average of 4·4° from the expected value of 120°. These distortions are similar to those observed in 5-anilino-pentadienylidenanilinium bromide (Brandl, Springer, Narayanan, Preuss, Hoppe & Scheibe, 1974) and are caused by repulsions between hydrogen atoms in the chain [Table 3(*b*)].

The geometry of the portion of the molecule involving the piperidine ring is closely similar to that found in 1-[*p*-(1-oxyminoethyl)phenoxyacetyl]piperidine (Tranqui, Cromer & Boucherle, 1974). The short C(14)–N(16) distance, 1·349 (4) Å, and the small displacement of the N(16) atom, 0·095 Å, out of the plane defined by the atoms C(14), C(17) and C(21) indicate the partial double-bond character of this linkage. The piperidine ring adopts the chair conformation with N(16) and C(19) displaced by −0·644 and 0·611 Å respectively out of the plane defined by the atoms C(17), C(18), C(20) and C(21). The basal plane of the chair makes a dihedral angle of 66·1° with respect to the pentadiene chain.

Fig. 3 is a stereo view of the unit cell contents looking along the *b* axis. The molecules lie approximately in planes parallel to (20$\bar{3}$). There are no intermolecular separations significantly less than the sum of the respective van der Waals radii.

References

BRANDL, F., SPRINGER, H. J., NARAYANAN, P., PREUSS, J., HOPPE, W. & SCHEIBE, G. (1974). *J. Cryst. Mol. Struct.* **4**, No. 6, 391–402.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.

KARLE, J. & KARLE, I. L. (1965). *Computing Methods in Crystallography*, edited by J. S. ROLLETT, Ch. 17, pp. 151–153. Oxford: Pergamon Press.

TRANQUI, D., CROMER, D. T. & BOUCHERLE, A. (1974). *Acta Cryst.* B**30**, 2237–2240.

The Crystal Structure of Tetraphenylarsonium Nitridotetrachlororuthenate(VI): a Square-Pyramidal Ruthenium Complex

BY FREDERICK L. PHILLIPS* AND ANDRZEJ C. SKAPSKI

Chemical Crystallography Laboratory, Imperial College, London SW7 2AY, England

(Ph₄As) [RuNCl₄] is tetragonal with $a = 12·607$ (3), $c = 7·842$ (2) Å, space group $P4/n$, $Z = 2$. The structure has been determined from diffractometer data, and least-squares refinement with 1188 independent reflexions has reached $R = 0·037$. In the square-pyramidal [RuNCl₄]⁻ anion the Ru and N atoms lie on a fourfold axis, with Ru–N and Ru–Cl 1·570 and 2·310 Å respectively. Electronic repulsion by the nitrido ligand is responsible for the large N–Ru–Cl angles of 104·6°. The cation has $\bar{4}$ (S_4) crystallographic symmetry, with As–C 1·909 Å and two independent C–As–C angles of 104·9 and 111·8°.

Introduction

Complexes containing a terminal nitrido ligand have highly distorted coordinations. The reasons for this may be steric or electronic. We have recently determined the structure of (Ph₄As) [OsNCl₄] (Fletcher, Griffith, Pawson, Phillips & Skapski, 1973; Phillips & Skapski, 1975), and the geometry found for the anion indicates that in this complex the electronic repulsion by the strongly π-donating nitrido ligand is the predominant factor.

We now report details of the analogous Ru complex.

* Present address: Department of Chemistry, University of Ghana, Legon, Ghana.

Experimental

Tetraphenylarsonium nitridotetrachlororuthenate(VI) was obtained as puce prisms by crystallization from methyl cyanide (Griffith & Pawson, 1973). Preliminary photographs showed the crystal to be tetragonal, with systematic absences $hk0$: $h + k = 2n + 1$ which uniquely determine space group $P4/n$ (No. 85). The distribution of intensities showed the compound to be isostructural with (Ph₄As) [OsNCl₄].

