

UC Santa Cruz

UC Santa Cruz Previously Published Works

Title

Synthesis and structures of ruthenium di- and tricarbonyl complexes derived from 4,5-diazafluoren-9-one

Permalink

<https://escholarship.org/uc/item/8r2769jq>

Journal

Acta Crystallographica Section C: Structural Chemistry, 71(11)

ISSN

0108-2701

Authors

Jimenez, Jorge
Chakraborty, Indranil
Mascharak, Pradip

Publication Date

2015-11-01

DOI

10.1107/s2053229615018100

Peer reviewed



Synthesis and structures of ruthenium di- and tricarbonyl complexes derived from 4,5-diazafluoren-9-one

Jorge Jimenez, Indranil Chakraborty and Pradip Mascharak*

Department of Chemistry, UC Santa Cruz, CA 95064, USA. *Correspondence e-mail: pradip@ucsc.edu

Received 12 August 2015

Accepted 27 September 2015

Edited by A. G. Oliver, University of Notre Dame, USA

Keywords: metal–carbonyl complexes; bite distance; CO releasing molecules; ruthenium complexes; crystal structure; therapeutics; mode of binding; biological effect.

CCDC references: 1427969; 1427968

Supporting information: this article has supporting information at journals.iucr.org/c

Carbon monoxide (CO) has recently been shown to impart beneficial effects in mammalian physiology and considerable research attention is now being directed toward metal–carbonyl complexes as a means of delivering CO to biological targets. Two ruthenium carbonyl complexes, namely *trans*-dicarbonyldichlorido(4,5-diazafluoren-9-one- κ^2N,N')ruthenium(II), $[\text{RuCl}_2(\text{C}_{11}\text{H}_6\text{N}_2\text{O})(\text{CO})_2]$, (1), and *fac*-tricarbonyldichlorido(4,5-diazafluoren-9-one- κN)ruthenium(II), $[\text{RuCl}_2(\text{C}_{11}\text{H}_6\text{N}_2\text{O})(\text{CO})_3]$, (2), have been isolated and structurally characterized. In the case of complex (1), the *trans*-directing effect of the CO ligands allows bidentate coordination of the 4,5-diazafluoren-9-one (dafo) ligand despite a larger bite distance between the N-donor atoms. In complex (2), the *cis* disposition of two chloride ligands restricts the ability of the dafo molecule to bind ruthenium in a bidentate fashion. Both complexes exhibit well defined ^1H NMR spectra confirming the diamagnetic ground state of Ru^{II} and display a strong absorption band around 300 nm in the UV.

1. Introduction

Carbon monoxide (CO) has recently been shown to impart salutary effects in mammalian physiology when applied in lower concentrations (Mottetlini & Otterbien, 2010). This surprising discovery has raised interest in metal–carbonyl complexes as potential CO donors. Although metal–carbonyl complexes have been studied extensively for their photo-physical and photochemical properties (Stufkens & Vlcek, 1998), considerable research attention has now been directed toward these species as a means of delivering CO to biological targets under controlled conditions as opposed to its administration in the gaseous form (Bernardes & Garcia-Gallego, 2014; Romao *et al.*, 2012). In such attempts, the photoactive CO-releasing molecules (photoCORMs) have emerged as promising therapeutics where CO release can be triggered upon illumination (Gonzalez & Mascharak, 2014; Chakraborty *et al.*, 2014; Schatzschneider, 2015). Herein we report the syntheses, properties and X-ray structures of two ruthenium carbonyl complexes, namely *trans*- $[\text{RuCl}_2(\text{dafo})(\text{CO})_2]$, (1), and *fac*- $[\text{RuCl}_2(\text{CO})_3(\text{dafo})(\text{CO})_3]$, (2), where dafo is 4,5-diazafluoren-9-one. The potentially bidentate ligand dafo binds the Ru^{II} center of (1) and (2) in a bidentate and a monodentate fashion, respectively. Both steric and electronic effects play concurrent roles in dictating the mode of binding of dafo in these two complexes.

2. Experimental

All reagents were of commercial grade and were used without further purification. The solvents were purified according to a

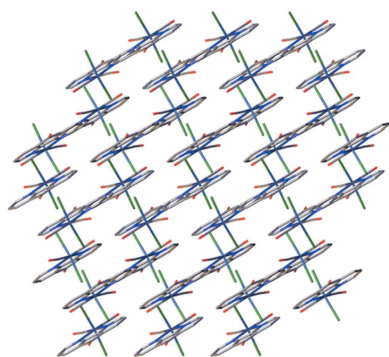
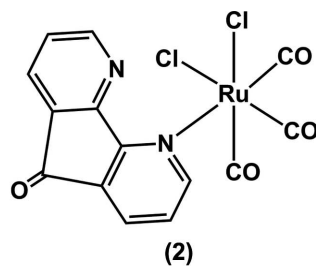
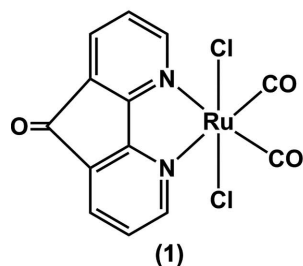


Table 1
Experimental details.

