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trans-Chloro[(*E*)-1,1,1,4,4,4-hexafluorobut-2-en-2-yl]bis(tricyclohexylphosphine)platinum(II)–*trans*-chloro[(*Z*)-1,1,1,4,4,4-hexafluorobut-2-en-2-yl]bis(tricyclohexylphosphine)platinum(II) (1/1) at 120 K

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.031
wR factor = 0.073
Data-to-parameter ratio = 16.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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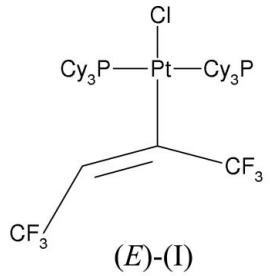
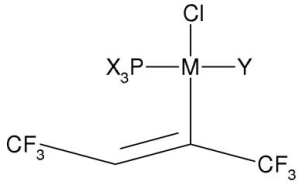
The title cocrystal, $[PtCl(C_4HF_6)(C_{18}H_{33}P)_2]$, contains molecules with a random distribution of *E* and *Z* alkenyl isomers in essentially equal numbers. This is indicative of the isomerization of the *E* form of the Pt complex in the course of attempting to carry out a reaction between it and tricyclohexyltin 4-chlorobenzenethiolate in acetone as solvent.

Comment

The cocrystal, (*E*/*Z*)-(I), a 1:1 mixture of *trans*-chloro[(*E*)-1,1,1,4,4,4-hexafluorobut-2-en-2-yl]bis(tricyclohexylphosphine)platinum(II), (*E*)-(I), and *trans*-chloro[(*Z*)-1,1,1,4,4,4-hexafluorobut-2-en-2-yl]bis(tricyclohexylphosphine)-platinum(II), (*Z*)-(I), was isolated from the attempted 1:1 reaction of a sample of (*E*)-(I) with tricyclohexyltin 4-chlorobenzenethiolate in Me_2CO. The starting compound, (*E*)-(I), had been prepared by the published procedure from *trans*-$[PtH\{P(C_6H_{11})_3\}_2(MeOH)]PF_6$ and $F_3CC{\equiv}CCF_3$, and had been shown by NMR to contain only an (*E*)-alkenyl group (Attig *et al.*, 1979).



(*E*)-(I)



(*Z*)-(I) X = Cy; Y = Cy_3P; M = Pt
(*Z*)-(II) X = Me; Y = Cp; M = Rh

Cy = Cyclohexyl
Cp = Cyclopentadienyl

The refinement of the structure was carried out on the basis of an asymmetric unit comprising a single 'average' molecule in which the alkenyl C atom not bonded to Pt and the CF_3 group attached to it are both distributed over pairs of sites of equal occupancy, with one set, C38*A* and C40*A* (Fig.1),

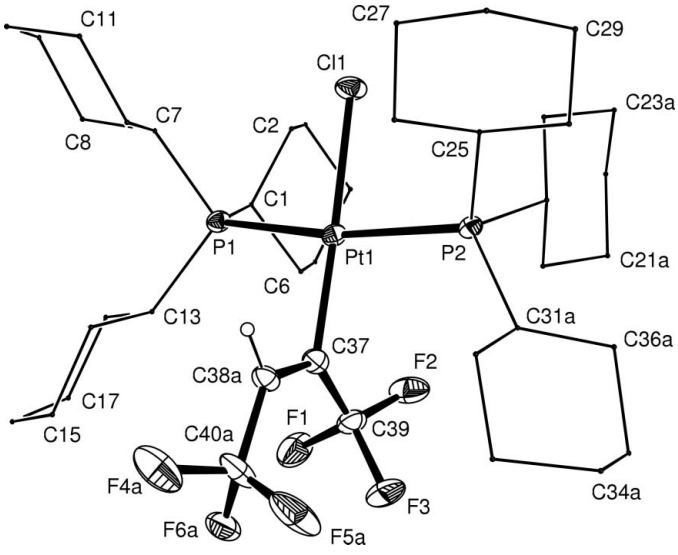


Figure 1
The *E* isomer of (I). Displacement ellipsoids are shown at the 20% probability level and the alkenyl H atom as a small sphere of arbitrary radius; other H atoms have been omitted. For clarity, the cyclohexyl groups are represented only by thin lines representing the bonds to their constituent C atoms, only some of which are labelled, because the strictly cyclic labelling of these groups allows the identity of the remainder to be worked out.

