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Di-μ-acetato-bis[dicarbonyl(pyrazole)ruthenium(I)] and Di-μ-acetato-bis[dicarbonyl(3,5-dimethylpyrazole)ruthenium(I)]†

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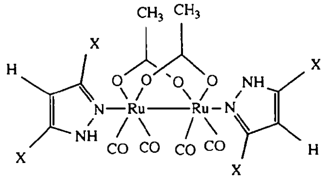
Abstract

The crystal structures of the title compounds, [Ru_2($C_2H_3O_2$)$_2$($C_3H_4N_2$)$_2$(CO)$_4$], (1), and [Ru_2($C_2H_3O_2$)$_2$($C_5H_8N_2$)$_2$(CO)$_4$], (2), have been determined. The octahedral coordination about the Ru^I ion is slightly distorted in (1) and more distorted in (2), with the two O atoms and two C atoms in the equatorial positions, and one N atom and another Ru ion in the axial positions. Compound (2) has mirror symmetry.

Comment

Diruthenium(I) carbonyl complexes are either involved as the active intermediates in homogeneously catalyzed reactions or catalytic precursors for the carbonylation of amines, the hydrogenation of carboxylic acids, and the addition of acetic acid to alkynes (Suss-Fink *et al.*, 1985; Matteoli *et al.*, 1985; Frediani *et al.*, 1995). The main purpose of this study is to explore the synthesis and reactivity of some diruthenium(I)–carbonyl complexes containing the μ-acetato linkage. Here, the crystal structures of di-μ-acetato-bis[dicarbonyl(pyrazole)ruthenium(I)] {[Ru_2(μ-O_2CMe)$_2$(HPz)$_2$(CO)$_4$], (1)} and di-μ-acetato-bis[dicarbonyl(3,5-dimethylpyrazole)ruthenium(I)] {[Ru_2(μ-O_2CMe)$_2$(HPz′)$_2$(CO)$_4$], (2), where HPz is pyrazole and HPz′ is 3,5-dimethylpyrazole} are presented.



(1) X=H (2) X=CH_3

Compound (2) has a mirror plane passing through the μ-acetato groups and bisecting the Ru—Ru bond. In compound (1), both Ru^I ions have distorted octahedral geometry, coordinated by two O atoms of μ-acetato groups and two C atoms of carbonyl groups in the equatorial positions, and the pyrazole N atom and another Ru ion are in the axial positions, whereas in (2), the Ru^I atom has a more distorted octahedral geometry, because the O4—C11—Ru1 system is not linear [O4—C11—Ru1 171 (2)°] and also, there is a non-bonded interaction between the O2 and C11 atoms. All the bond lengths and angles are normal with respect to related compounds in the literature. The Ru—Ru bond length is 2.675 (1) and 2.682 (1) Å in compounds (1) and (2), respectively, shorter than that in [Ru_2(μ-Pz′)(μ-O_2CMe)(CO)$_4$(PPh_3)$_2$] [2.726 (1) Å] and [Ru_2(μ-Pz′)$_2$(CO)$_2$(μ_1,η^2-dppm)$_2$] [2.738 (1) Å], and similar to that in [Ru_2(μ-Pz′)(μ-O_2CMe)(CO)$_4$(HPz′)$_2$] [2.682 (1) Å] and [Ru_2(μ-Pz′)(μ-CO)$_2$(CO)$_2$(μ_1,η^2-phen)$_2$]$^+$ [2.685 (1) Å; Shiu *et al.*, 1996]. The pyrazole moieties in (1) and (2) are planar to within 0.005 (2) and 0.014 (6) Å, respectively. Both crystal structures are stabilized by a three-dimensional network of N—H···O hydrogen bonds.

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† Alternative names: di(μ-acetato-1:2$\kappa^2$$O$:$O'$)tetracarbonyl-1$\kappa^2$$C$,2$\kappa^2$$C$-bis(pyrazole)-1$\kappa N^2$,2$\kappa N^2$-diruthenium(I)(*Ru*—*Ru*) and di(μ-acetato-1:2$\kappa^2$$O$:$O'$)tetracarbonyl-1$\kappa^2$$C$,2$\kappa^2$$C$-bis(3,5-dimethylpyrazole)-1κN^2,2κN^2-diruthenium(I)(*Ru*—*Ru*).

