Bovio, B., Bonati, F., Burini, A. & Pietroni, B. R. (1984). Z. Naturforsch. Teil B, 39, 1747–1754.

Britten, J. F., Lock, C. J. L. & Wang, Z. (1992). Acta Cryst. C48, 1600–1603.

Canty, A. J., Minchin, N. J., Healy, P. C. & White, A. H. (1982). J. Chem. Soc. Dalton Trans. pp. 1795–1802.

Cotton, F. A. & Wilkinson, G. (1988). Advanced Inorganic Chemistry, 15th ed., pp. 948–949. New York: John Wiley.

Fehlhammer, W. P. & Finck, W. (1991). J. Organomet. Chem. 414, 261–270.

French, S. & Wilson, K. (1978). Acta Cryst. A34, 517–525.

Howard-Lock, H. E., Lock, C. J. L., Penny, S. & Turner, M. (1989). Can. J. Chem. 67, 1051–1055.

Lock, C. J. L. & Turner, M. A. (1987). Acta Cryst. C43, 2096–2099.

Rosopulos, Y., Nagel, U. & Beck, N. (1985). Chem. Ber. 118, 931–942.

Sheldrick, G. M. (1990). SHELXTL PC. Release 4.1. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

(tert-Butyl isocyano-C)(carbonyl)(η5-cyclopentadienyl)(triphenylphosphine-P)-ruthenium(II) Hexafluorophosphate

STEPHEN J. SIMPSON

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, England

Abstract

The crystal structure of the title compound consists of discrete $[Ru(CN'Bu)(CO)(PPh_3)(\eta^5\text{-}C_5H_5)]^+$ cations and $[PF_6]^-$ anions. The cation has pseudo-octahedral symmetry with the cyclopentadienyl group occupying three sites in a facial arrangement.

Comment

The chemistry of the $[Ru(CN'Bu)(PPh_3)(\eta^5\text{-}C_5H_5)]^+$ moiety has been extensively studied as it is able to ligate molecules such as dihydrogen, iodoalkanes and mercaptans (Conroy-Lewis, Redhouse & Simpson, 1989; Conroy-Lewis & Simpson, 1986, 1991); these molecules normally undergo oxidative addition at late-transition-metal centres. The variation in structural parameters of the triphenylphosphine and tert-butyl isocyanide ligands for a series of compounds containing this moiety might illuminate the unusual electronic character responsible for this reactivity. We previously reported the crystal structure of $[Ru(CN'Bu)(PPh_3)(NH_3)(\eta^5\text{-}C_5H_5)]PF_6$, where the additional ligand was a pure σ-donor (Conroy-Lewis

& Simpson, 1990), and we present here the structure of $[Ru(CN'Bu)(CO)(PPh_3)(\eta^5\text{-}C_5H_5)]PF_6$, where the carbonyl ligand is an archetypal good π-acceptor and poor σ-donor. The compound has been reported previously (Conroy-Lewis, Redhouse & Simpson, 1989).

The cation has the expected pseudo-octahedral geometry with the cyclopentadienyl group occupying three fac sites. Both the Ru—P bond length, 2.328 (1) Å, and Ru—C(N) distance, 1.961 (4) Å, are longer than the 2.290 (1) and 1.934 (5) Å, respectively, found in $[Ru(CN'Bu)(PPh_3)(NH_3)(\eta^5\text{-}C_5H_5)]PF_6$ (Conroy-Lewis & Simpson, 1990). This reflects the increased competition for π-electron density at the metal as a result of replacing an ammine group with a carbonyl group. The Ru—C(O) bond length of 1.901 (6) Å in $[Ru(CN'Bu)(CO)(PPh_3)(\eta^5\text{-}C_5H_5)]PF_6$ is at the high end of the range reported for this class of molecule: 1.880 (6) Å for $[Ru(CO)\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5)]BF_4$ (Frank & Selegue, 1991), 1.869 (2) Å for $[Ru(CO)(PPh_3)_2(\eta^5\text{-}C_5H_5)]BPh_4$ (Wisner, Bartczak & Ibers, 1985) and 1.890 (2) Å for $[Ru(CO)(PPh_3)_2(\eta^5\text{-}C_5H_5)][Co(CO)_4]$ (Doyle & Van Engen, 1985). The carbonyl stretching frequencies in the infrared spectra of these cations, at 2014, 2022, 1987 and 1978 cm^{-1}, respectively, illustrate more clearly the electron density at the metal centre available for back donation. The values of $\nu(C\equiv N)$ for $[Ru(CN'Bu)(PPh_3)(CO)(\eta^5\text{-}C_5H_5)]PF_6$ and $[Ru(CN'Bu)(PPh_3)(NH_3)(\eta^5\text{-}C_5H_5)]PF_6$ are 2186 and 2126 cm^{-1}, respectively, confirming the effect of the carbonyl group.

