Synthesis and Crystal Structure of Tetracarbonyl(triphenylstibine)-ruthenium

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Irradiation of $[Ru_3(CO)_{12}]$ in hexane in the presence of $SbPh_3$ gives the title complex as the major product. *X*-Ray diffraction has shown that the environment around the ruthenium atom is distorted trigonal bipyramidal in which the $SbPh_3$ occupies an equatorial site. The angle (C–Ru–C) between the equatorial carbonyl groups is 137° and that (C–Ru–C) between the axial carbonyl groups is 173°. This geometry represents an intermediate configuration in the dynamic rearrangement path between trigonal-bipyramidal and square-pyramidal co-ordination. The crystals are triclinic. The unit cell chosen has space group $B1$ with $a = 14.02$, $b = 10.42$, $c = 17.49$ Å, $\alpha = 121.0$, $\beta = 89.2$, $\gamma = 81.7°$, and $Z = 4$. The structure has been refined by least squares to R 0.036 for 4 157 counter amplitudes.

THE structures of a number of $[Fe(CO)_4L]$ complexes ($L = PPh_2H$, $AsMe_3$, $SbPh_3$, *etc.*) have been determined by *X*-ray diffraction.[1-4] In all these cases the structures are trigonal bipyramids in which the ligand (L) occupies an axial position. A similar assignment of structure can be made for other $[Fe(CO)_4L]$ complexes on the basis of their i.r. spectra.[5,6] Only one $[Ru(CO)_4L]$ complex has been made ($L = PPh_3$) and it is clear from the i.r. data quoted,[7,8] and our own, that it is a trigonal bipyramid with triphenylphosphine occupying an axial site. The structure of $[Os(CO)_4(PPh_3)]$ can be similarly assigned on the basis of its i.r. spectrum.[8]

In our photochemical studies on $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ we have used Group 5B ligands to trap intermediate fragments.[9] From the reaction between triphenylstibine and $[Ru_3(CO)_{12}]$ we have isolated as the major product tetracarbonyl(triphenylstibine)ruthenium. Its i.r. spectrum indicated that the ligand (L) could not be axial in a trigonal bipyramid, but it was compatible with it being equatorial. The *X*-ray analysis now described shows this to be the case. We have thus made and determined the structure of the first trigonal-bipyramidal $[M(CO)_4L]$ complex in which the ligand (L = Group 5B ligand) occupies an equatorial site.†

EXPERIMENTAL

Preparation of Tetracarbonyl(triphenylstibine)ruthenium.—A mixture of $[Ru_3(CO)_{12}]$ (0.19 g, 3×10^{-4} mol) and triphenylstibine (0.32 g, 9×10^{-4} mol) in pure deoxygenated n-hexane (150 cm³) under an atmosphere of oxygen-free nitrogen was irradiated with a tungsten–halogen lamp at 25 °C and $\lambda > 390$ nm using 1 mol dm^{-3} sodium nitrite as a filter. When the reaction was complete (4 h) the solution was filtered and the filtrate evaporated. The residue was chromatographed on alumina (200 mesh). Elution with n-hexane (under nitrogen) gave, on evaporation of the solvent, small yellow needles {0.113 g, 22% based on $[Ru_3(CO)_{12}]$} of tetracarbonyl(triphenylstibine)ruthenium, m.p. 91—92 °C (Found: C, 47.2; H, 3.0%; *m/e* 567. $C_{22}H_{15}O_4RuSb$ requires C, 46.7; H, 2.7%; *m/e* 567); $\nu_{max.}$ (in hexane) at 2 097w, 2 076s, 2 059m, 2 029w, 1 997vs, 1 988s, 1 971vs, and 1 936w cm^{-1}. Crystals suitable for *X*-ray analysis were obtained by careful evaporation of n-hexane solutions.