	(1)	(2)
Crystal data		
Chemical formula	[RuCl ₂ (C ₁₁ H ₆ N ₂ O)(CO) ₂]	[RuCl ₂ (C ₁₁ H ₆ N ₂ O)(CO) ₃]
<i>M_r</i>	410.17	438.18
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	296	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.5589 (2), 16.9199 (6), 12.7585 (5)	7.458 (2), 9.701 (2), 11.594 (9)
α , β , γ (°)	90, 100.69, 90	90.43 (3), 108.60 (4), 98.41 (2)
<i>V</i> (Å ³)	1391.30 (8)	785.1 (7)
<i>Z</i>	4	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	1.52	1.36
Crystal size (mm)	0.20 × 0.15 × 0.12	0.15 × 0.10 × 0.08
Data collection		
Diffractometer	Bruker APEXII CCD diffractometer	Bruker APEXII CCD diffractometer
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2008)	Multi-scan (<i>SADABS</i> ; Bruker, 2008)
<i>T</i> _{min} , <i>T</i> _{max}	0.668, 0.745	0.682, 0.745
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	13644, 2840, 2598	7433, 2934, 2141
<i>R</i> _{int}	0.055	0.049
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.625	0.609
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.029, 0.076, 1.01	0.037, 0.060, 1.13
No. of reflections	2840	2934
No. of parameters	190	202
No. of restraints	0	1
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	1.02, -0.42	0.74, -0.60

Computer programs: *APEX2* (Bruker, 2008), *SAINT* (Bruker, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *SHELXTL* (Bruker 2008), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

standard procedure (Armarego & Chai, 2003). 4,5-Diazafluoren-9-one (dafo) was synthesized according to a reported procedure (Eckhard & Summers, 1973). A PerkinElmer Spectrum-One FT-IR spectrophotometer was employed to monitor the IR spectra of the compounds. UV-Vis spectra were obtained with a Varian Cary 50 UV-Vis spectrophotometer. ¹H NMR spectra were recorded at 298 K on a Varian Unity Inova 500 MHz instrument. Microanalyses were carried out with a PerkinElmer Series II Elemental Analyzer.



2.1. Synthesis and crystallization

2.1.1. Synthesis of complex (1). A slurry of [RuCl₂(CO)₃]₂ (100 mg, 0.195 mmol) in dry methanol (15 ml) was heated under reflux (338 K) while stirring for 3 h. Next, 4,5-diazafluoren-9-one (dafo; 71.1 mg, 0.370 mmol) was added and the reaction mixture was allowed to reflux for an additional 3 h. The color of the solution changed from pale yellow to bright

yellow during this time. Upon cooling, a yellow precipitate was observed which was filtered off, washed with a minimum amount of CH₂Cl₂, and dried under reduced pressure (yield 72.8 mg, 48%). Elemental analysis (%) found: C 38.11, N 6.89, H 1.52; calculated for C₁₃H₆Cl₂N₂O₃Ru: C 38.06, N 6.83, H 1.47. IR: ν (CO) (KBr, cm⁻¹) 2078, 1993. ¹H NMR (CDCl₃): δ 8.96 (*d*, 2H), 8.24 (*d*, 2H), 7.73 (*t*, 2H).

2.1.2. Synthesis of complex (2). A batch of [RuCl₂(CO)₃]₂ (100 mg, 0.195 mmol) in dry methanol (20 ml) was allowed to stir at 318 K for 3 h. Next, dafo (71.2 mg, 0.370 mmol) was added and the solution was allowed to stir at 318 K for an additional 3 h. The white precipitate that formed during this time was filtered off, washed with a small amount of CH₂Cl₂, and dried under vacuum (yield 90.9 mg, 56%). Elemental analysis (%) found: C 38.42, N 6.43, H 1.43; calculated for C₁₄H₆Cl₂N₂O₄Ru: C 38.37, N 6.39, H 1.38. IR: ν (CO) (KBr, cm⁻¹) 2062, 1998. ¹H NMR (CDCl₃): δ 9.70 (*d*, 1H), 8.76 (*d*, 1H), 8.20 (*d*, 1H), 8.15 (*d*, 1H), 7.70 (*d*, 1H), 7.62 (*t*, 1H).

2.1.3. Isolation of complexes (1) and (2). Single crystals of both complexes were obtained by layering hexanes over their CH₂Cl₂ solutions. One crystal of each complex was selected and fixed on top of MiTiGen micromounts using Paratone Oil and transferred to the diffractometer.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The metal atoms were

Table 2
Selected geometric parameters (Å, °) for (1).

Ru1—C2	1.879 (3)	Ru1—N1	2.203 (2)
Ru1—C1	1.923 (3)	Ru1—Cl2	2.3844 (9)
Ru1—N2	2.161 (2)	Ru1—Cl1	2.3974 (8)
C2—Ru1—C1	90.05 (13)	N2—Ru1—Cl2	84.47 (6)
C2—Ru1—N2	95.24 (10)	N1—Ru1—Cl2	89.61 (6)
C1—Ru1—N2	174.48 (11)	C2—Ru1—Cl1	88.54 (9)
C2—Ru1—N1	175.16 (10)	C1—Ru1—Cl1	94.06 (10)
C1—Ru1—N1	93.90 (11)	N2—Ru1—Cl1	87.65 (6)
N2—Ru1—N1	80.89 (8)	N1—Ru1—Cl1	88.39 (6)
C2—Ru1—Cl2	92.93 (9)	Cl2—Ru1—Cl1	172.08 (3)
C1—Ru1—Cl2	93.72 (10)		

located by direct methods and the remaining non-H atoms emerged from successive Fourier syntheses. H atoms were included in calculated positions riding on the C atom to which they are bonded, with $C-H = 0.93 \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(C)$. Carbonyl atoms C1 and O1 in (2) were constrained to have equivalent atomic displacement parameters and the C6—C7 bond was restrained to emulate rigid-body motion.