It seems likely that the ability of the $[Ru(CN'Bu)(PPh_3)(\eta^5\text{-}C_5H_5)]^+$ moiety to stabilize unusual ligands results from the presence of both a good σ-donor ('BuNC) and a good π-acceptor (PPh$_3$) in the coordination sphere.
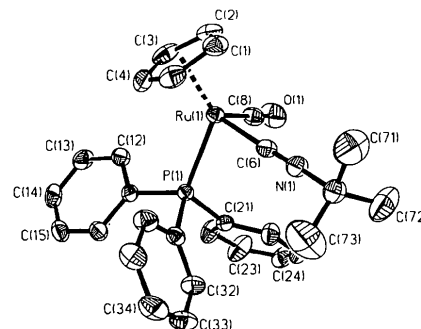

Fig. 1. Plot showing 30% thermal ellipsoids for the cation present in $[Ru(CN'Bu)(CO)(PPh_3)(\eta^5\text{-}C_5H_5)]PF_6$.

Experimental

Crystal data

$[Ru(C_{18}H_{15}P)(C_5H_9N)-$	$Z = 2$
$(C_5H_5)(CO)][PF_6]$	$D_x = 1.505$ Mg m^{-3}

$M_r = 684.5$
Triclinic
$P\bar{1}$
$a = 10.574\ (3)$ Å
$b = 11.037\ (3)$ Å
$c = 13.580\ (4)$ Å
$\alpha = 86.96\ (2)°$
$\beta = 76.70\ (2)°$
$\gamma = 78.32\ (2)°$
$V = 1510.4\ (8)$ Å^3

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 6.2–13.7°$
$\mu = 0.671$ mm^{-1}
$T = 294\ (1)$ K
Block
$0.45 \times 0.35 \times 0.30$ mm
Yellow

Data collection

Nicolet $R3m/V$ diffractometer
θ–2θ scans
Absorption correction: empirical based on ψ scans
$T_{min} = 0.5850,\ T_{max} = 0.6600$
5601 measured reflections
5284 independent reflections

4508 observed reflections $[F > 6\sigma(F)]$
$R_{int} = 0.0429$
$\theta_{max} = 25°$
$h = 0 \rightarrow 12$
$k = -12 \rightarrow 13$
$l = -15 \rightarrow 16$
3 standard reflections monitored every 100 reflections intensity variation: <1%

Refinement

Refinement on F
Final $R = 0.0436$
$wR = 0.0604$
$S = 2.12$
4508 reflections

371 parameters
$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{max} = 0.263$
$\Delta\rho_{max} = 0.93$ e Å^{-3}
$\Delta\rho_{min} = -0.70$ e Å^{-3}