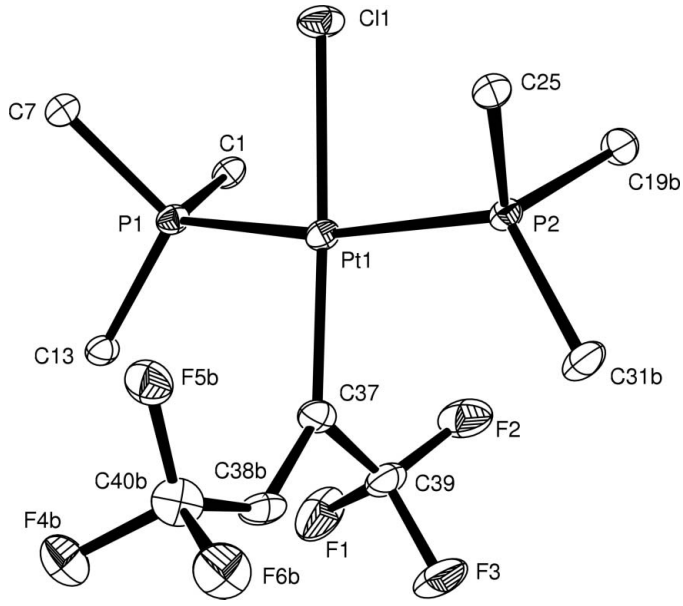


Figure 2
The *Z* isomer of (I). Displacement ellipsoids are shown at the 20% probability level. For clarity the cyclohexyl groups are represented by only the C atoms directly bonded to P, and all H atoms have been omitted.

corresponding to the *E* isomer with *cis* CF_3 groups and the other, C38*B* and C40*B* (Fig. 2), to the *Z* isomer with *trans* CF_3 groups. This is the justification for the presumption of a random distribution of essentially equal numbers of molecules with *E* and *Z* forms in the cocrystal. There is also disorder in two of the cyclohexyl groups attached to P2, which is not related in any obvious way to the disorder of the alkenyl group. In these groups defined, respectively, by C19–C24 and C30–C36, all of the atoms have been dealt with in pairs of equal occupancy, with suffix *A* for one orientation of the group and suffix *B* for the other. Selected geometric parameters for cocrystalline (*E*/*Z*)-(I) are given in Table 1. The coordination of Pt is square planar but with slight tetrahedral distortion, as shown by the displacements, all approximately 0.11 Å, of P1 and P2 to one side, and Cl1 and C37 to the other, of the plane defined by these four atoms. The displacement of the Pt atom from this plane is only 0.0283 (12) Å. The *E* and *Z* conformations of the butenyl groups are clearly seen from the torsion angles given in Table 1. The C—C distances in these groups are disappointingly disparate, with C═C distances of 1.327 (13) and 1.402 (13) Å and C—C (to the CF_3 groups) ranging over 1.398 (16)–1.496 (6) Å. This, along with the variation in bond angles in the butenyl groups, may be attributable to the superposition of the two conformations in the disordered 'average' molecule rather than to real differences in the bonding of the (*E*)- and (*Z*)-butenyl groups. The other bond lengths and bond angles in (*E*/*Z*)-(I), summarized in Table 2, are unremarkable. The only interaction between the molecules is in the form of van der Waals contacts. The content of the unit cell is shown in a highly schematic manner in Fig. 3.