3. Results and discussion

The complexes *trans*-[RuCl₂(dafo)(CO)₂] (dafo is 4,5-diazafluoren-9-one), (1), and *fac*-[RuCl₂(dafo)(CO)₃], (2), were isolated from the reaction of [RuCl₂(CO)₃]₂ with two equivalents of dafo in methanol. Complex (1) was isolated from the methanolic reaction mixture under refluxing conditions. Quite in contrast, stirring of the reaction mixture in methanol at 318 K resulted in (2). In accordance with our previous report on *cis*- and *trans*-[RuCl₂(azpy)(CO)₂] [where azpy is 2-(phenyldiazenyl)pyridine] complexes (Carrington *et al.*, 2013), warming of [RuCl₂(CO)₃]₂ at 318 K presumably resulted in the intermediate solvento species *fac*-[RuCl₂(MeOH)(CO)₃]. Addition of dafo displaced the solvent molecule to furnish complex (2), where the dafo ligand binds the Ru^{II} center in a monodentate fashion. This finding is unusual compared to that observed for other analogous carbonyl complexes derived from rigid heterocycles like bipyridine (bpy), where, under similar conditions, the complex isolated is of formula *cis*-[RuCl₂(bpy)(CO)₂] (Haukka *et al.*, 1995). In the case of complex (2), the relatively larger bite distance between

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

Ru1—C1	1.865 (5)	Ru1—N1	2.168 (3)
Ru1—C3	1.882 (5)	Ru1—Cl2	2.4037 (16)
Ru1—C2	1.914 (4)	Ru1—Cl1	2.4128 (12)
C1—Ru1—C3	93.5 (2)	C2—Ru1—Cl2	86.04 (12)
C1—Ru1—C2	89.90 (18)	N1—Ru1—Cl2	88.62 (10)
C3—Ru1—C2	95.34 (16)	C1—Ru1—Cl1	85.99 (15)
C1—Ru1—N1	173.34 (18)	C3—Ru1—Cl1	86.50 (12)
C3—Ru1—N1	90.43 (15)	C2—Ru1—Cl1	175.60 (11)
C2—Ru1—N1	95.11 (13)	N1—Ru1—Cl1	88.86 (9)
C1—Ru1—Cl2	87.35 (18)	Cl2—Ru1—Cl1	92.18 (5)
C3—Ru1—Cl2	178.40 (13)		

the two N atoms of the dafo ligand (compared to bpy) most likely restricts bidentate coordination to the metal center (Pal *et al.*, 2014). In the case of (1), the intermediate species *fac*-[RuCl₂(MeOH)(CO)₃] undergoes a *facial*→*meridional* isomerization upon refluxing (338 K). In this *meridional* intermediate, the *trans* disposition of two of the CO ligands facilitates removal of one CO ligand. This vacancy finally allows binding of the dafo ligand in a bidentate fashion in (1).

The coordination geometry of Ru^{II} in both complexes is distorted octahedral (Tables 2 and 3). The two CO ligands are *cis* to each other in complex (1) (Fig. 1), while in complex (2) (Fig. 2), the three CO ligands are arranged in a *facial* disposition. The two Cl[−] ligands are in *trans* and *cis* dispositions in (1) and (2), respectively. In complex (1), the chelate ring composed of atoms Ru1, N1, C7, C9, and N2 is almost planar, with a mean deviation of 0.007 (3) Å. The equatorial plane of (1) is comprised of the bidentate dafo ligand and two CO ligands (atoms C1, C2, N2, and N1), with a mean deviation of 0.040 (3) Å, and the Ru^{II} atom is displaced by 0.010 (3) Å towards the Cl2 atom. The coordinated dafo ligand is planar [mean deviation = 0.020 (3) Å] in complex (1). In the case of complex (2), the equatorial plane is comprised of one N atom of the monodentate dafo ligand, one chloride and two CO

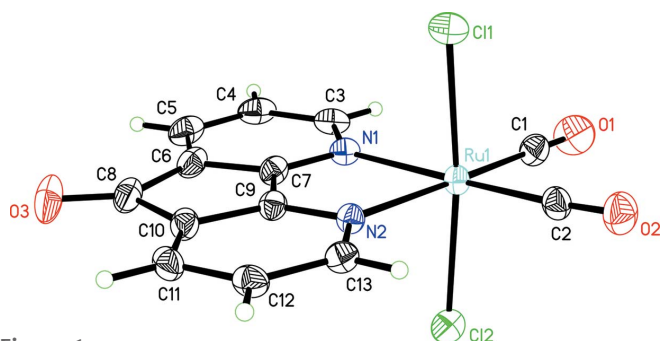


Figure 1
A perspective view of complex (1), showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level.

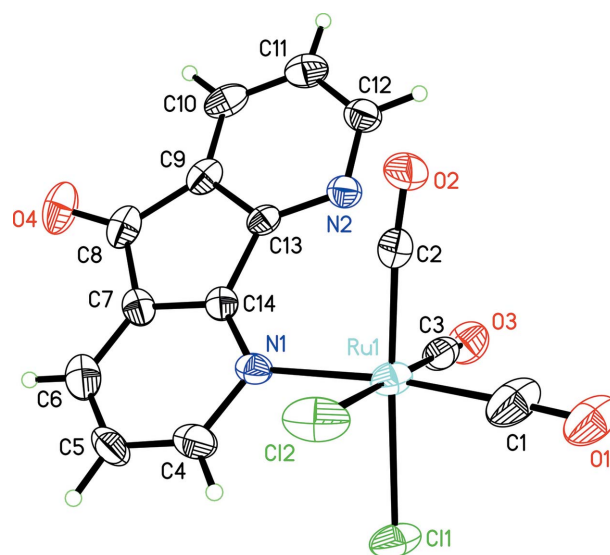


Figure 2
A perspective view of complex (2), showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level.

