Dirhodium(II,II) Tetra-acetate Complexes with Axially Co-ordinated Triphenylstibine, Triphenylarsine, and Dibenzyl Sulphide Ligands. The Syntheses, Properties, and X-Ray Crystal Structures of $[Rh_2(O_2CMe)_4(SbPh_3)_2]$, $[Rh_2(O_2CMe)_4(AsPh_3)_2]$, and $[Rh_2(O_2CMe)_4\{S(CH_2Ph)_2\}_2]$*

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The triphenylstibine and dibenzyl sulphide complexes $[Rh_2(O_2CMe)_4(SbPh_3)_2]$ and $[Rh_2(O_2CMe)_4\{S(CH_2Ph)_2\}_2]$ have been synthesised for the first time, and their electronic and Raman spectra recorded together with those of $[Rh_2(O_2CMe)_4(AsPh_3)_2]$. The triphenylstibine complex was isolated as light brown crystals belonging to space group $P\bar{1}$, with one centrosymmetric molecule per unit cell. The structure has been refined to an R value of 0.027 for 3 608 observed intensities measured on a diffractometer. The triphenylarsine complex was isolated as maroon needles also belonging to space group $P\bar{1}$ with one centrosymmetric molecule per unit cell. The structure has been refined to R 0.022 for 2 969 observed intensities. The dibenzyl sulphide complex crystallises as burgundy-coloured thin plates with two centrosymmetric molecules per unit cell, space group $P2_1/c$. The final R value was 0.056 for 2 469 observed intensities. The dirhodium tetra-acetate nuclei in the three complexes are essentially identical with each other and with the nuclei found in analogous bis adducts. The Rh–Rh bond lengths are 2.421(4), 2.427(1), 2.406(3) Å for the triphenylstibine, triphenylarsine, and dibenzyl sulphide complexes, respectively, and the Rh–Sb, Rh–As, and Rh–S bond lengths are 2.732(4), 2.576(1), and 2.561(5) Å, respectively. The Rh–Sb distance is the longest (by 0.13 Å) axial rhodium-to-donor-atom bond length known for a bis adduct of dirhodium tetra-acetate. The syntheses of these complexes further demonstrate the versatility of the dirhodium tetra-acetate nucleus in co-ordinating a wide variety of different axial ligands.

In the course of extensive electronic and vibrational studies of dirhodium(II,II) tetracarboxylate complexes with two axially co-ordinated ligands, we have synthesised new tetra-acetate complexes in which the axial ligands are triphenylstibine and dibenzyl sulphide. The former is the first complex of this type to be reported containing a Rh–Sb bond. In this paper we report the single-crystal X-ray structure determinations of these two complexes together with that of the analogous complex with triphenylarsine as axial ligand, and compare the bond lengths and angles with those of related complexes. We also report briefly on the Raman and electronic spectra of the complexes.

Experimental

Tetrakis-μ-acetato-bis(triphenylstibine)dirhodium(II,II), (1), was prepared by the dropwise addition of a saturated methanol solution of triphenylstibine to a solution of dirhodium tetra-acetate in methanol. Light brown crystals of the adduct were precipitated and then recrystallised from dichloromethane. Tetrakis-μ-acetato-bis(triphenylarsine)dirhodium(II,II), (2), was prepared as maroon needles[1] and tetrakis-μ-acetato-bis(dibenzyl sulphide)dirhodium(II,II), (3), as burgundy crystals by an analogous procedure (Found: C, 45.8; H, 3.60. Calc. for $[Rh_2(O_2CMe)_4(SbPh_3)_2]$: C, 46.0; H, 3.70. Found: C, 49.5; H, 3.90. Calc. for $[Rh_2(O_2CMe)_4(AsPh_3)_2]$: C, 50.1; H, 4.00. Found: C, 49.4; H, 4.55; S, 7.30. Calc. for $[Rh_2(O_2CMe)_4\{S(CH_2Ph)_2\}_2]$: C, 49.6; H, 4.65; S, 7.35%).

Suitable crystals for X-ray diffraction purposes were obtained by slow evaporation from solutions of complexes (1) and (3) in dichloromethane and from a solution of (2) in dichloromethane–ethanol (10:1).

The electronic spectra of the complexes are as follows: (1), solid, $\lambda_{max.}$ 264 (sh), 306m, 361s, and 543w nm; solution in dichloromethane (in the presence of 0.01 mol dm^{-3} triphenylstibine), 362 (42 000) and 558 nm (ε = 720 dm^3 mol^{-1} cm^{-1}); (2), solid, 252s, 303s, 352s, and 509w nm; solution in dichloromethane (in the presence of 0.01 mol dm^{-3} triphenylarsine), 340 (44 000) and 527 nm (ε = 700 dm^3 mol^{-1} cm^{-1}); (3), solid, 262s, 290s, 320 (sh), 430 (sh), and 550w nm; solution in dichloromethane (in the presence of 0.01 mol dm^{-3} dibenzyl sulphide), 308 (35 000), 432 (sh), and 546 nm (ε = 370 dm^3 mol^{-1} cm^{-1}).