Recourse to the Cambridge Structural Database (CSD; Version 5.26; Allen, 2002) by means of the Chemical Database Service of the EPSRC (CDS; Fletcher *et al.*, 1996) reveals the presence of data for only one analogue of (*E*/*Z*)-(I). This is the compound chloro-(*trans*-1,1,1,4,4,4-hexafluorobut-2-en-2-yl)-(η^5-pentamethylcyclopentadienyl)(trimethylphosphine)-rhodium (CSD code WIYZOT; Selmeczy & Jones, 2000), in which the CF_3 groups of the hexafluorobutenyl substituent are *trans* to one another and the compound is therefore here designated (*Z*)-(II). Although the *Z* conformation of the butenyl substituent is clearly established in the proposed structure of (*Z*)-(II), the internal geometry of the group is rather poorly defined; for example, the C═C bond length, calculated from the coordinates extracted from the CSD entry, is only 1.11 (3) Å, and the C—C bond lengths are very long. Nevertheless, the structure of (*Z*)-(II) clearly provides an authentic example of the butenyl substituent in the *Z* conformation. The paper of Selmeczy & Jones (2000) and the references within it also provide much information regarding the unpredictability of reactions such as those producing (*E*)-(I) and (*Z*)-(II), especially where hexafuorobut-2-yne is involved. Furthermore, Selmeczy & Jones (2000) also discuss, and summarize mechanisms for, the isomerization of such compounds. Thus, although no specific mechanism is invoked, the paper of Selmeczy & Jones (2000) clearly supports the interpretation of the structure of (*E*/*Z*)-(I) reported here as resulting from the partial isomerization of (*E*)-(I).

Experimental

A solution of (*E*)-(I) (Attig *et al.*, 1979) and $(C_6H_{11})_3SnSC_6H_4Cl$-*p* (each 1 mmol) in Me_2CO (15 ml) was refluxed for 30 min. Crystals of (*E*/*Z*)-(I) were formed on slow evaporation of the solvent at room temperature. IR (KBr): 1600 cm^{-1} (C═C).

Crystal data

$[PtCl(C_4HF_6)(C_{18}H_{33}P)_2]$	D_x = 1.524 Mg m^{-3}
M_r = 954.42	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 44847 reflections
a = 14.3933 (2) Å	θ = 2.9–27.5°
b = 17.5714 (3) Å	μ = 3.57 mm^{-1}
c = 17.5270 (3) Å	T = 120 (2) K
β = 110.2621 (10)°	Block, colourless
V = 4158.45 (12) Å^3	0.36 × 0.18 × 0.12 mm
Z = 4	

Data collection

Nonius KappaCD diffractometer	7588 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.042
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	θ_{max} = 27.5°
T_{min} = 0.457, T_{max} = 0.652	$h = -18 \rightarrow 18$
53705 measured reflections	$k = -22 \rightarrow 21$
9510 independent reflections	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0283P)^2 + 5.1608P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.031	$(\Delta/\sigma)_{max}$ = 0.003
$wR(F^2)$ = 0.074	$\Delta\rho_{max}$ = 0.88 e Å^{-3}
S = 1.04	$\Delta\rho_{min}$ = −0.98 e Å^{-3}
9510 reflections	
568 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Pt1—C37	2.033 (4)	C37—C38*A*	1.402 (13)
Pt1—P1	2.3426 (9)	C37—C39	1.496 (6)
Pt1—P2	2.3535 (9)	C38*A*—C40*A*	1.493 (13)
Pt1—Cl1	2.3688 (9)	C38*B*—C40*B*	1.398 (16)
C37—C38*B*	1.327 (13)		
C37—Pt1—P1	94.52 (10)	C38*A*—C37—C39	128.7 (5)
C37—Pt1—P2	95.55 (10)	C38*B*—C37—Pt1	138.9 (6)
P1—Pt1—P2	168.08 (3)	C38*A*—C37—Pt1	111.0 (5)
C37—Pt1—Cl1	175.69 (11)	C39—C37—Pt1	120.3 (3)
P1—Pt1—Cl1	86.29 (3)	C37—C38*A*—C40*A*	123.5 (10)
P2—Pt1—Cl1	84.14 (3)	C37—C38*B*—C40*B*	125.7 (10)
C38*B*—C37—C39	100.8 (6)		
Pt1—C37—C38*A*—C40*A*	178.6 (8)	C39—C37—C38*A*—C40*A*	−2.8 (14)
Pt1—C37—C38*B*—C40*B*	−2.2 (19)	C39—C37—C38*B*—C40*B*	178.5 (11)

Table 2
Geometric parameters (Å, °) for structural components of (*E*/*Z*)-(I) expressed as ranges; the ranges are somewhat extended by the inclusion of values associated with disordered atoms.