Crystallographic Measurements.—After initial examination by oscillation, precession, and Weissenberg photographs, final cell dimensions and intensity data were measured with a Stoe two-circle computer-controlled diffractometer using graphite-monochromated Mo-K_α radiation. The crystal ($0.6 \times 0.4 \times 0.2$ mm) was mounted inside a Pantak capillary tube and aligned about the crystallographic *x* axis. The ω-scan technique was employed with a stepping interval of 0.02° and a step time of 1 s. Backgrounds were measured for 10 s at each end of the scan. The intensities of three $0kl$ reflections were remeasured after each layer of data collection to monitor the stability of the system. There was no systematic variation of intensity with time. Of 5 498 reflections scanned within the range $0.1 < (\sin \theta)/\lambda < 0.65$ Å^{-1}, 4 157 for which $I > 2.5\sigma(I)$ were considered to be observed and were used in the analysis. Intensities were converted into structure amplitudes by use of the appropriate conversion factors, but absorption corrections were not applied.

Crystal data. $C_{22}H_{15}O_4RuSb$, $M = 566.2$, Triclinic, $a = 14.02(1)$, $b = 10.42(1)$, $c = 17.49(1)$ Å, $\alpha = 121.0(1)$, $\beta = 89.2(1)$, $\gamma = 81.7(1)°$. $U = 2\,155.3$ Å³, $Z = 4$, $D_c = 1.745$ g cm^{-3}, $F(000) = 1\,096$, systematic absences hkl with $h + l$ odd, space group $B1$ or $B\bar{1}$ [$B\bar{1}(C_i^1)$ established as a result of this analysis],† λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 18.1 cm^{-1}.

Structure determination. The positions of the ruthenium and antimony atoms were determined by direct methods using SHELX.[11] The electron-density map phased on the heavy-atom positions then revealed the positions of all the non-hydrogen atoms. Least-squares refinement, first with isotropic and then with anisotropic temperature factors, resulted in an R value of 0.040. At this stage hydrogen atoms were placed in their theoretical positions and were included in the least-squares calculations without, however, refining their parameters. The refinement process was terminated when all calculated shifts were $<0.1\sigma$ and R 0.036 for the 4 157 observed amplitudes. Complex neutral-atom scattering factors [11] were employed. The final atomic co-ordinates are listed in Table 1. Anisotropic thermal parameters, observed and calculated structure factors, the results of mean-plane calculations, and full lists of bond lengths and angles are available as Supplementary Publication No. SUP 22462 (30 pp.).‡

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† Complexes $[Fe(CO)_4L]$ in which the ligand is an alkene are essentially trigonal bipyramids where the alkene occupies an equatorial site.[10]

† Equivalent positions for this non-standard unit cell are $(0,0,0;\ \frac{1}{2},0,\frac{1}{2}) \pm (x,y,z)$. An equivalent primitive unit cell has dimensions $a = 11.13$, $b = 10.42$, $c = 11.28$ Å, $\alpha = 108.0$, $\beta = 102.55$, and $\gamma = 60.3°$.

‡ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

The weighting scheme employed in the final cycles of least-squares calculations was $w = 1/[\sigma^2(F) + 0.000\ 2|F|^2]$. Computations were carried out on the University of Birmingham ICL 1906A computer and on the CDC 7600 at the University of Manchester Regional Computer Centre.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$)