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ru(1)	0.1439 (1)	0.3582 (1)	0.1873 (1)	0.037 (1)
C(1)	0.2270 (5)	0.5272 (4)	0.1329 (4)	0.064 (2)
C(2)	0.1119 (6)	0.5327 (4)	0.0977 (4)	0.063 (2)
C(3)	0.0040 (5)	0.5370 (4)	0.1832 (5)	0.069 (2)
C(4)	0.0561 (6)	0.5347 (4)	0.2705 (4)	0.069 (2)
C(5)	0.1929 (5)	0.5280 (4)	0.2400 (5)	0.065 (2)
C(8)	0.0941 (5)	0.2624 (5)	0.0955 (4)	0.054 (2)
O(1)	0.0603 (5)	0.2108 (4)	0.0406 (3)	0.092 (2)
P(1)	0.0775 (1)	0.2265 (1)	0.3203 (1)	0.036 (1)
C(11)	-0.0866 (4)	0.2771 (4)	0.4021 (3)	0.041 (1)
C(12)	-0.1894 (4)	0.3420 (4)	0.3598 (4)	0.053 (2)
C(13)	-0.3171 (5)	0.3729 (5)	0.4197 (5)	0.065 (2)
C(14)	-0.3424 (5)	0.3405 (5)	0.5220 (4)	0.066 (2)
C(15)	-0.2426 (5)	0.2774 (5)	0.5632 (4)	0.060 (2)
C(16)	-0.1143 (5)	0.2448 (4)	0.5060 (3)	0.052 (2)
C(21)	0.0706 (4)	0.0739 (4)	0.2777 (3)	0.042 (1)
C(22)	-0.0477 (5)	0.0334 (5)	0.2944 (4)	0.064 (2)
C(23)	-0.0529 (6)	-0.0774 (5)	0.2523 (6)	0.090 (3)
C(24)	0.0602 (7)	-0.1465 (5)	0.1935 (5)	0.080 (3)
C(25)	0.1760 (7)	-0.1132 (5)	0.1830 (4)	0.078 (2)
C(26)	0.1856 (5)	0.0009 (4)	0.2220 (4)	0.060 (2)
C(31)	0.1859 (4)	0.1956 (4)	0.4095 (3)	0.042 (1)
C(32)	0.2354 (5)	0.0792 (5)	0.4420 (4)	0.059 (2)
C(33)	0.3168 (6)	0.0641 (6)	0.5104 (4)	0.071 (2)
C(34)	0.3457 (6)	0.1625 (6)	0.5492 (4)	0.077 (3)
C(35)	0.2968 (6)	0.2793 (6)	0.5205 (4)	0.073 (2)
C(36)	0.2192 (5)	0.2963 (5)	0.4501 (4)	0.062 (2)
N(1)	0.4324 (4)	0.2085 (4)	0.1582 (3)	0.055 (1)
C(6)	0.3233 (4)	0.2579 (4)	0.1681 (3)	0.046 (2)
C(7)	0.5710 (4)	0.1520 (5)	0.1537 (4)	0.061 (2)
C(71)	0.6528 (7)	0.2457 (7)	0.1069 (8)	0.121 (4)
C(72)	0.6068 (8)	0.0431 (7)	0.0806 (9)	0.126 (5)
C(73)	0.5833 (8)	0.1195 (14)	0.2605 (7)	0.183 (7)
P(2)	0.4071 (1)	0.3500 (1)	-0.1755 (1)	0.070 (1)
F(1)	0.3491 (4)	0.3612 (4)	-0.2702 (2)	0.163 (3)
F(2)	0.3039 (3)	0.4634 (3)	-0.1302 (3)	0.140 (3)
F(3)	0.3116 (3)	0.2653 (3)	-0.1259 (3)	0.246 (5)
F(4)	0.5102 (3)	0.2368 (3)	-0.2213 (3)	0.198 (3)
F(5)	0.5026 (3)	0.4349 (3)	-0.2255 (3)	0.177 (4)
F(6)	0.4651 (4)	0.3391 (5)	-0.0812 (2)	0.333 (8)

Table 2. *Geometric parameters* (Å, °)