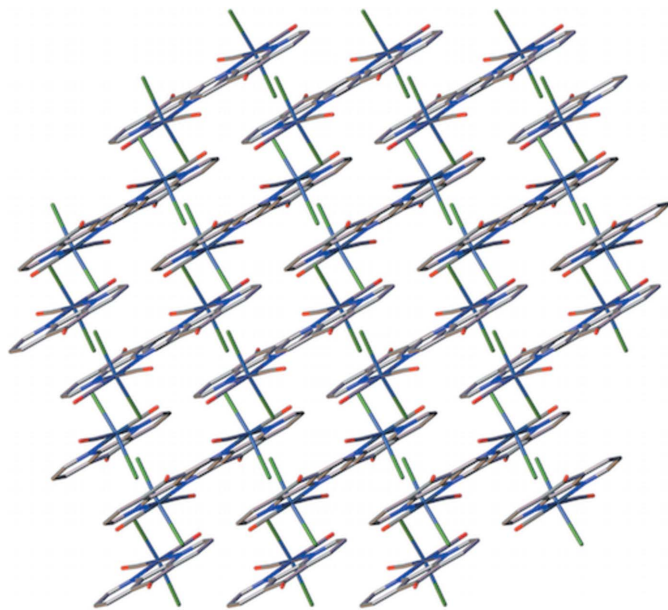


Figure 3
The crystal packing of complex (1), showing a view along the *b* axis.

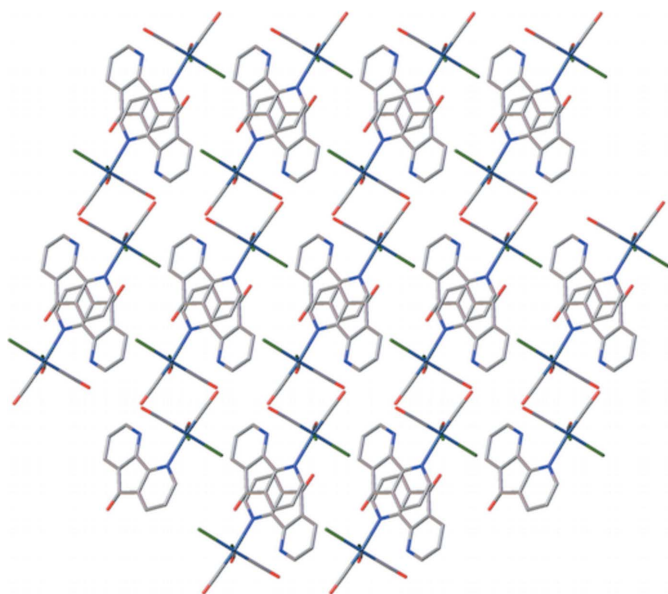


Figure 4
The crystal packing of complex (2), showing a view along the *b* axis.

ligands (atoms N1, Cl2, C1, and C3), with a mean deviation of 0.034 (4) Å. The Ru^{II} atom is displaced by 0.059 (4) Å towards the carbonyl C2 atom. In this case, the dafo ligand frame is also fairly planar, with a mean deviation of 0.028 (3) Å. The

monodentate dafo ligand in (2) forms a dihedral angle of 52.16 (8)° with the equatorial plane constituted by atoms C1, C3, N1, and Cl2. The crystal packing (Dolomanov *et al.*, 2009; Spek, 2009) for the complexes reveal no significant stacking or other nonbonded interactions (Figs. 3 and 4). The distances between the two N atoms (N1 and N2) of the dafo ligand in (1) and (2) are 2.833 (4) and 3.146 (5) Å, respectively, due to the different modes of binding. The bidentate coordination of dafo in (1) appears to promote pronounced competition in π back-bonding between the dafo and CO ligands for the same metal orbitals compared to complex (2). This is corroborated by the apparent CO release rate (k_{CO}) values of these complexes. In CH₂Cl₂ solution under 305 nm UV illumination, complex (1) exhibits a much higher k_{CO} value (15.34 ± 0.02 min⁻¹, conc. 2.4 × 10⁻⁴ M) compared to complex (2) (6.08 ± 0.02 min⁻¹, conc. 2.4 × 10⁻⁴ M).

Acknowledgements

Financial support from NSF grant DMR-1409335 is gratefully acknowledged. JJ is supported by NIH grant 2R25GM058903.