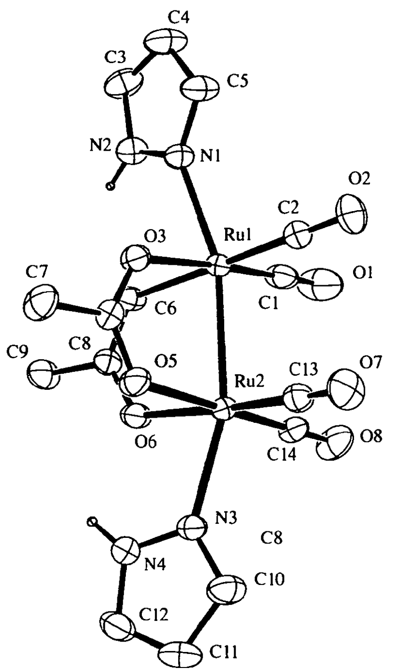

Fig. 1. The molecular structure of compound (1) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. For clarity, all H atoms except the for the imino H atom have been omitted.

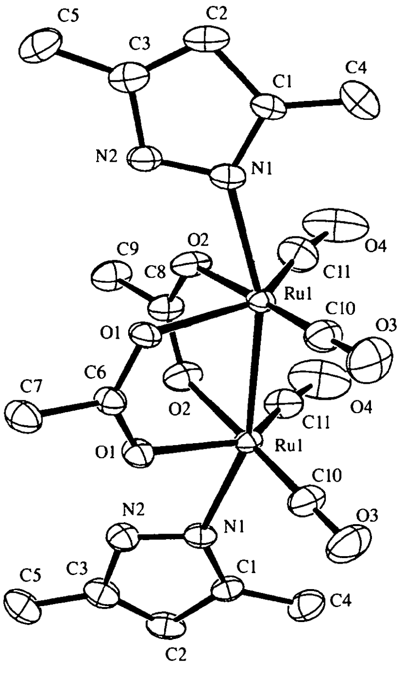

Fig. 2. The molecular structure of compound (2) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

Experimental

For the synthesis of compound (1), *catena*-[Ru(O_2CMe)(CO)$_2$] (0.305 g, 1.412 m*M*) and 40 ml of THF were added to a 100 ml Schlenk flask at room temperature. The suspension was then heated under reflux for 5 h, forming a clear orange–yellow solution. A THF solution of pyrazole (HPz) (0.12 g, 1.76 m*M*) dissolved in 2 ml of THF was added dropwise. The solution changed color to yellow and the resulting solution was stirred for 30 min and cooled to room temperature. The volume of the solution was reduced to *ca* 2 ml and 50 ml of deaerated H_2O was added, producing a yellow precipitate. The solid was collected and washed twice with 5 ml of deaerated H_2O, and dried under vacuum to afford 0.337 g product in 84% yield. Yellow crystals suitable for X-ray diffraction study were obtained from a CH_2Cl_2–hexane solution at room temperature. Yellow compound (2) was prepared from *catena*-[Ru(O_2CMe)(CO)$_2$] and 3,5-dimethylpyrazole (Hpz′) in a procedure similar to that used for compound (I). The yield was 89%. Crystals for crystallographic study were grown from a CH_2Cl_2–hexane solution at room temperature.

Compound (1)

Crystal data

$[Ru_2(C_2H_3O_2)_2(C_3H_4N_2)_2(CO)_4]$
M_r = 568.43
Triclinic
$P\bar{1}$
a = 8.332 (1) Å
b = 9.524 (1) Å
c = 13.539 (2) Å
α = 90.02 (1)°
β = 100.32 (2)°
γ = 111.33 (1)°
V = 982.0 (2) Å^3
Z = 2
D_x = 1.922 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 9.48–31.86°
μ = 1.586 mm^{-1}
T = 293 (2) K
Pillar
0.45 × 0.35 × 0.30 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.550, T_{max} = 0.621
4516 measured reflections
4516 independent reflections