Atom	x	y	z
Sb	7 574.9(2)	−72.4(3)	−706.7(2)
Ru	7 044.7(2)	2 894.6(3)	256.3(2)
O(1)	4 920(4)	2 573(8)	−11(4)
O(2)	6 917(5)	4 659(6)	−721(4)
O(3)	9 088(3)	3 659(5)	606(3)
O(4)	6 710(4)	3 835(5)	2 223(3)
C(1)	5 701(5)	2 701(7)	99(4)
C(2)	6 970(5)	3 948(7)	−389(4)
C(3)	8 331(4)	3 345(5)	470(3)
C(4)	6 828(4)	3 448(6)	1 492(3)
C(5)	7 723(3)	−1 121(5)	67(3)
C(6)	8 486(3)	−2 281(5)	−111(3)
C(7)	8 577(4)	−2 871(6)	442(4)
C(8)	7 916(5)	−2 327(7)	1 167(4)
C(9)	7 145(5)	−1 193(7)	1 347(4)
C(10)	7 049(4)	−579(6)	813(3)
C(11)	8 929(3)	−1 119(4)	−1 521(2)
C(12)	9 767(3)	−562(5)	−1 191(3)
C(13)	10 657(4)	−1 285(6)	−1 704(3)
C(14)	10 721(4)	−2 556(5)	−2 541(3)
C(15)	9 887(4)	−3 099(5)	−2 885(3)
C(16)	8 992(3)	−2 403(5)	−2 381(3)
C(17)	6 640(3)	−1 408(4)	−1 637(3)
C(18)	6 147(4)	−896(5)	−2 129(3)
C(19)	5 549(5)	−1 772(7)	−2 751(4)
C(20)	5 447(4)	−3 146(7)	−2 871(4)
C(21)	5 927(5)	−3 651(6)	−2 378(4)
C(22)	6 534(4)	−2 804(5)	−1 763(3)
H(6)	9 012	−2 726	−684
H(7)	9 176	−3 768	298
H(8)	7 996	−2 784	1 598
H(9)	6 613	−784	1 911
H(10)	6 451	326	970
H(12)	9 727	441	−531
H(13)	11 305	−838	−1 440
H(14)	11 416	−3 131	−2 930
H(15)	9 933	−4 080	−3 555
H(16)	8 348	−2 852	−2 653
H(18)	6 222	194	−2 032
H(19)	5 167	−1 365	−3 138
H(20)	4 986	−3 830	−3 354
H(21)	5 835	−4 731	−2 470
H(22)	6 919	−3 229	−1 385

RESULTS AND DISCUSSION

The structure of the molecule is illustrated in Figure 1 which also shows the atom numbering. Selected molecular parameters are listed in Table 2. A view of the crystal structure along the b axis is shown in Figure 2. All intermolecular contact distances correspond to normal van der Waals interactions.

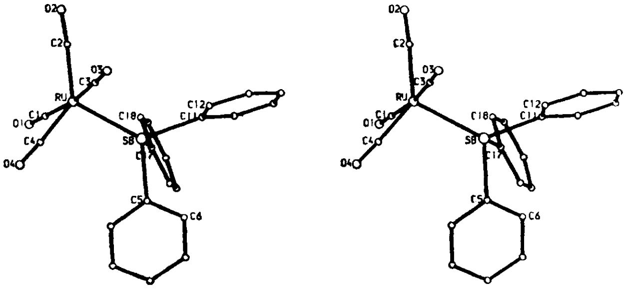


FIGURE 1 Stereoscopic view of the $[Ru(CO)_4(SbPh_3)]$ molecule

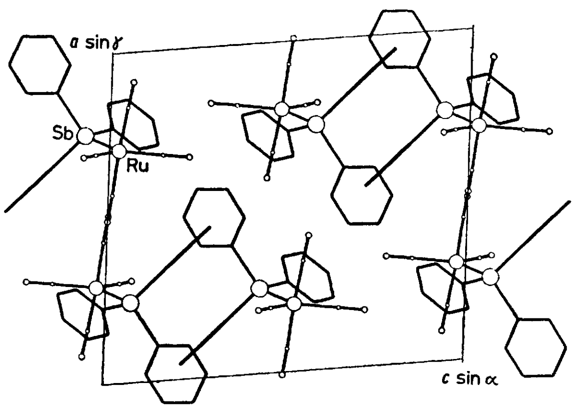


FIGURE 2 The contents of the unit cell projected along the b axis

The environment of the antimony atom is distorted tetrahedral. The C–Sb–C angles are compressed by *ca.* 10° to a mean value of 99.4° and the C–Sb–Ru are enlarged to a mean value of 118.2°. Similar, but somewhat smaller, distortions from tetrahedral geometry at antimony occur in $[Fe(CO)_4(SbMe_3)]$,[2] $[Fe(CO)_4(SbPh_3)]$,[3] $[Co(NO)(CO)_2(SbPh_3)]$,[12] and at the terminal antimony atom in $[(Ph_3Sb)(OC)_3PhFe(SbPh_2)Fe(CO)_4]$.[4] In each of these molecules the groups attached to antimony are bent away from the adjoining metal atom. This distortion is generally rationalised on the basis of the Sb–C bonds having enhanced p character, whilst the antimony–metal bond has enhanced s character.

