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Structure of μ_3-Pentafluorophenylimido-μ_3-phenylimido-tris[tricarbonylruthenium(0)]

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Abstract. $[Ru_3(C_6H_5N)(C_6F_5N)(CO)_9]$, $M_r = 827{\cdot}48$, monoclinic, $P2_1/c$, $a = 9{\cdot}323$ (1), $b = 13{\cdot}462$ (2), $c = 19{\cdot}892$ (3) Å, $\beta = 93{\cdot}00$ (1)°, $V = 2493{\cdot}2$ (6) Å^3, $Z = 4$, $D_x = 2{\cdot}205$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 17{\cdot}00$ cm^{-1}, $F(000) = 1576$, $T = 295$ K, $R = 0{\cdot}0381$ for 3721 observed reflections. The three Ru atoms form an isosceles triangle, with Ru—Ru 2·659 (1) and 2·656 (1) Å, Ru···Ru 3·285 (1) Å, Ru—Ru—Ru 76·3 (1)°. The NPh and NC_6F_5 ligands are triply bridging, with Ru—N 2·039 (3) to 2·152 (3) Å. All the carbonyl groups are terminal.

Introduction. Reaction of $Ru_3(CO)_{12}$ and azoarenes, ArN=NAr′, gives $Ru_3(\mu_3\text{-NAr})(\mu_3\text{-NAr}')(CO)_9$ in moderate yields (Bruce, Humphrey, Omar bin Shawkataly, Snow & Tiekink, 1987). X-ray study of $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ (1) (Clegg, Sheldrick, Stalke, Bhaduri & Gopalkrishnan, 1984) and $Ru_3(\mu_3\text{-NPh})(\mu_3\text{-NC}_6H_4F\text{-}3)(CO)_9$ (2) (Bruce *et al.*, 1987) reveals that in both (1) and (2), the Ru_3 triangle with a non-bonded Ru···Ru vector is capped on both sides by a μ_3-arylimido moiety. We now report the structure of $Ru_3(\mu_3\text{-NPh})(\mu_3\text{-NC}_6F_5)(CO)_9$ (3).

Experimental. Pentafluoroazobenzene, $PhN{=}NC_6F_5$ reacts with $Ru_3(CO)_{12}$ under N_2 to give an orange crystalline product in very low yield after separation by column chromotography. The product has an IR spectrum ν_{CO} (cyclohexane) similar to $Ru_3(\mu_3\text{-NAr})(\mu_3\text{-NAr}')(CO)_9$ (Bruce *et al.*, 1987). Orange crystals suitable for X-ray analysis were obtained by recrystallization from *n*-hexane.

Preliminary Weissenberg and Buerger precession photographs yielded approximate cell dimensions and showed a monoclinic system with space group $P2_1/c$ from systematic absences $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$. Data collection on crystal 0·7 × 0·6 × 0·2 mm was obtained with Syntex $P2_1$ diffractometer using $2\theta/\theta$ scan for two octants of the sphere ($0 < h < 9$, $0 < k < 13$, $-19 < l < 19$) out to the 2θ limit of 52°. A variable scan speed of 5·0–29·3° min^{-1} was used. Lattice parameters refined using 25 reflections in the range $35 \leq \theta \leq 43°$. Standard reflection (304) checked every 15 reflections: no significant deviation. The data were corrected for Lorentz and polarization effects. 4976 reflections were collected, 4177 unique ($R_{\text{int}} = 0{\cdot}1253$), of which 3721 observed reflections with $I > 2{\cdot}5\sigma(I)$ were used for refinement of the structure.