Measurement of some high-angle α_1 and α_2 reflexions on a diffractometer gave $a = 12·607(3)$, $c = 7·842(2)$ Å, $U = 1246·4$ Å³, $D_o = 1·70$ (by flotation), $D_c = 1·706$ g cm⁻³ for $Z = 2$ and a molecular formula C₂₄H₂₀AsCl₄NRu; M.W. 640·24, $F(000) = 632$.

Intensities were measured, to $\theta = 70°$, on a Siemens off-line automatic four-circle diffractometer. A crystal of approximate dimensions $0.34 \times 0.44 \times 0.19$ mm was mounted with **a** parallel to the φ axis of the diffractometer, and a 'five-value' measuring procedure was employed (Allen, Rogers & Troughton, 1971). Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) at a take-off angle of $3.0°$, Ni filter and Na(Tl)I scintillation counter were used. 1194 independent reflexions were measured, of which 28 were judged to be 'unobserved' as the net count of each was less than 2.58σ. The $05\bar{6}$ reflexion was monitored as a reference every 50 reflexions, and its net count did not alter significantly during data collection (*ca* 2 days). The intensities were scaled by use of the reference reflection, and Lorentz and polarization corrections applied.

Solution and refinement of the structure

An updated version of July 1970 of the X-RAY 63 system (Stewart, 1964) was used for the solution and refinement of the structure. The calculations were carried out on the University of London CDC 7600 computer with the full-matrix *ORFLS* program. Structural illustrations were drawn with the aid of the Imperial College CDC 6400.

Atomic coordinates from the structure of (Ph₄As) [OsNCl₄] could not be used initially as a different choice of axes had been made in data collection. Indices were therefore transformed to be consistent with those of the isostructural Os compound, and isotropic least-squares refinement of the non-hydrogen atoms gave $R = 0.131$. Application of an absorption correction [μ(Cu $K\alpha$) = 109·8 cm^{-1}] according to the method of Busing & Levy (1957), with a $10 \times 10 \times 10$ grid and crystal path lengths determined by the vector analysis procedure of Coppens, Leiserowitz & Rabinovich (1965), and refinement as previously reduced R to 0·107. Anisotropic refinement gave $R = 0.046$.

The five independent H atoms were located from a difference synthesis, and their inclusion as a fixed-atom contribution, with isotropic temperature factors of the parent C atoms, gave $R = 0.040$. Introduction of a weighting scheme, and the removal of six strong low-angle reflexions most affected by extinction, re-

duced R to its final value of 0.037. The largest remaining feature on the final difference synthesis was a region of electron density of up to 0.6 e Å^{-3} approximately midway along the Ru≡N bond.

The weighting scheme used was that suggested by Hughes (1941), where $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geq F^*$, with $F^* = 38$ as the final value. Scattering factors were from Cromer & Waber (1965), and for H from Stewart, Davidson & Simpson (1965). Anomalous dispersion corrections for Ru, As and Cl were those given by Cromer (1965).

Atomic coordinates† are given in Table 1, while Table 2 lists the coefficients in the expression for the anisotropic temperature factor $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ and the root-mean-square amplitudes of vibration along the principal axes of the thermal ellipsoids.‡

---

† Coordinates are in terms of an alternative unit cell in space group $P4/n$ with origin on $\bar{1}$ at $\frac{1}{4},\frac{1}{4},0$ from $\bar{4}$.

‡ A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31099 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic coordinates with estimated standard deviations in parentheses*

The hydrogen atom positions are unrefined, and these atoms have the same numbers as the parent carbon atoms.

	x	y	z
Ru(1)	$\frac{1}{4}$	$\frac{1}{4}$	0·11828 (8)
N(1)	$\frac{1}{4}$	$\frac{1}{4}$	−0·0819 (9)
Cl(1)	0·33873 (12)	0·09649 (11)	0·19242 (17)
As(1)	$\frac{1}{4}$	$\frac{3}{4}$	0
C(1)	0·3692 (3)	0·7646 (3)	0·1483 (5)
C(2)	0·4461 (3)	0·8419 (4)	0·1172 (6)
C(3)	0·5266 (4)	0·8542 (4)	0·2318 (7)
C(4)	0·5321 (4)	0·7924 (5)	0·3751 (6)
C(5)	0·4574 (4)	0·7127 (4)	0·4035 (6)
C(6)	0·3753 (3)	0·6990 (4)	0·2900 (5)
H(2)	0·447	0·895	0·008
H(3)	0·578	0·920	0·217
H(4)	0·584	0·795	0·469
H(5)	0·472	0·661	0·513
H(6)	0·316	0·645	0·302