3947 reflections with $I > 2\sigma(I)$
θ_{max} = 27.46°
$h = -10 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 17$
3 standard reflections frequency: 60 min intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.060
S = 1.035
4516 reflections
253 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 0.6013P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.004$
$\Delta\rho_{max}$ = 0.382 e Å^{-3}
$\Delta\rho_{min}$ = −0.660 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ru1—C2	1.822 (3)	Ru2—C13	1.827 (3)
Ru1—C1	1.826 (3)	Ru2—C14	1.828 (3)
Ru1—O3	2.122 (2)	Ru2—O5	2.113 (2)
Ru1—O4	2.126 (2)	Ru2—O6	2.134 (2)
Ru1—N1	2.202 (2)	Ru2—N3	2.203 (2)
Ru1—Ru2	2.6746 (6)		
C2—Ru1—C1	87.2 (2)	C13—Ru2—C14	90.3 (1)
C2—Ru1—O3	96.2 (1)	C13—Ru2—O5	92.3 (1)
C1—Ru1—O3	175.9 (1)	C14—Ru2—O5	177.2 (1)
C2—Ru1—O4	179.7 (1)	C13—Ru2—O6	175.2 (1)
C1—Ru1—O4	92.8 (1)	C14—Ru2—O6	94.2 (1)
O3—Ru1—O4	83.9 (1)	O5—Ru2—O6	83.2 (1)
C2—Ru1—N1	97.7 (1)	C13—Ru2—N3	98.9 (1)
C1—Ru1—N1	96.6 (1)	C14—Ru2—N3	95.9 (1)
O3—Ru1—N1	85.4 (1)	O5—Ru2—N3	84.6 (1)
O4—Ru1—N1	82.0 (1)	O6—Ru2—N3	82.3 (1)
C2—Ru1—Ru2	96.1 (1)	C13—Ru2—Ru1	94.6 (1)
C1—Ru1—Ru2	94.0 (1)	C14—Ru2—Ru1	94.5 (1)
O3—Ru1—Ru2	83.3 (1)	O5—Ru2—Ru1	84.3 (1)
O4—Ru1—Ru2	84.2 (1)	O6—Ru2—Ru1	83.4 (1)
N1—Ru1—Ru2	163.0 (1)	N3—Ru2—Ru1	162.9 (1)

Table 2. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1N2···O7^{i}	0.86	2.713	3.412 (3)	139.4 (1)
N4—H1N4···O2^{ii}	0.86	2.594	3.195 (4)	127.8 (1)

Symmetry code: (i) $x, 1 + y, z$; (ii) $x - 1, y, z$.

Compound (2)

Crystal data

$[Ru_2(C_2H_3O_2)_2(C_5H_8N_2)_2$-$(CO)_4]$
$M_r = 624.54$
Orthorhombic
$Bb2_1m$
$a = 9.292$ (1) Å
$b = 13.731$ (1) Å
$c = 18.639$ (2) Å
$V = 2378.2$ (4) Å^3
$Z = 4$
$D_x = 1.744$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 14.78$–$32.90°$
$\mu = 1.318$ mm^{-1}
$T = 293$ (2) K
Lump
$0.44 \times 0.31 \times 0.25$ mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.675$, $T_{\max} = 0.719$
1853 measured reflections
1853 independent reflections

1705 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 29.90°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 26$
3 standard reflections frequency: 3600 min intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.169$
$S = 1.199$
1853 reflections
151 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.1137P)^2 + 3.8418P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.048$
$\Delta\rho_{\max} = 0.861$ e Å^{-3}
$\Delta\rho_{\min} = -0.848$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (2)*

Ru1—C11	1.769 (16)	Ru1—O1	2.136 (7)
Ru1—C10	1.802 (12)	Ru1—N1	2.204 (7)
Ru1—O2	2.097 (8)	Ru1—Ru1^{i}	2.682 (1)
C11—Ru1—C10	125.3 (8)	O2—Ru1—N1	81.7 (3)
C11—Ru1—O2	56.1 (7)	O1—Ru1—N1	83.2 (3)
C10—Ru1—O2	178.7 (5)	C11—Ru1—Ru1^{i}	94.0 (4)
C11—Ru1—O1	140.6 (7)	C10—Ru1—Ru1^{i}	96.2 (3)
C10—Ru1—O1	94.0 (5)	O2—Ru1—Ru1^{i}	83.5 (2)
O2—Ru1—O1	84.6 (4)	O1—Ru1—Ru1^{i}	83.6 (2)
C11—Ru1—N1	87.5 (5)	N1—Ru1—Ru1^{i}	161.0 (2)
C10—Ru1—N1	98.4 (4)		

Symmetry code: (i) $x, y, 2 - z$.

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1N2···O3^{i}	0.86	2.41	3.22 (1)	157.4 (3)

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

For (1), the H atoms were placed in calculated positions and refined on their corresponding non-H atoms. The displacement parameters were fixed at 0.08 Å^2. For (2), H atoms were introduced at calculated positions and refined as riding on the corresponding N and C atoms with common isotropic displacement parameters fixed at 0.08 Å^2 for all H atoms. The H atoms of the special position methyl group were neglected.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *NRCVAX*; software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1175). Services for accessing these data are described at the back of the journal.

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