The three heavy atoms of Ru were first located through *SHELXS*86 (Sheldrick, 1986) and were then used to initiate the starting phase model for the difference Fourier method to reveal the other atoms through *SHELX*76 (Sheldrick, 1976). Scattering factors for C, H, N and O inlaid in *SHELX*76; scattering factors and anamolous-scattering factors for Ru from the *International Tables for X-ray Crystallography* (1974). Structure determination and refinement performed on IBM 4361/4381. Refinement by full-matrix least squares based on F, anisotropic refinement for non-H atoms; H atoms fixed (C—H 0·96 Å) but not refined. In order to correct the observed structure factors for absorption effects, *ABSORB* (Ugozzoli, 1987) was used (transmission factors min.–max.: 0·6801–1·6465). The final agreement factors were $R = 0{\cdot}0381$, $wR = 0{\cdot}0453$, $S = 1{\cdot}41$. Weight for every observed structure factor calculated according to $w = 1/[\sigma^2(F) + 0{\cdot}001904F^2]$. $(\Delta/\sigma)_{\max} = 0{\cdot}096$; $\Delta\rho_{\max} = 0{\cdot}7402$, $\Delta\rho_{\min} = -0{\cdot}6853$ e Å^{-3}; no extinction correction. Geometrical calculations performed with *XANADU* (Roberts & Sheldrick, 1975) and illustrations drawn with *ORTEP* (Johnson, 1965).

Discussion. The final atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1.¶ Bond distances and

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¶ Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52791 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* (× 10^4, × 10^5 *for* Ru) *and* B_{eq} ($Å^2$) *with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33}).$$

	x	*y*	*z*	B_{eq}
Ru(1)	29680 (3)	5889 (2)	11816 (2)	2·81 (1)
Ru(2)	8098 (3)	18408 (2)	9071 (2)	2·88 (1)
Ru(3)	27748 (3)	29590 (3)	15589 (2)	3·21 (1)
N(1)	3081 (3)	1984 (2)	789 (2)	2·80 (8)
N(2)	2011 (3)	1577 (3)	1833 (2)	2·96 (8)
C(2)	5153 (5)	2751 (3)	273 (3)	3·92 (12)
C(3)	5921 (5)	2933 (4)	−272 (3)	4·81 (16)
C(4)	5487 (6)	2609 (5)	−908 (3)	5·51 (17)
C(5)	4209 (6)	2075 (4)	−981 (3)	5·06 (14)
C(6)	3423 (5)	1860 (3)	−427 (2)	3·84 (12)
C(1)	3859 (4)	2208 (3)	204 (2)	3·05 (10)
C(15)	3342 (4)	−148 (3)	387 (2)	3·25 (15)
C(7)	1622 (4)	1307 (3)	2479 (2)	3·36 (11)
C(16)	−329 (5)	655 (4)	947 (3)	4·23 (14)
C(14)	2249 (5)	−604 (3)	1597 (3)	3·79 (13)
C(18)	171 (5)	2097 (4)	−6 (3)	4·75 (15)
O(2)	1799 (4)	−1284 (3)	1832 (2)	5·58 (11)
O(6)	−270 (4)	2247 (4)	−538 (2)	6·99 (15)
F(1)	4040 (3)	941 (3)	2812 (2)	5·80 (10)
F(5)	−887 (3)	1655 (3)	2292 (2)	6·38 (11)
F(4)	−1483 (4)	1119 (3)	3510 (2)	7·62 (13)
C(8)	2629 (5)	974 (4)	2963 (3)	4·26 (13)
F(2)	3344 (4)	351 (3)	4032 (2)	7·43 (13)
F(3)	600 (5)	438 (4)	4397 (2)	8·33 (15)
O(5)	−1436 (5)	3324 (3)	1334 (3)	7·06 (15)
O(7)	1232 (5)	4142 (4)	2616 (3)	7·00 (14)
O(1)	6040 (4)	357 (4)	1757 (3)	6·72 (14)
C(11)	−116 (6)	1064 (4)	3337 (3)	5·07 (16)
C(12)	219 (5)	1366 (3)	2696 (2)	3·86 (12)
C(19)	1813 (5)	3715 (4)	2227 (3)	4·61 (14)
C(9)	2307 (6)	680 (4)	3599 (3)	5·08 (16)
C(10)	919 (8)	723 (4)	3783 (3)	5·42 (17)
C(13)	4891 (5)	419 (4)	1560 (3)	4·32 (13)
C(17)	−589 (5)	2773 (4)	1183 (3)	5·14 (16)
O(3)	3510 (4)	−580 (3)	−87 (2)	4·86 (11)
O(4)	−1003 (4)	−26 (3)	980 (3)	6·33 (10)
O(9)	3196 (6)	4803 (3)	698 (3)	7·65 (16)
C(21)	3056 (5)	4131 (4)	1015 (3)	4·45 (14)
O(20)	5695 (5)	3072 (5)	2299 (3)	9·19 (20)
C(20)	4605 (6)	3047 (4)	2037 (3)	4·99 (15)