Table 2. *Anisotropic thermal parameters* (Ru, As, Cl × 10⁵; N, C × 10⁴) *and root-mean-square amplitudes of vibration* (Å)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Min.	Inter.	Max.
Ru(1)	697 (7)	697 (7)	1044 (11)	0	0	0	0·180	0·237	0·237
N(1)	74 (6)	74 (6)	149 (12)	0	0	0	0·216	0·245	0·245
Cl(1)	1168 (12)	905 (10)	2137 (24)	212 (8)	97 (13)	377 (12)	0·222	0·276	0·329
As(1)	496 (7)	496 (7)	966 (13)	0	0	0	0·173	0·200	0·200
C(1)	49 (2)	65 (3)	122 (6)	6 (2)	−6 (3)	−12 (3)	0·187	0·196	0·237
C(2)	63 (3)	70 (3)	190 (8)	−6 (2)	−13 (4)	−10 (4)	0·209	0·243	0·253
C(3)	74 (3)	87 (4)	260 (11)	−5 (3)	−31 (5)	−20 (5)	0·217	0·266	0·303
C(4)	72 (3)	116 (5)	189 (9)	19 (3)	−39 (5)	−39 (5)	0·197	0·244	0·334
C(5)	75 (3)	107 (4)	147 (7)	29 (3)	−16 (4)	3 (5)	0·196	0·231	0·316
C(6)	60 (3)	84 (3)	151 (7)	9 (2)	2 (4)	11 (4)	0·213	0·216	0·267

Description of the structure and discussion

Fig. 1 shows the two ionic species present in the crystal structure, together with the thermal vibration ellipsoids (Johnson, 1965) of the non-hydrogen atoms. The more important interatomic distances and bond angles are given in Table 3.
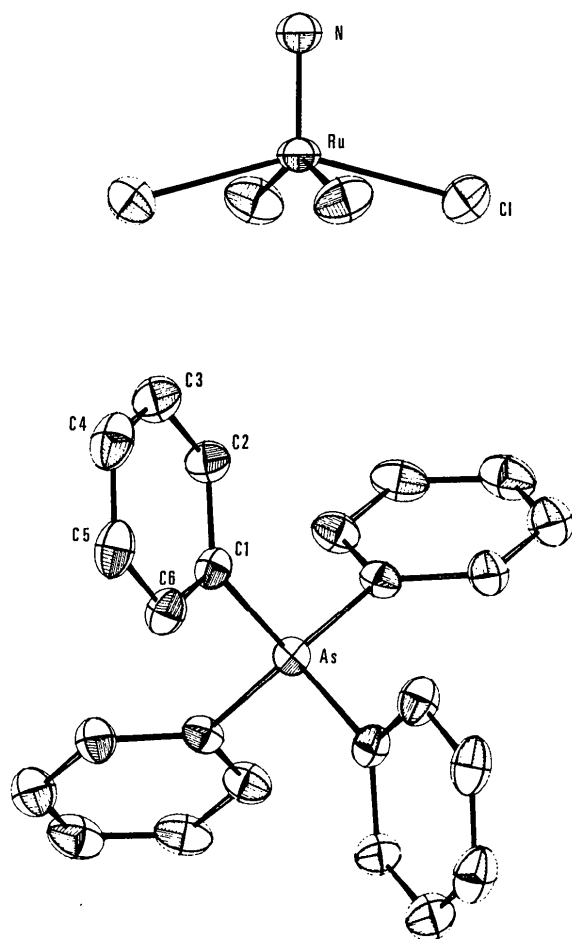

Fig. 1. The [RuNCl₄]⁻ and (Ph₄As)⁺ ions. Thermal vibration ellipsoids are scaled to enclose 30% probability.