References

- Armarego, W. L. F. & Chai, C. L. L. (2003). In *Purification of Laboratory Chemicals*. Oxford: Butterworth Heinemann.
- Bernardes, G. J. L. & Garcia-Gallego, S. (2014). *Angew. Chem. Int. Ed.* **53**, 9712–9721.
- Bruker (2008). *APEX2, SAINT and SADABS*. Bruker–Nonius AXS Inc., Madison, Wisconsin, USA.
- Carrington, S. J., Chakraborty, I., Alvarado, J. R. & Mascharak, P. K. (2013). *Inorg. Chim. Acta*, **407**, 121–125.
- Chakraborty, I., Carrington, S. J. & Mascharak, P. K. (2014). *Acc. Chem. Res.* **47**, 2603–2611.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Eckhard, I. F. & Summers, L. A. (1973). *Aust. J. Chem.* **26**, 2727–2728.
- Gonzalez, M. A. & Mascharak, P. K. (2014). *J. Inorg. Biochem.* **133**, 127–135.
- Haukka, M., Kiviahio, L., Ahlgrh, M. & Pakkanen, T. A. (1995). *Organometallics*, **14**, 825–833.
- Motterlini, R. & Otterbien, L. E. (2010). *Nat. Rev. Drug. Discov.* **9**, 728–743.
- Pal, A., Biswas, B., Mitra, M., Purohit, C. S., Lin, C. H. & Ghosh, R. (2014). *J. Chem. Sci.* **126**, 717–725.
- Romao, C. C., Blatter, W. A., Seixas, J. D. & Bernardes, G. D. L. (2012). *Chem. Soc. Rev.* **41**, 3571–3583.
- Schatzschneider, U. (2015). *Br. J. Pharmacol.* **172**, 1638–1650.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Stufkens, D. J. & Vlcek, A. Jr (1998). *Coord. Chem. Rev.* **177**, 127–179.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2015). C71, 965-968 [doi:10.1107/S2053229615018100]

Synthesis and structures of ruthenium di- and tricarbonyl complexes derived from 4,5-diazafluoren-9-one

Jorge Jimenez, Indranil Chakraborty and Pradip Mascharak

Computing details

For both compounds, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Bruker 2008) and *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(1) *trans*-Dicarbonyldichlorido(4,5-diazafluoren-9-one- κ^2N,N')ruthenium(II)

Crystal data

[RuCl₂(C₁₁H₆N₂O)(CO)₂]

$M_r = 410.17$

Monoclinic, $P2_1/n$

$a = 6.5589$ (2) Å

$b = 16.9199$ (6) Å

$c = 12.7585$ (5) Å

$\beta = 100.69^\circ$

$V = 1391.30$ (8) Å³

$Z = 4$

$F(000) = 800$

$D_x = 1.958$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9050 reflections

$\theta = 2.4\text{--}26.3^\circ$

$\mu = 1.52$ mm⁻¹

$T = 296$ K

Block, colorless

0.20 × 0.15 × 0.12 mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Detector resolution: 8.33 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2008)

$T_{\min} = 0.668$, $T_{\max} = 0.745$

13644 measured reflections

2840 independent reflections

2598 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.055$

$\theta_{\max} = 26.4^\circ$, $\theta_{\min} = 2.0^\circ$

$h = -8 \rightarrow 8$

$k = -21 \rightarrow 21$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.076$

$S = 1.01$

2840 reflections

190 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 1.2351P]$

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

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.02$ e Å⁻³

$\Delta\rho_{\min} = -0.42$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ru1	0.70714 (3)	0.37385 (2)	0.63595 (2)	0.03500 (10)
Cl1	0.94807 (12)	0.34857 (5)	0.79811 (6)	0.05222 (19)
Cl2	0.49226 (13)	0.38504 (5)	0.46405 (7)	0.0547 (2)
O3	0.7415 (4)	0.01600 (13)	0.5327 (3)	0.0766 (8)
O2	0.9657 (4)	0.51454 (14)	0.6069 (2)	0.0628 (6)
O1	0.4360 (5)	0.47572 (18)	0.7402 (2)	0.0803 (8)
N1	0.5457 (3)	0.26370 (14)	0.66326 (18)	0.0392 (5)
N2	0.8830 (3)	0.29170 (13)	0.55820 (17)	0.0352 (5)
C3	0.3910 (4)	0.2398 (2)	0.7137 (2)	0.0481 (7)
H3	0.3207	0.2775	0.7465	0.058*
C4	0.3349 (5)	0.1611 (2)	0.7178 (2)	0.0564 (8)
H4	0.2307	0.1473	0.7548	0.068*
C5	0.4305 (5)	0.1020 (2)	0.6679 (3)	0.0590 (9)
H5	0.3912	0.0493	0.6699	0.071*
C6	0.5859 (5)	0.12555 (16)	0.6158 (3)	0.0489 (7)
C7	0.6332 (4)	0.20550 (16)	0.6183 (2)	0.0401 (6)
C9	0.8043 (4)	0.21970 (15)	0.5641 (2)	0.0373 (6)
C13	1.0409 (4)	0.29571 (17)	0.5048 (2)	0.0396 (6)
H13	1.1021	0.3445	0.4978	0.048*
C12	1.1159 (4)	0.23020 (18)	0.4600 (2)	0.0446 (6)
H12	1.2257	0.2360	0.4239	0.054*
C11	1.0311 (5)	0.15600 (19)	0.4678 (2)	0.0474 (7)
H11	1.0814	0.1117	0.4378	0.057*
C10	0.8679 (4)	0.15088 (17)	0.5223 (2)	0.0434 (6)
C8	0.7321 (5)	0.08520 (17)	0.5532 (3)	0.0531 (8)
C2	0.8658 (5)	0.46283 (17)	0.6145 (2)	0.0431 (6)
C1	0.5301 (5)	0.43934 (19)	0.7038 (3)	0.0514 (7)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ru1	0.03214 (14)	0.03422 (14)	0.04105 (15)	0.00096 (7)	0.01306 (10)	-0.00192 (8)
Cl1	0.0427 (4)	0.0715 (5)	0.0438 (4)	-0.0011 (3)	0.0117 (3)	0.0017 (3)
Cl2	0.0477 (4)	0.0553 (4)	0.0600 (5)	-0.0021 (3)	0.0075 (4)	0.0063 (3)
O3	0.0714 (17)	0.0331 (12)	0.120 (2)	0.0023 (11)	0.0029 (16)	-0.0037 (13)
O2	0.0662 (15)	0.0503 (13)	0.0734 (16)	-0.0131 (12)	0.0170 (13)	-0.0006 (11)
O1	0.0791 (19)	0.090 (2)	0.0798 (19)	0.0227 (16)	0.0357 (16)	0.0011 (16)
N1	0.0333 (11)	0.0471 (13)	0.0383 (11)	-0.0028 (9)	0.0099 (9)	0.0030 (10)
N2	0.0339 (11)	0.0349 (11)	0.0381 (11)	0.0020 (9)	0.0102 (9)	-0.0008 (9)

