	1.807 (4)		
C11—P—C1—I	−63.1 (2)	C13—P—C1—I	60.3 (2)
C12—P—C1—I	179.2 (2)		

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.056$
$S = 1.09$
4653 reflections
236 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.2481P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 1.28$ e Å^{-3}
$\Delta\rho_{\min} = -1.28$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00069 (9)

H atoms were treated as riding atoms, with C—H distances in the range 0.95–0.99 Å and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$, or $1.5U_{\rm eq}({\rm C})$ for the methyl group.

For both compounds, data collection: *KM*-4 *CCD Software* (Kuma, 1995–1999); cell refinement: *KM*-4 *CCD Software*; data reduction: *KM*-4 *CCD Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1349). Services for accessing these data are described at the back of the journal.

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