Ru(1)—C(1)	2.240 (5)	Ru(1)—C(2)	2.232 (5)
Ru(1)—C(3)	2.221 (4)	Ru(1)—C(4)	2.225 (5)
Ru(1)—C(5)	2.236 (6)	Ru(1)—C(6)	1.961 (4)
Ru(1)—P(1)	2.328 (1)	Ru(1)—C(8)	1.901 (6)
N(1)—C(6)	1.152 (5)	C(8)—O(1)	1.121 (8)
C(6)—Ru(1)—P(1)	88.1 (1)	C(6)—Ru(1)—C(8)	93.3 (2)
P(1)—Ru(1)—C(8)	90.8 (1)	Ru(1)—C(6)—N(1)	173.9 (4)
C(6)—N(1)—C(7)	174.8 (5)	Ru(1)—C(8)—O(1)	176.6 (4)

The sample for structural determination was recrystallized by slow diffusion of a layer of diethyl ether into a dichloromethane solution. Cell parameters were determined by least-squares refinement. Data were corrected for Lorentz and polarization effects. Neutral-atom scattering factors and complex anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations were performed using *SHELXTL-Plus* (Sheldrick, 1987) on a MicroVAX II computer. The Ru and P atoms were located from a Patterson synthesis. Subsequent difference maps located all remaining non-H atoms. All non-H atoms were refined with anisotropic thermal parameters and H atoms were placed in calculated positions and allowed to ride with fixed U_{iso}. The hexafluorophosphate anion was constrained to octahedral symmetry and the P—F bond length was refined. Refinement was by full-matrix least squares. The shift in the final refinement (maximum $\Delta/\sigma = 0.263$, mean $\Delta/\sigma = 0.011$) was concerned with the anion. The highest unassigned electron-density peaks were adjacent to the hexafluorophosphate anion.

References

Conroy-Lewis, F. M., Redhouse, A. D. & Simpson, S. J. (1989). *J. Organomet. Chem.* **366**, 357–367.
Conroy-Lewis, F. M. & Simpson, S. J. (1986). *J. Chem. Soc. Chem. Commun.* pp. 506–507.
Conroy-Lewis, F. M. & Simpson, S. J. (1990). *J. Organomet. Chem.* **396**, 83–94.
Conroy-Lewis, F. M. & Simpson, S. J. (1991). *J. Chem. Soc. Chem. Commun.* pp. 388–389.
Doyle, G. & Van Engen, D. (1985). *J. Organomet. Chem.* **280**, 253–259.
Frank, K. G. & Selegue, J. P. (1991). *Acta Cryst.* C47, 35–37.

Sheldrick, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet *R3m/V* crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

Wisner, J. M., Bartczak, T. J. & Ibers, J. A. (1985). *Inorg. Chim. Acta*, **100**, 115–123.

Acta Cryst. (1993). C**49**, 1335–1336

Structure of Guanidinium Hexafluorogallate, [C(NH₂)₃]₃GaF₆

$[C(NH_2)_3]_3GaF_6$

HANNA MAŁUSZYŃSKA

Institute of Physics, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Abstract

The guanidinium cation is planar within experimental error and does not exhibit any symmetry. The two inequivalent GaF₆ anions have 3 symmetry. The cation is strongly hydrogen bonded to the GaF₆ anions utilizing all H atoms. The molecular packing can be described as a framework of GaF₆ ions (where Ga atoms occupy octahedral voids) hydrogen bonded to guanidinium cations lying approximately parallel to (100) planes.

Comment

This work is part of a series of X-ray diffraction and NMR studies of crystal structure and ionic motion in various guanidinium salts (Pająk, Grottel & Kozioł, 1982; Kozak, Grottel, Kozioł & Pająk, 1987; Grottel, Kozak, Kozioł & Pająk, 1989).

The title compound is isostructural with guanidinium hexafluoroaluminate (Grottel, Kozak, Małuszyńska & Pająk, 1992). No essential differences in crystal and molecular structures of the aluminium derivative [$Pa\bar{3}$, $a = 13.953\,(2)$ Å] and the gallium analogue have been observed, except for a longer Ga—F bond length of $1.901\,(1)$ Å, compared to the length of the Al—F bond of $1.818\,(1)$ Å.