The geometry around the ruthenium atom is more striking. It is distorted trigonal bipyramidal in which the $SbPh_3$ moiety surprisingly occupies an *equatorial* site. In the analogous Fe–Sb complexes [2,3] the iron likewise has trigonal-bipyramidal co-ordination but with the

TABLE 2

Selected molecular dimensions

(*a*) Bond lengths (Å)

Sb–Ru	2.623(0.4)	C(2)–O(2)	1.149(7)
Ru–C(1)	1.932(7)	C(3)–O(3)	1.148(7)
Ru–C(2)	1.933(7)	C(4)–O(4)	1.126(6)
Ru–C(3)	1.923(6)	Sb–C(5)	2.130(4)
Ru–C(4)	1.935(5)	Sb–C(11)	2.132(4)
C(1)–O(1)	1.130(8)	Sb–C(17)	2.135(4)

(*b*) Bond angles (°)

C(5)–Sb–Ru	113.8(1)	C(1)–Ru–C(2)	89.1(3)
C(11)–Sb–Ru	121.7(1)	C(1)–Ru–C(3)	173.1(2)
C(17)–Sb–Ru	119.0(1)	C(1)–Ru–C(4)	90.6(3)
C(5)–Sb–C(11)	98.7(2)	C(2)–Ru–C(3)	86.7(2)
C(5)–Sb–C(17)	99.7(2)	C(2)–Ru–C(4)	136.6(3)
C(11)–Sb–C(17)	99.9(2)	C(3)–Ru–C(4)	88.7(2)
C(1)–Ru–Sb	90.7(2)	O(1)–C(1)–Ru	178.7(6)
C(2)–Ru–Sb	116.5(2)	O(2)–C(2)–Ru	175.7(6)
C(3)–Ru–Sb	96.0(1)	O(3)–C(3)–Ru	177.9(5)
C(4)–Ru–Sb	106.9(2)	O(4)–C(4)–Ru	176.9(5)

(*c*) Torsion angles (°)

C(5)–Sb–Ru–C(1)	−94.3	C(11)–Sb–Ru–C(3)	−30.8
C(5)–Sb–Ru–C(3)	87.1	C(17)–Sb–Ru–C(1)	22.8
C(5)–Sb–Ru–C(4)	−3.5	C(17)–Sb–Ru–C(2)	−66.5
C(11)–Sb–Ru–C(2)	58.6		

$SbPh_3$ ligand in an *axial* position. Also in $[(Ph_3Sb)(OC)_3PhFe(SbPh_2)Fe(CO)_4]$, where the terminal iron atom has trigonal-bipyramidal co-ordination, the adjoining antimony atom occupies an axial position.

The i.r. spectrum (Figure 3) of $[Ru(CO)_4(SbPh_3)]$ differs from those of other $[M(CO)_4L]$ complexes and is compatible with the structure in which the triphenylstibine is bonded equatorially in a distorted trigonal bipyramid. Whereas the spectra of the related $[Fe(CO)_4(PPh_3)]$,[6] $[Fe(CO)_4(SbPh_3)]$,[6] and $[Ru(CO)_4(PPh_3)]$ [7] show three principal bands as required for C_{3v} symmetry, that of $[Ru(CO)_4(SbPh_3)]$ shows four principal bands (2 076, 1 997, 1 988, and 1 971 cm^{-1}) as required for C_{2v} symmetry.[5,8,13] Examples of trigonal-bipyramidal geometry around Ru^0 are rare, occurring, as far as we are aware, only in $[Ru(CO)_4(PPh_3)]$,[7,8] $[Ru(CO)_5]$,[14] $[Ru(NO)H(PPh_3)_3]$,[15] $[Ru(NO)(Ph_2PCH_2CH_2PPh_2)_2]^+$,[15] and $[RuI(CO)(NO)(PPh_3)_2]$.[16] Precise structural data are available for the latter three complexes, but because of the nature of the ligands direct comparison with the present structure is not possible.