Group		Min.	Max.
CF_3	C—F	1.297 (10)	1.368 (9)
	F—C—F	102.0 (9)	106.5 (7)
	F—C—C	110.0 (10)	119.3 (9)
Phosphine	C—P	1.843 (3)	1.858 (4)
	C—P—Pt	108.61 (12)	118.53 (15)
	C—P—C	102.30 (17)	109.17 (19)
Cyclohexyl	C—C	1.402 (9)	1.628 (9)
	C—C—P	110.6 (2)	125.2 (4)
	C—C—C	103.5 (7)	116.7 (9)

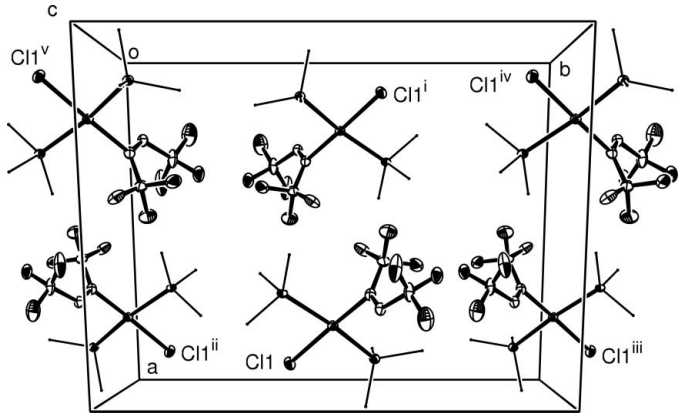


Figure 3
The packing of the molecules in the cell of (*E*/*Z*)-(I). Displacement ellipsoids are shown at the 20% probability level. For clarity, all H atoms have been omitted and the cyclohexyl groups are indicated simply by thin line P—C bonds. Selected atoms are labelled. The example shown employs molecules of the *E* form, as in Fig. 1. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (iv) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (v) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$.]

The disorder in the hexafluorobutenyl substituent and in two of the four cyclohexyl groups noted in the *Comment* text was dealt with by standard techniques. Although subsidiary calculations, with isotropic displacement parameters constrained to be equal for atoms in pairs of the same type and connectivity, indicated occupancies of 0.441 (4) and 0.559 (4) for the disordered atoms of the *cis* (E form) and *trans* (*Z* form) hexafluorobutenyl groups, respectively, fixing these at 0.5 rather than at the refined values produced slightly better *R* values for the same mode of refinement. Some residual disorder is still apparent in this part of the molecule, as evidenced by rather extreme anisotropic displacement parameters as, for example, in the case of F4*A* and F5*A*. In order to permit interatomic distances within the disordered cyclohexyl groups to be restrained to be equal (within 0.02 Å) to those within a comparatively ordered cyclohexyl group (that defined by C1–C6 was used for this purpose), ordered atoms such as C19, C31, C32 and C35 were artificially split into pairs as, for example, C19*A*/C19*B*. For each such pair, the atomic coordinates were refined as free variables and the anisotropic displacement parameters of the two atoms were constrained to be equal. In this way, all six C atoms of the cyclohexyl group were made available for application of similarity restraints to the geometry of both orientations of the disordered groups. In the final stage of the calculations, H atoms were introduced in calculated positions, taking full account of the disorder noted above, with C—H set to 0.95, 0.99 and 1.00 Å for H atoms attached to alkene, methylene and tertiary C atoms, respectively, and refined with a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$ in all cases.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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