Experimental

Crystal data

[C(NH₂)₃]₃[GaF₆]
$M_r = 363.95$
Cubic
$Pa\bar{3}$
$a = 14.073\,(1)$ Å

Cu *Kα* radiation
$\lambda = 1.54178$ Å
Cell parameters from 15 reflections
$\theta = 22.3\text{–}26.5°$

$V = 2787.1\,(1)$ Å³
$Z = 8$
$D_x = 1.735$ Mg m⁻³
$D_m = 1.74$ Mg m⁻³

$\mu = 3.44$ mm⁻¹
$T = 293$ K
Cube
$0.2 \times 0.2 \times 0.1$ mm
Transparent

Data collection

Syntex *P2₁* diffractometer
$\theta/2\theta$ scans
2272 measured reflections
638 independent reflections
526 observed reflections
[$I \geq 1.96\sigma(I)$]
$R_{int} = 0.049$
$\theta_{max} = 58°$

$h = 0 \rightarrow 17$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 17$
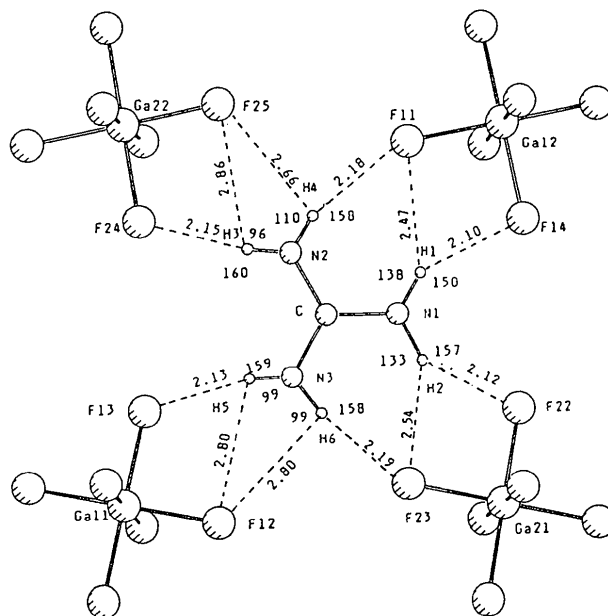3 standard reflections monitored every 100 reflections
intensity variation: ±2%

Fig. 1. The hydrogen-bond geometry (Å, °) of [C(NH₂)₃]₃GaF₆. σ(H···F) = 0.02 Å, σ(N—H···F) = 2°. Symmetry codes are: GaII $-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; Ga21 $0, \frac{1}{2}, \frac{1}{2}$; Ga12 $0, 1, \frac{1}{2}$; Ga22 $-\frac{1}{2}, 1, \frac{1}{2}$; F12 $y - 1, -z + \frac{1}{2}, x + \frac{1}{2}$; F13 $x - \frac{1}{2}, y, -z + \frac{1}{2}$; F23 $-y + \frac{1}{2}, -z + 1, x + \frac{1}{2}$; F22 none; F14 $1 + x, \frac{3}{2} - y, \frac{1}{2} + z$; F24 $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; F25 $y - 1, -z + \frac{3}{2}, x + \frac{1}{2}$.
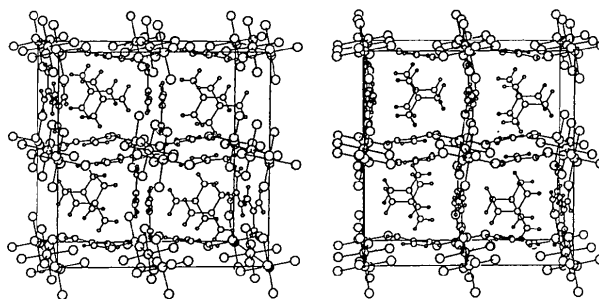

Fig. 2. Stereoscopic view of the unit-cell contents.