Table 2. *Bond distances* (Å) *and angles* (°) *involving* Ru *atoms only, with e.s.d.'s in parentheses*

Ru(2)—Ru(1)	2·659 (1)	C(16)—Ru(2)	1·921 (5)
N(1)—Ru(1)	2·039 (3)	C(18)—Ru(2)	1·913 (6)
N(2)—Ru(1)	2·089 (3)	C(17)—Cu(2)	1·911 (5)
C(15)—Ru(1)	1·914 (4)	N(1)—Ru(3)	2·048 (3)
C(14)—Ru(1)	1·941 (5)	N(2)—Ru(3)	2·075 (3)
C(13)—Ru(1)	1·921 (5)	C(19)—Ru(3)	1·931 (5)
Ru(3)—Ru(2)	2·656 (1)	C(21)—Ru(3)	1·939 (6)
N(1)—Ru(2)	2·152 (3)	C(20)—Ru(3)	1·913 (6)
N(2)—Ru(2)	2·134 (3)		

N(1)—Ru(1)—Ru(2)	52·5 (1)	N(1)—Ru(3)—Ru(2)	52·5 (1)
N(2)—Ru(1)—Ru(2)	51·7 (1)	N(2)—Ru(3)—Ru(2)	51·9 (1)
N(2)—Ru(1)—N(1)	71·5 (1)	N(2)—Ru(3)—N(1)	71·6 (1)
C(15)—Ru(1)—Ru(2)	109·1 (1)	C(19)—Ru(3)—Ru(2)	107·5 (1)
C(15)—Ru(1)—N(1)	98·4 (2)	C(19)—Ru(3)—N(1)	160·1 (2)
C(15)—Ru(1)—N(2)	160·8 (1)	C(19)—Ru(3)—N(2)	96·5 (2)
C(14)—Ru(1)—Ru(2)	109·7 (1)	C(21)—Ru(3)—Ru(2)	107·4 (2)
C(14)—Ru(1)—N(1)	162·0 (2)	C(21)—Ru(3)—N(1)	94·3 (2)
C(14)—Ru(1)—N(2)	95·5 (2)	C(21)—Ru(3)—N(2)	159·2 (2)
C(14)—Ru(1)—C(15)	90·2 (2)	C(21)—Ru(3)—C(19)	92·1 (2)
C(13)—Ru(1)—Ru(2)	146·8 (2)	C(20)—Ru(3)—Ru(2)	148·4 (2)
C(13)—Ru(1)—N(1)	101·2 (2)	C(20)—Ru(3)—N(1)	104·8 (2)
C(13)—Ru(1)—N(2)	104·7 (2)	C(20)—Ru(3)—N(2)	103·5 (2)
C(13)—Ru(1)—C(15)	93·2 (2)	C(20)—Ru(3)—C(19)	93·4 (2)
C(13)—Ru(1)—C(14)	94·1 (2)	C(20)—Ru(3)—C(21)	94·8 (2)
Ru(3)—Ru(2)—Ru(1)	76·3 (1)	Ru(2)—N(1)—Ru(1)	78·7 (1)
N(1)—Ru(2)—Ru(1)	48·8 (1)	Ru(3)—N(1)—Ru(1)	107·0 (2)
N(1)—Ru(2)—Ru(3)	49·1 (1)	Ru(3)—N(1)—Ru(2)	78·4 (1)
N(2)—Ru(2)—Ru(1)	50·2 (1)	C(1)—N(1)—Ru(1)	122·9 (2)
N(2)—Ru(2)—Ru(3)	49·9 (1)	C(1)—N(1)—Ru(2)	130·5 (3)
N(2)—Ru(2)—N(1)	68·5 (1)	C(1)—N(1)—Ru(3)	124·6 (2)
C(16)—Ru(2)—Ru(1)	83·0 (1)	Ru(2)—N(2)—Ru(1)	78·1 (1)
C(16)—Ru(2)—Ru(3)	145·0 (2)	Ru(3)—N(2)—Ru(1)	104·2 (1)
C(16)—Ru(2)—N(1)	128·9 (2)	Ru(3)—N(2)—Ru(2)	78·2 (1)
C(16)—Ru(2)—N(2)	95·3 (2)	C(7)—N(2)—Ru(1)	122·9 (3)
C(18)—Ru(2)—Ru(1)	120·3 (2)	C(7)—N(2)—Ru(2)	133·2 (3)
C(18)—Ru(2)—Ru(3)	122·3 (2)	C(7)—N(2)—Ru(3)	125·6 (3)
C(18)—Ru(2)—N(1)	98·0 (2)	O(3)—C(15)—Ru(1)	177·5 (3)
C(18)—Ru(2)—N(2)	166·5 (2)	O(4)—C(16)—Ru(2)	178·7 (5)
C(18)—Ru(2)—C(16)	92·5 (2)	O(2)—C(14)—Ru(1)	178·2 (4)
C(17)—Ru(2)—Ru(1)	151·4 (2)	O(6)—C(18)—Ru(2)	176·9 (5)
C(17)—Ru(2)—Ru(3)	87·2 (2)	O(7)—C(19)—Ru(3)	178·6 (5)
C(17)—Ru(2)—N(1)	131·5 (2)	O(1)—C(13)—Ru(1)	176·2 (5)
C(17)—Ru(2)—N(2)	101·4 (2)	O(5)—C(17)—Ru(2)	178·6 (5)
C(17)—Ru(2)—C(16)	98·5 (2)	O(9)—C(21)—Ru(3)	178·9 (5)
C(17)—Ru(2)—C(18)	88·3 (2)	O(20)—C(20)—Ru(3)	177·3 (6)