Table 3. *Interatomic distances* (Å) *and bond angles* (°) *with estimated standard deviations in parentheses*

Superscripts refer to atoms in the following positions:

(I)	$y,\frac{1}{2}-x,z$	(III)	$\frac{1}{2}-x,1\frac{1}{2}-y,z$
(II)	$\frac{1}{2}-x,\frac{1}{2}-y,z$	(IV)	$1-y,x-\frac{1}{2},-z$

(*a*) [RuNCl₄]⁻ anion

Ru(1)–N(1)	1·570 (7)	Ru(1)–Cl(1)	2·310 (1)
N(1)—Ru(1)–Cl(1)	104·58 (4)	Cl(1) –Ru(1)–Cl(1ᴵ)	86·37 (5)
Cl(1) –Ru(1)–Cl(1ᴵᴵ)	150·84 (6)		
N(1)···Cl(1)	3·102 (5)	Cl(1)···Cl(1ᴵ)	3·161 (3)

(*b*) (Ph₄As)⁺ cation

As(1)–C(1)	1·909 (4)	C(4)–C(5)	1·395 (8)
C(1)—C(2)	1·396 (6)	C(5)–C(6)	1·376 (6)
C(2)—C(3)	1·365 (7)	C(6)–C(1)	1·387 (6)
C(3)—C(4)	1·369 (8)	Mean C–C	1·381
C(1)—As(1)–C(1ᴵᴵᴵ)	104·9 (2)	C(1)–As(1)–C(1ᴵⱽ)	111·8 (2)
As(1)–C(1)—C(2)	120·5 (3)	C(2)–C(3)—C(4)	120·9 (5)
As(1)–C(1)—C(6)	118·3 (3)	C(3)–C(4)—C(5)	120·4 (5)
C(2)—C(1)—C(6)	121·2 (4)	C(4)–C(5)—C(6)	119·7 (4)
C(1)—C(2)—C(3)	118·7 (4)	C(5)–C(6)—C(1)	119·0 (4)

In the anion both the Ru and N atoms lie on a fourfold rotation axis. The metal atom therefore has a square-pyramidal coordination with the four Cl atoms constituting the base of the pyramid, and the point symmetry of the anion is 4*mm* (C_{4v}).

Hitherto the only nitrido complexes of Ru for which structural information existed have been binuclear species with a bridging N atom: in the centrosymmetric [Ru₂NCl₈]³⁻ ion the observed Ru–N distances are 1·720 Å in the K⁺ salt (Ciechanowicz & Skapski, 1969, 1971) and 1·725 Å in the NH₄⁺ salt (Gee & Powell, 1971). Therefore there are no Ru–N (terminal) distances to compare with that of 1·570(7) Å found here. This triple bond may be slightly shorter than the equivalent one of 1·604(10) Å in [OsNCl₄]⁻ (Phillips & Skapski, 1975); the difference between the two bond lengths is on the border line of significance.

The Ru–Cl bond lengths of 2·310 Å are identical with the corresponding ones in [OsNCl₄]⁻. Somewhat longer Ru–Cl distances (mean 2·388 Å) are found in the square-pyramidal complex RuCl₂(PPh₃)₃ (La Placa & Ibers, 1965), but as the latter is a d^6 complex as

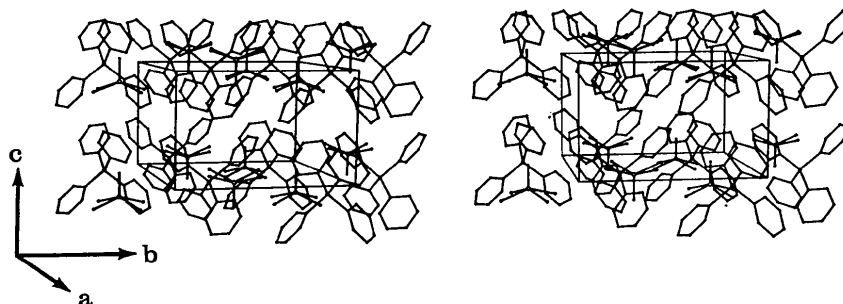Fig. 2. Packing of the (Ph₄As)⁺ and [RuNCl₄]⁻ ions.

against d^2 in the present case the two are not strictly comparable.