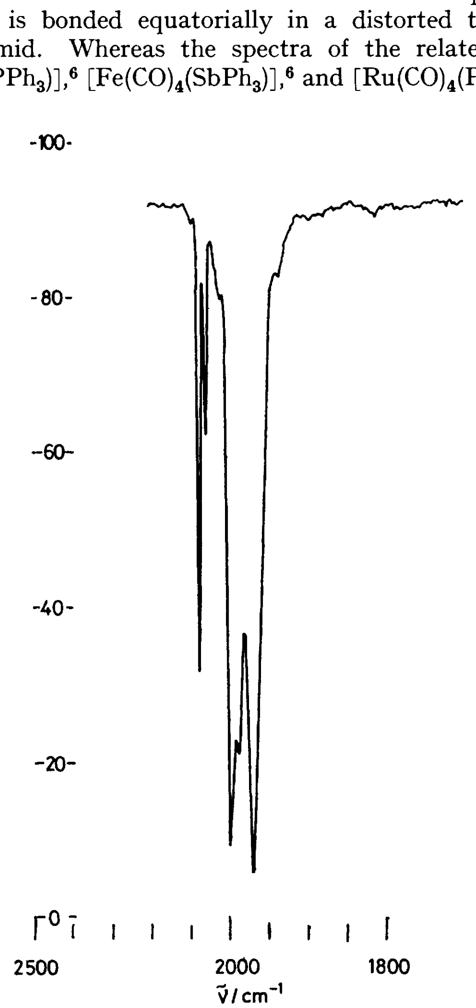


FIGURE 3 The i.r. spectrum of $[Ru(CO)_4(SbPh_3)]$ in n-hexane

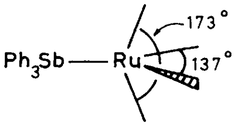
The major deviations from ideal geometry in $[Ru(CO)_4(SbPh_3)]$ involve the equatorial substituents. The C(2)–Ru–C(4) angle is enlarged to 136.6° while the other two equatorial angles, C(2)–Ru–Sb and C(4)–Ru–Sb, are compressed to 116.5 and 106.9°, respectively. The two equatorial carbonyl groups are thus bent towards the triphenylstibine moiety. The four atoms Sb, Ru, C(2), and C(4) are, however, coplanar to within ±0.001 Å. The axial C(1)–Ru–C(3) angle is 173° compared with the ideal value of 180°. Similar distortions from ideal trigonal bipyramidal have been observed in two other d^8 complexes, the pentacyanonickelate(II) ion,[17] and in $[Ni(CN)_2\{PPh(OEt)_2\}_3]$.[18]

The conformation about the Sb–Ru bond is defined by the torsion angles listed in Table 2. The shortest contact distances between atoms of the phenyl rings and the carbonyl groups are C(10) $\cdots$ C(4) 3.69, C(18) $\cdots$ C(1) 3.72, and C(18) $\cdots$ O(1) 3.74 Å. The shortest distances involving hydrogen atoms are H(12) $\cdots$ O(3) 2.86 and H(12) $\cdots$ C(3) 2.96 Å. There does not, therefore, appear to be any unfavourable steric interaction between these groups, which would necessitate deviations from ideal geometry.