angles involving the Ru atoms are listed in Table 2. Fig. 1 shows a perspective view of the molecule. The structure of complex (3) is shown in Fig. 1. The molecular geometry for (3) is essentially the same as that found for (1) and (2). One of the three Ru—Ru bonds present in $Ru_3(CO)_{12}$ has been broken on replacement of three CO groups by two NAr ligands. This is in agreement with the formulation that the CO ligand is a two-electron donor while its NAr ligand is a four-electron donor ligand. The Ru(1)···Ru(3) separation of 3·285 (1) Å is similar to complexes (1) and (2) [3·290 (1)–3·291 (1) Å].

However, there are some differences between the structures of (3) and (1) and (2) based on their bond lengths and angles. One very interesting feature in this complex is that the asymmetry in the Ru(1)—Ru(2) [2·710 (1) for (1), 2·702 (1) for (2), 2·659 (1) Å for (3)] and Ru(2)—Ru(3) [2·626 (1) for (1), 2·615 (1) for (2), 2·656 (1) Å for (3)] bonds in both (1) and (2) are not found in complex (3). As expected, the presence of five fluorine atoms on one of the phenyl groups in (3) does exert a significant influence on the structure.

It has been suggested (Clegg, Sheldrick, Stalke, Bhaduri & Gopalkrishnan, 1984) that the relative disposition of the ligands is responsible for the

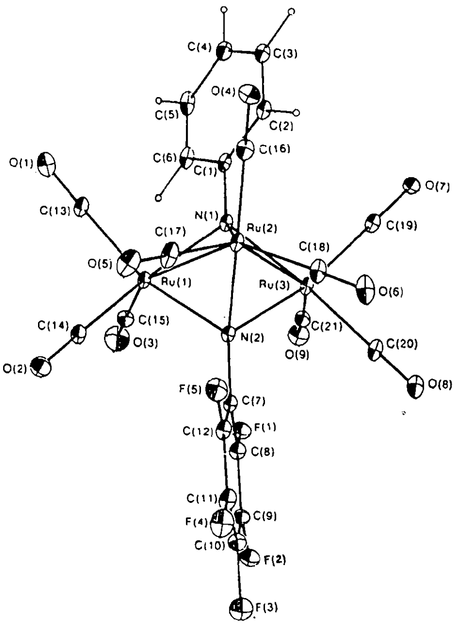

Fig. 1. A perspective view of the molecule.

disparate Ru—Ru distances. This has been further explained (Bruce *et al.*, 1987) in terms of a 'semi-bridging' carbonyl that leads to a weak Ru–CO interaction and which contributes to the minor asymmetry observed in the Ru—Ru bonds. For compounds (1) and (2) there is an asymmetrical arrangement of the three CO ligands on the central Ru atom, Ru(2) in Fig. 1, relative to the other two Ru atoms and the 'semi-bridging' carbonyl thereby invoked corresponds to one of these three CO ligands. In these compounds the phenyl rings lie essentially perpendicularly to the plane of the three metal atoms and almost parallel to one another and the bond equivalent to Ru(1)–Ru(2). In the present compound the phenyl rings are significantly non-parallel, and the fluorinated ring is twisted (presumably because of steric factors) almost perpendicularly to the Ru(1)–Ru(3) direction; the