C3	0.0355 (14)	0.071 (2)	0.0372 (14)	-0.0094 (13)	0.0063 (12)	0.0048 (14)
C4	0.0457 (17)	0.078 (2)	0.0445 (16)	-0.0208 (16)	0.0050 (14)	0.0157 (16)
C5	0.0563 (19)	0.0563 (19)	0.0586 (19)	-0.0226 (16)	-0.0041 (16)	0.0186 (16)
C6	0.0472 (17)	0.0401 (16)	0.0555 (18)	-0.0052 (12)	-0.0009 (14)	0.0106 (12)
C7	0.0366 (13)	0.0383 (14)	0.0447 (15)	-0.0038 (11)	0.0058 (11)	0.0052 (11)
C9	0.0342 (13)	0.0361 (13)	0.0411 (14)	0.0025 (10)	0.0058 (11)	0.0006 (11)
C13	0.0369 (14)	0.0436 (14)	0.0395 (14)	0.0010 (11)	0.0101 (11)	0.0032 (11)
C12	0.0421 (15)	0.0553 (17)	0.0376 (14)	0.0100 (13)	0.0104 (12)	-0.0025 (12)
C11	0.0463 (16)	0.0481 (16)	0.0447 (15)	0.0156 (13)	0.0004 (13)	-0.0103 (13)
C10	0.0416 (15)	0.0366 (13)	0.0480 (16)	0.0055 (12)	-0.0023 (12)	-0.0023 (12)
C8	0.0511 (17)	0.0360 (15)	0.065 (2)	0.0023 (13)	-0.0069 (15)	0.0035 (14)
C2	0.0473 (16)	0.0381 (14)	0.0453 (15)	0.0033 (12)	0.0122 (13)	-0.0059 (12)
C1	0.0531 (18)	0.0444 (17)	0.0552 (18)	0.0069 (14)	0.0063 (15)	0.0029 (14)

Geometric parameters (Å, °)

Ru1—C2	1.879 (3)	C4—C5	1.395 (5)
Ru1—C1	1.923 (3)	C4—H4	0.9300
Ru1—N2	2.161 (2)	C5—C6	1.375 (5)
Ru1—N1	2.203 (2)	C5—H5	0.9300
Ru1—Cl2	2.3844 (9)	C6—C7	1.387 (4)
Ru1—Cl1	2.3974 (8)	C6—C8	1.519 (5)
O3—C8	1.204 (4)	C7—C9	1.443 (4)
O2—C2	1.108 (4)	C9—C10	1.377 (4)
O1—C1	1.040 (4)	C13—C12	1.379 (4)
N1—C7	1.323 (4)	C13—H13	0.9300
N1—C3	1.360 (3)	C12—C11	1.384 (4)
N2—C9	1.330 (3)	C12—H12	0.9300
N2—C13	1.343 (3)	C11—C10	1.383 (4)
C3—C4	1.385 (5)	C11—H11	0.9300
C3—H3	0.9300	C10—C8	1.521 (4)
C2—Ru1—C1	90.05 (13)	C6—C5—H5	121.6
C2—Ru1—N2	95.24 (10)	C4—C5—H5	121.6
C1—Ru1—N2	174.48 (11)	C5—C6—C7	117.0 (3)
C2—Ru1—N1	175.16 (10)	C5—C6—C8	136.2 (3)
C1—Ru1—N1	93.90 (11)	C7—C6—C8	106.8 (3)
N2—Ru1—N1	80.89 (8)	N1—C7—C6	128.5 (3)
C2—Ru1—Cl2	92.93 (9)	N1—C7—C9	121.5 (2)
C1—Ru1—Cl2	93.72 (10)	C6—C7—C9	110.0 (3)
N2—Ru1—Cl2	84.47 (6)	N2—C9—C10	127.1 (3)
N1—Ru1—Cl2	89.61 (6)	N2—C9—C7	121.6 (2)
C2—Ru1—Cl1	88.54 (9)	C10—C9—C7	111.3 (2)
C1—Ru1—Cl1	94.06 (10)	N2—C13—C12	122.5 (3)
N2—Ru1—Cl1	87.65 (6)	N2—C13—H13	118.7
N1—Ru1—Cl1	88.39 (6)	C12—C13—H13	118.7
Cl2—Ru1—Cl1	172.08 (3)	C13—C12—C11	121.4 (3)
C7—N1—C3	114.0 (3)	C13—C12—H12	119.3

C7—N1—Ru1	107.51 (17)	C11—C12—H12	119.3
C3—N1—Ru1	138.5 (2)	C12—C11—C10	116.8 (3)
C9—N2—C13	114.8 (2)	C12—C11—H11	121.6
C9—N2—Ru1	108.51 (16)	C10—C11—H11	121.6
C13—N2—Ru1	136.70 (18)	C9—C10—C11	117.4 (3)
N1—C3—C4	122.0 (3)	C9—C10—C8	106.5 (3)
N1—C3—H3	119.0	C11—C10—C8	136.1 (3)
C4—C3—H3	119.0	O3—C8—C6	127.9 (3)
C3—C4—C5	121.8 (3)	O3—C8—C10	126.8 (3)
C3—C4—H4	119.1	C6—C8—C10	105.4 (2)
C5—C4—H4	119.1	O2—C2—Ru1	176.3 (3)
C6—C5—C4	116.7 (3)	O1—C1—Ru1	178.9 (3)