The strong π-donating ability of the N atom, and the resulting Ru≡N triple bond, leads to a depression of the Cl atoms so that the basal plane is 0·58 Å below the Ru atom (Table 4) and the N–Ru–Cl angles are 104·6° (104·5° in [OsNCl₄]⁻). This electronic effect brings the Cl atoms closer together until it is counterbalanced by the Cl(basal)···Cl(basal) interactions. A more detailed discussion has been given for [OsNCl₄]⁻ (Phillips & Skapski, 1975).

Table 4. *Planarity of groups of atoms in the structure and distances from least-squares planes*

The equations of the planes are expressed as $Px + Qy + Rz = S$ in direct space. Superscripts have the same meaning as in Table 3, in addition: (V) $\frac{1}{2} - y, x, z$.

P	Q	R	S	Deviation (Å) of atoms from plane
−6·97	8·29	4·01	4·35	C(1) 0·013, C(2) −0·007, C(3) −0·008, C(4) 0·016, C(5) −0·010, C(6) −0·005
				Not defining plane: As(1) 0·128
0	0	7·84	1·51	Cl(1), Cl(1ᴵ), Cl(1ᴵᴵ), Cl(1ᴵⱽ), all zero by symmetry.
				Not defining plane: Ru(1) −0·581, N(1) −2·151

In the cation the As atom lies on a fourfold rotation-inversion axis, and the As–C distances of 1·909 Å are unexceptional. Its tetrahedral geometry is distorted, with four C–As–C angles of 111·8° and two of 104·9°. This slight elongation of the tetrahedron may be caused by weak repulsion between the nitrido ligand and the phenyl rings. This can be seen in the stereoscopic diagram (Johnson, 1965) in Fig. 2 showing the packing of the ionic species. The shortest interionic non-bonded distance of 3·32 Å is N(1)···C(3ⱽᴵ) [(VI) $x - \frac{1}{2}, y - \frac{1}{2}, -z$].

Table 4 also gives details of the planarity of the phenyl rings. The As atom lies 0·13 Å out of these planes.

References

ALLEN, F. H., ROGERS, D. & TROUGHTON, P. G. H. (1971). *Acta Cryst.* B27, 1325–1337.
BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* 10, 180–182.
CIECHANOWICZ, M. & SKAPSKI, A. C. (1969). *Chem. Commun.* pp. 574–575.
CIECHANOWICZ, M. & SKAPSKI, A. C. (1971). *J. Chem. Soc. (A)*, pp. 1792–1794.
COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* 18, 1035–1038.
CROMER, D. T. (1965). *Acta Cryst.* 18, 17–23.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* 18, 104–109.
FLETCHER, S. R., GRIFFITH, W. P., PAWSON, D., PHILLIPS, F. L. & SKAPSKI, A. C. (1973). *Inorg. Nucl. Chem. Lett.* 9, 1117–1120.
GEE, R. J. D. & POWELL, H. M. (1971). *J. Chem. Soc. (A)*, pp. 1795–1797.
GRIFFITH, W. P. & PAWSON, D. (1973). *J. Chem. Soc. Dalton*, pp. 1315–1320.
HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* 63, 1737–1752.
JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
LA PLACA, S. J. & IBERS, J. A. (1965). *Inorg. Chem.* 4, 778–783.
PHILLIPS, F. L. & SKAPSKI, A. C. (1975). *J. Cryst. Mol. Struct.* 5, 83–92.
STEWART, J. M. (1964). Univ. of Maryland Technical Report TR-64-6.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.