dihedral angle between the two phenyl ring planes is 36·8 (1)°. In turn this disposition of the ligands causes the arrangement of the CO groups on the central Ru atom to be far more symmetric with respect to the remaining Ru atoms; the Ru—C—O ligands are also more linear with the smallest angle being 176·2 (5)°. These alterations of the relative orientations of the ligands are consistent with the symmetry observed in the Ru—Ru bond lengths.

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Structure du Bis(2-propanol)-bis-μ-(2-propanolato)-hexakis(2-propanolato)-dicérium(IV)

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Abstract. $[Ce_2(C_3H_7O)_8(C_3H_8O)_2]$, $M_r = 873{\cdot}1$, triclinic, $P\bar{1}$, $a = 10{\cdot}001\ (2)$, $b = 11{\cdot}032\ (2)$, $c = 12{\cdot}154\ (4)$ Å, $\alpha = 67{\cdot}99\ (2)$, $\beta = 69{\cdot}03\ (2)$, $\gamma = 71{\cdot}79\ (1)$°, $V = 1136\ (1)$ Å^3, $Z = 1$, $D_x = 1{\cdot}28$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71069$ Å, $\mu = 2{\cdot}01$ mm^{-1}, $F(000) = 450$, $T = 293$ K, final $R = 0{\cdot}046$ for 2239 unique observed reflections with $I \geq 3\sigma(I)$. The structure contains one discrete dimeric molecule. Each Ce atom is octahedrally coordinated by one isopropyl alcohol and five isopropoxy groups, two of which are bridging between the Ce atoms. The following mean distances have been obtained: Ce–Ce = 3·743, four Ce—O = 2·32 and two Ce—O = 2·04 Å. The two latter distances correspond to in-plane terminal isopropoxy groups.

Introduction. Les alcoxydes métalliques $M(OR)_n$ (M = Si, Ti, Zr, Y,...) (OR = OEt, OPr^i, OPr^n...) sont des précurseurs très utilisés dans la chimie du procédé sol–gel (Klein, 1988). Ce procédé met en jeu des réactions d'hydrolyse et de condensation qui conduisent à la formation d'un réseau d'oxyde macromoléculaire. Selon la taille et la concentration des macromolécules, des sols ou des gels peuvent être obtenus.

Le séchage et la calcination de ces solutions colloïdales permet d'obtenir des céramiques de haute pureté sous des formes très diverses (films, fibres,

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* L'auteur auquel toute correspondance doit être adressée.

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