(2) *fac*-Tricarbonyldichlorido(4,5-diazafluoren-9-one- κ N)ruthenium(II)*Crystal data*[RuCl₂(C₁₁H₆N₂O)(CO)₃] $M_r = 438.18$ Triclinic, $P\bar{1}$ $a = 7.458$ (2) Å $b = 9.701$ (2) Å $c = 11.594$ (9) Å $\alpha = 90.43$ (3)° $\beta = 108.60$ (4)° $\gamma = 98.41$ (2)° $V = 785.1$ (7) Å³ $Z = 2$ $F(000) = 428$ $D_x = 1.853$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2934 reflections

 $\theta = 2.7$ – 26.0 ° $\mu = 1.36$ mm⁻¹ $T = 296$ K

Block, colorless

 $0.15 \times 0.10 \times 0.08$ mm*Data collection*

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Detector resolution: 8.33 pixels mm⁻¹ ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2008)

 $T_{\min} = 0.682$, $T_{\max} = 0.745$

7433 measured reflections

2934 independent reflections

2141 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.049$ $\theta_{\max} = 25.7$ °, $\theta_{\min} = 1.9$ ° $h = -9 \rightarrow 9$ $k = -11 \rightarrow 11$ $l = -14 \rightarrow 14$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.037$ $wR(F^2) = 0.060$ $S = 1.13$

2934 reflections

202 parameters

1 restraint

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2)]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.74$ e Å⁻³ $\Delta\rho_{\min} = -0.60$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ru1	0.34512 (5)	0.19385 (3)	0.80951 (3)	0.05637 (13)
Cl1	0.31437 (16)	−0.05628 (10)	0.78187 (11)	0.0812 (4)
Cl2	0.01300 (14)	0.19209 (12)	0.69578 (13)	0.0944 (4)
O1	0.2193 (5)	0.1340 (3)	1.0283 (3)	0.0996 (9)
O2	0.3520 (4)	0.5013 (3)	0.8646 (2)	0.0701 (8)
O4	0.7583 (4)	0.4634 (3)	0.4104 (3)	0.0928 (10)
O3	0.7628 (4)	0.1844 (3)	0.9465 (3)	0.0816 (9)
N1	0.4091 (4)	0.2135 (3)	0.6401 (3)	0.0517 (8)
N2	0.7099 (4)	0.4535 (3)	0.8075 (3)	0.0539 (8)
C1	0.2690 (8)	0.1590 (5)	0.9463 (5)	0.0996 (9)
C2	0.3567 (5)	0.3899 (4)	0.8389 (3)	0.0543 (10)
C14	0.5432 (5)	0.3041 (4)	0.6140 (3)	0.0472 (9)
C13	0.6820 (5)	0.4209 (4)	0.6922 (4)	0.0460 (9)
C9	0.7831 (5)	0.4932 (4)	0.6231 (4)	0.0558 (10)
C8	0.7136 (6)	0.4259 (5)	0.4978 (4)	0.0647 (12)
C7	0.5671 (6)	0.3054 (4)	0.5003 (4)	0.0552 (10)
C6	0.4577 (7)	0.2099 (5)	0.4087 (4)	0.0749 (13)
H6	0.4751	0.2088	0.3328	0.090*
C5	0.3210 (7)	0.1158 (5)	0.4337 (4)	0.0775 (14)
H5	0.2432	0.0489	0.3740	0.093*
C4	0.2986 (6)	0.1201 (4)	0.5465 (4)	0.0706 (12)
H4	0.2029	0.0560	0.5602	0.085*
C10	0.9183 (6)	0.6085 (4)	0.6741 (5)	0.0684 (12)
H10	0.9866	0.6593	0.6297	0.082*
C11	0.9465 (6)	0.6442 (4)	0.7941 (5)	0.0739 (13)
H11	1.0349	0.7218	0.8331	0.089*
C12	0.8448 (6)	0.5657 (4)	0.8559 (4)	0.0644 (11)
H12	0.8703	0.5913	0.9377	0.077*
C3	0.6052 (7)	0.1911 (4)	0.8956 (4)	0.0611 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ru1	0.0571 (2)	0.0437 (2)	0.0766 (3)	0.00962 (15)	0.03234 (18)	0.00607 (16)
Cl1	0.0980 (8)	0.0420 (6)	0.1220 (10)	0.0094 (6)	0.0617 (8)	0.0079 (6)
Cl2	0.0528 (7)	0.0710 (8)	0.1545 (12)	0.0099 (6)	0.0270 (7)	−0.0064 (8)
O1	0.129 (2)	0.0729 (17)	0.141 (3)	0.0402 (16)	0.094 (2)	0.0351 (17)
O2	0.089 (2)	0.0517 (19)	0.073 (2)	0.0212 (17)	0.0251 (16)	−0.0041 (16)
O4	0.099 (2)	0.131 (3)	0.074 (2)	0.044 (2)	0.0520 (19)	0.0392 (19)

