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Di-μ-propionato-bis[dicarbonyl(triphenylphosphine)ruthenium(I)](*Ru*—*Ru*)

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Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.008 Å
Disorder in main residue
R factor = 0.037
wR factor = 0.089
Data-to-parameter ratio = 13.3

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

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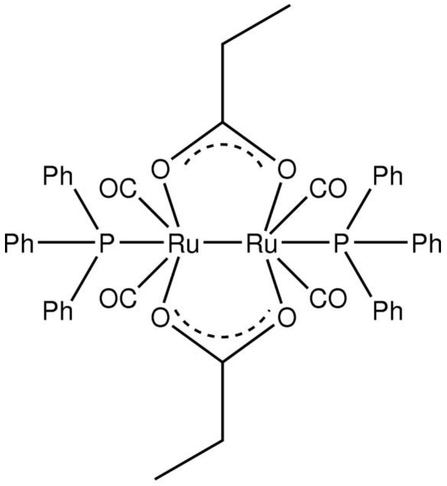
The title compound, $[Ru_2(C_3H_5O_2)_2(C_{18}H_{15}P)_2(CO)_4]$, has a dimeric structure displaying a 'sawhorse' configuration, with the two carboxylate groups bridging two $[Ph_3PRu(CO)_2]$ fragments. The compound resides on a special position, with a crystallographic twofold rotation axis lying normal to the Ru—Ru bond.

Comment

On continuing our studies (Legrand *et al.*, 1994) of catalytic olefin hydroesterification using a CO/CH_3OH mixture, we observed the inhibitory effect of triphenylphosphine upon the reaction system. In order to obtain further insight and, possibly, to isolate some of the reaction intermediates, we decided to determine the crystal structure of the adduct formed. Although some similar compounds are known to be important catalysts or catalytic precursors, in our case, the title compound, (I), proved to be completely inactive.



(I)

The IR spectrum of the precipitate revealed three strong, easily discernible carbonyl stretching frequencies, implying the presence of more than two carbonyl ligands in either a *cis* or a *fac* orientation. The gap between the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ vibrational modes is *ca* 125 cm^{-1}, in agreement with the range reported for some μ-*O*,*O*′-carboxylate complexes (Deacon & Phillips, 1980). The present X-ray diffraction study showed that the product is a dimeric Ru^I complex, with four *cisoid* carbonyl groups and two μ-*O*,*O*′-propionate ligands in a 'sawhorse' configuration (Fig. 1), capped by triphenylphosphine ligands, such that the coordinating P atom approaches the axis of the Ru—Ru bond.

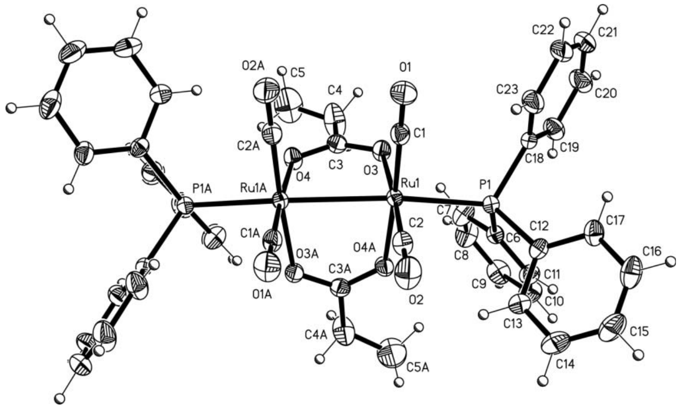


Figure 1

A view of the molecule of (I) (disorder excluded), showing the atom-labelling scheme. Symmetry-related atoms (suffix A) are generated by $(1-x, y, \frac{1}{2}-z)$. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary size.

The molecule of (I) is located on a crystallographic twofold rotation axis normal to the Ru—Ru bond, but it possesses non-crystallographic symmetry close to C_{2v}, only perturbed by the relative disposition of the aromatic rings and the orientational disorder of the carboxylate alkyl substituent. The pair of Ru atoms are six-coordinated with identical environments. The phosphine ligand lies approximately collinear with the Ru—Ru bond and the pair of carbonyl and μ-*O*,*O*′-carboxylate ligands are mutually *cis* in the equatorial plane of a distorted octahedron.

The selected geometric parameters in Table 1 show that there are no significant differences from other phosphine-substituted ruthenium carbonyl carboxylates (Schumann *et al.*, 1977; Shiu *et al.*, 1993; Matteoli *et al.*, 1995).