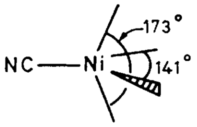
The Sb–Ru bond length is 2.623 Å and this appears to be the first recorded measurement of a bond between antimony and ruthenium in a molecular complex. It is in very good agreement with Sb–Ru distances of 2.618 and 2.656 Å in the binary compound $RuSb_2$.[19] The Sb–C(phenyl) bond lengths are all in the range 2.130—2 135 Å (mean 2.132 Å) in good agreement with those found [3,4,12] in other structures, and with the sum of the accepted single-bond covalent radii of sp^2-hybridised carbon (0.74 Å) and antimony (1.41 Å).[20] The Ru–C(carbonyl) bonds range from 1.923 to 1.935 Å (mean 1.931 Å). The axially orientated bonds are slightly shorter than the equatorial ones, but the difference is not significant. These lengths are typical for bonds of this type, *e.g.* in $[\{Ru(SnMe_3)(CO)_4\}_2]$ [21] they average 1.94 Å (range 1.932—1.947 Å). If the covalent radius of ruthenium is taken as 1.42 Å,[21] and of sp-hybridised carbon as 0.70 Å,[20] the length of a Ru–CO single bond would be 2.12 Å. The measured lengths, some 0.2 Å less than this, therefore indicate a considerable degree of π bonding. The measured length of the Sb–Ru bond (2.623 Å) is also shorter by 0.2 Å than the expected single-bond value obtained from the sum of covalent radii of Sb and Ru^0.

Two structural features of $[Ru(CO)_4(SbPh_3)]$ call for comment. First, the triphenylstibine moiety is sited equatorially and not axially as would be expected from previous examples of analogous $[M(CO)_4L]$ complexes. Theoretical considerations also indicate [22] that poor σ donors that are good π acceptors (such as CO) should preferably occupy equatorial sites. Secondly, the large C–Ru–C bond angle (137°) between the two equatorial carbonyl groups represents a considerable distortion from a regular trigonal-bipyramidal arrangement.

A detailed comparison with the $[Ni(CN)_5]^{3-}$ ion in the crystal structure [17] of $[Cr(NH_2CH_2CH_2NH_2)_3][Ni(CN)_5]\cdot 1.5\ H_2O$ is relevant in this context. There are two crystallographically independent $[Ni(CN)_5]^{3-}$ ions in the structure; one is a regular square pyramid and the other is a distorted trigonal bipyramid. In the trigonal bipyramid one of the equatorial Ni–C bonds is significantly longer than the other two. If we equate the equatorial cyanide with the longest Ni–C bond with our $SbPh_3$ ligand, as indicated in (I) and (II) below, the close similarity between the $SbRu(CO)_4$ moiety and the trigonal-bipyramidal $[Ni(CN)_5]^{3-}$ ion is evident. Ibers and his co-workers[17] pointed out that this $[Ni(CN)_5]^{3-}$ ion had a geometry intermediate between trigonal bipyramidal (D_{3h} symmetry) and square pyramidal (C_{4v} symmetry), but rather nearer the former than the latter, although its symmetry was reduced to essentially C_{2v}. The same conclusion applies to the $SbRu(CO)_4$ moiety. Clearly, the energy difference between trigonal bipyramids and square pyramids in five-co-ordinate complexes must be rather small. {In this context it is of interest that $[Ru^0(CO)_4(PPh_3)]$ is trigonal bipyramidal,[7,8] whereas $[Ru^{II}Cl_2(PPh_3)_3]$ is square pyramidal.[23]}



(I)



(II)

Five-co-ordinate complexes are stereochemically nonrigid.[24] The energy barrier to trigonal-bipyramidal–square-pyramidal interconversion in solution is low, <42 kJ mol^{-1},[25] and is believed[24,25] to follow the Berry mechanism.[26] The $SbRu(CO)_4$ moiety possesses to a reasonable approximation the C_{2v} symmetry required for the Berry rearrangement, and its geometry, like that of the $[Ni(CN)_5]^{3-}$ ion,[24] corresponds to a reaction coordinate in the Berry reaction path between trigonal bipyramidal and square pyramidal. Were the coordination geometry to swing over completely to square pyramidal, the $SbPh_3$ ligand would occupy the apical site.

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