O3	0.074 (2)	0.082 (2)	0.089 (2)	0.0230 (18)	0.0218 (19)	0.0225 (17)
N1	0.054 (2)	0.0403 (19)	0.058 (2)	0.0090 (16)	0.0139 (17)	-0.0020 (16)
N2	0.056 (2)	0.049 (2)	0.056 (2)	0.0045 (16)	0.0185 (18)	0.0003 (17)
C1	0.129 (2)	0.0729 (17)	0.141 (3)	0.0402 (16)	0.094 (2)	0.0351 (17)
C2	0.051 (2)	0.062 (3)	0.050 (3)	0.010 (2)	0.016 (2)	0.009 (2)
C14	0.047 (2)	0.049 (3)	0.049 (3)	0.0187 (19)	0.016 (2)	0.004 (2)
C13	0.047 (2)	0.040 (2)	0.057 (3)	0.0170 (18)	0.019 (2)	0.011 (2)
C9	0.050 (2)	0.059 (3)	0.071 (3)	0.023 (2)	0.030 (2)	0.020 (2)
C8	0.064 (3)	0.082 (3)	0.068 (3)	0.039 (2)	0.035 (3)	0.026 (3)
C7	0.057 (3)	0.062 (3)	0.050 (3)	0.027 (2)	0.014 (2)	-0.001 (2)
C6	0.085 (3)	0.088 (4)	0.059 (3)	0.042 (3)	0.021 (3)	0.005 (3)
C5	0.094 (4)	0.064 (3)	0.057 (3)	0.019 (3)	-0.003 (3)	-0.021 (2)
C4	0.067 (3)	0.053 (3)	0.079 (4)	0.006 (2)	0.008 (3)	-0.007 (3)
C10	0.052 (3)	0.055 (3)	0.108 (4)	0.010 (2)	0.039 (3)	0.024 (3)
C11	0.064 (3)	0.058 (3)	0.096 (4)	0.003 (2)	0.023 (3)	0.005 (3)
C12	0.066 (3)	0.055 (3)	0.065 (3)	0.007 (2)	0.012 (2)	-0.004 (2)
C3	0.080 (3)	0.046 (3)	0.069 (3)	0.012 (2)	0.039 (3)	0.011 (2)

Geometric parameters (Å, °)

Ru1—C1	1.865 (5)	C13—C9	1.394 (5)
Ru1—C3	1.882 (5)	C9—C10	1.377 (5)
Ru1—C2	1.914 (4)	C9—C8	1.488 (5)
Ru1—N1	2.168 (3)	C8—C7	1.486 (5)
Ru1—C12	2.4037 (16)	C7—C6	1.365 (5)
Ru1—C11	2.4128 (12)	C6—C5	1.370 (6)
O1—C1	1.141 (5)	C6—H6	0.9300
O2—C2	1.128 (4)	C5—C4	1.372 (5)
O4—C8	1.206 (4)	C5—H5	0.9300
O3—C3	1.146 (4)	C4—H4	0.9300
N1—C14	1.344 (4)	C10—C11	1.373 (5)
N1—C4	1.369 (4)	C10—H10	0.9300
N2—C13	1.314 (4)	C11—C12	1.362 (5)
N2—C12	1.350 (4)	C11—H11	0.9300
C14—C7	1.385 (5)	C12—H12	0.9300
C14—C13	1.490 (5)		
C1—Ru1—C3	93.5 (2)	C10—C9—C8	131.2 (4)
C1—Ru1—C2	89.90 (18)	C13—C9—C8	108.6 (4)
C3—Ru1—C2	95.34 (16)	O4—C8—C7	126.6 (4)
C1—Ru1—N1	173.34 (18)	O4—C8—C9	128.1 (4)
C3—Ru1—N1	90.43 (15)	C7—C8—C9	105.2 (4)
C2—Ru1—N1	95.11 (13)	C6—C7—C14	121.1 (4)
C1—Ru1—C12	87.35 (18)	C6—C7—C8	129.3 (4)
C3—Ru1—C12	178.40 (13)	C14—C7—C8	109.5 (4)
C2—Ru1—C12	86.04 (12)	C7—C6—C5	117.0 (4)
N1—Ru1—C12	88.62 (10)	C7—C6—H6	121.5
C1—Ru1—C11	85.99 (15)	C5—C6—H6	121.5

C3—Ru1—C11	86.50 (12)	C6—C5—C4	120.2 (4)
C2—Ru1—C11	175.60 (11)	C6—C5—H5	119.9
N1—Ru1—C11	88.86 (9)	C4—C5—H5	119.9
C12—Ru1—C11	92.18 (5)	N1—C4—C5	123.6 (4)
C14—N1—C4	115.2 (3)	N1—C4—H4	118.2
C14—N1—Ru1	129.1 (3)	C5—C4—H4	118.2
C4—N1—Ru1	115.7 (3)	C11—C10—C9	116.3 (4)
C13—N2—C12	114.9 (3)	C11—C10—H10	121.9
O1—C1—Ru1	177.9 (5)	C9—C10—H10	121.9
O2—C2—Ru1	172.3 (3)	C12—C11—C10	119.8 (4)
N1—C14—C7	122.9 (4)	C12—C11—H11	120.1
N1—C14—C13	129.2 (3)	C10—C11—H11	120.1
C7—C14—C13	107.9 (4)	N2—C12—C11	125.0 (4)
N2—C13—C9	123.9 (4)	N2—C12—H12	117.5
N2—C13—C14	127.4 (3)	C11—C12—H12	117.5
C9—C13—C14	108.7 (3)	O3—C3—Ru1	177.4 (4)
C10—C9—C13	120.1 (4)		