Experimental

The title compound was prepared according to the following procedure. $RuCl_3 \cdot 3H_2O$ (0.22 mmol), NEt_4I (0.44 mmol) and $LiClO_4$ (0.44 mmol) dissolved in 30 ml of dimethylformamide were added to a gaseous mixture of C_2H_4 (30 bar; 1 bar = 100 000 Pa) and CO (15 bar) and heated to 433 K in an autoclave. Once the reaction had reached its maximum activity (after 3 h), two equivalents (based on $RuCl_3 \cdot 3H_2O$) of triphenylphosphine dissolved in dimethylformamide (2 ml) were added. Suitable crystals of (I) were obtained by very slow cooling of a hot solution of the compound in dimethylformamide. Spectroscopic analysis: IR (KBr, ν, cm^{-1}): 2014, 1971, 1939, 1563, 1429 and 1090.

Crystal data

$[Ru_2(C_3H_5O_2)_2(C_{18}H_{15}P)_2(CO)_4]$
$M_r = 984.86$
Monoclinic, $C2/c$
$a = 24.643$ (2) Å
$b = 9.394$ (1) Å
$c = 18.857$ (1) Å
$\beta = 101.97$ (1)°
$V = 4270.4$ (6) Å^3
$Z = 4$

$D_x = 1.532$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 39
reflections
$\theta = 5.1$–12.5°
$\mu = 0.84$ mm^{-1}
$T = 294$ (2) K
Prism, yellow
0.50 × 0.40 × 0.16 mm

Data collection

Siemens *P*4/PC diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical
[face-indexed; *SHELXTL*
(Sheldrick, 2000)]
$T_{min} = 0.720$, $T_{max} = 0.877$
3860 measured reflections
3767 independent reflections
2962 reflections with $I > 2\sigma(I)$

$R_{int} = 0.031$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 29$
$k = 0 \rightarrow 11$
$l = -22 \rightarrow 21$
3 standard reflections
every 97 reflections
intensity decay: 4.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.089$
$S = 1.04$
3767 reflections
283 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Ru1—C2	1.844 (5)	P1—C6	1.836 (5)
Ru1—C1	1.846 (5)	O1—C1	1.143 (6)
Ru1—P1	2.457 (1)	O2—C2	1.144 (6)
Ru1—Ru1^i	2.7421 (7)	O3—C3	1.258 (5)
P1—C18	1.830 (4)	O4—C3	1.249 (5)
P1—C12	1.833 (4)		
C2—Ru1—C1	88.1 (2)	O3—Ru1—Ru1^i	83.13 (8)
C2—Ru1—O4^i	92.06 (19)	P1—Ru1—Ru1^i	163.54 (3)
C1—Ru1—O4^i	176.87 (15)	C18—P1—C12	103.79 (19)
C2—Ru1—O3	176.72 (15)	C18—P1—C6	103.1 (2)
C1—Ru1—O3	92.54 (18)	C12—P1—C6	102.8 (2)
C2—Ru1—P1	96.38 (14)	C18—P1—Ru1	117.03 (13)
C1—Ru1—P1	99.30 (13)	C12—P1—Ru1	114.70 (14)
O4^i—Ru1—P1	83.78 (8)	C6—P1—Ru1	113.74 (13)
O3—Ru1—P1	86.69 (8)	O1—C1—Ru1	178.9 (5)
C2—Ru1—Ru1^i	93.62 (13)	O2—C2—Ru1	179.3 (5)
C1—Ru1—Ru1^i	94.05 (13)	O4—C3—O3	125.5 (4)
O4^i—Ru1—Ru1^i	82.82 (8)		
P1—Ru1—P1^i—Ru1^i	171.64 (15)		

Symmetry code: (i) $1-x, y, \frac{1}{2}-z$.

Difference maps late in the refinement showed that C4 and C5 are approximately equally distributed between two positions [occupancy factors for C4 and C5 are 0.500 (17)]. Even after inclusion of the disorder in the model, standard deviations, displacement parameters and bond lengths indicated that the affected ethyl group was not described very precisely. All H atoms, except those involved in the disordered ethyl group, were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry, with C—H = 0.96 Å and $U_{iso}(H) = 0.08$ Å^2, but each group was allowed to rotate freely about its C—C bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å and $U_{iso}(H) = 0.08$ Å^2.

Data collection: *XSCANS* (Siemens, 1993); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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