The additional ligand in each case prevented possible dissociation of the axial ligands.

Disc electronic absorption spectra, solution electronic absorption spectra, and Raman spectra were obtained as previously described.[2] Raman spectra in the region 25—400 cm^{-1} were measured using both double and triple monochromators, bands in the region of 300 cm^{-1} being used to scale the relative intensities obtained in the two modes. Owing to the thermal sensitivity of the complexes, the samples were held at *ca.* 80 K with laser powers of *ca.* 50 mW for 514.5-nm excitation, a line rather than a point focus being used.

X-Ray Structure Determinations.—Intensity data were collected on a CAD-4 diffractometer with Mo-K_α radiation and an

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* Tetra-μ-acetato-bis-[triphenylstibinerhodium(II)], -[triphenylarsinerhodium(II)], and -[dibenzyl sulphiderhodium(II)](*Rh–Rh*).

Supplementary data available (No. SUP 56237, 13 pp.): thermal parameters, H-atom co-ordinates, full lists of bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Crystal data for complexes (1)—(3)

	$[Rh_2(O_2CMe)_4(SbPh_3)_2]$ (1)	$[Rh_2(O_2CMe)_4(AsPh_3)_2]$ (2)	$[Rh_2(O_2CMe)_4\{S(CH_2Ph)_2\}_2]$ (3)
M	1 148.10	1 054.47	870.62
Crystal system	Triclinic	Triclinic	Monoclinic
a/Å	9.205(1)	9.214(1)	15.448(1)
b/Å	15.074(3)	9.580(1)	8.248(3)
c/Å	9.170(2)	13.047(1)	16.049(2)
α/°	99.22(2)	101.077(9)	90
β/°	117.11(1)	109.895(7)	115.447(8)
γ/°	87.93(1)	89.484(7)	90
U/Å^3	1 116.85	1 060.706	1 846.46
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
D_c/g cm^{-3}	1.71	1.65	1.57
Z	1	1	2
$F(000)$	562	526	884
μ/cm^{-1}	18.06	22.48	9.47
Crystal size/mm	0.45 × 0.25 × 0.12	0.43 × 0.22 × 0.12	0.39 × 0.14 × 0.03
θ range/°	1.5—25	1.5—25	1.5—25
No. of unique data	3 916	3 721	3 233
No. of observed data	3 608	2 969	2 469
Significance test	$F > 3\sigma(F)$	$F > 3\sigma(F)$	$F > 3\sigma(F)$
No. of variables	333	337	279
Coefficient g in weighting scheme $w = 1/[\sigma^2(F_o) + gF_o^2]$	0.000 25	0.0002	0.0003
Final $R = \Sigma\Delta F/\Sigma F_o$	0.027	0.022	0.056
$R' = (\Sigma w\Delta F^2/\Sigma wF_o^2)^{\frac{1}{2}}$	0.036	0.028	0.054

ω—2θ scan procedure.[3] Complex (**1**) crystallised as well formed blocks which were cut to suitable dimensions. Complex (**2**) crystallised as maroon needles. Complex (**3**) crystallised as thin plates and, to compensate for their weakly diffracting nature, the data collection pre-scan acceptance parameter, $\sigma(I)/I$, normally 0.5—0.677, was raised to 1.0. Crystal data for the three complexes are summarised in Table 1.

The structures were solved *via* the heavy-atom method and refined by full-matrix least squares. Empirical absorption corrections were applied together with a further correction for complex (**1**) using the DIFABS procedure.[4] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. All hydrogen atoms were located for complexes (**1**) and (**2**) and included in the refinement with individual isotropic thermal parameters. For complex (**3**) the methyl hydrogen atoms were assigned idealised positions, with a C–H distance of 1.08 Å, and the methyl groups refined as rigid bodies. All three molecules contain a crystallographic centre of inversion.

All calculations were carried out on a DEC VAX 11/750 computer using the SHELX 76 program.[5] Final fractional coordinates for the three complexes are given in Table 2.

Results and Discussion

Electronic and Raman Spectra.—It is well known that the colours of dirhodium tetracarboxylate complexes are strongly dependent on the nature of the axial ligands.[6,7] Low-temperature disc transmission electronic spectra for the three complexes are shown in Figure 1; they are characterised by strong bands in the near-u.v. region, these probably arising from axial ligand-to-rhodium charge-transfer transitions. The electronic spectrum of the dibenzyl sulphide complex is consistent with those of other thioether adducts, whilst those of the triphenylstibine and triphenylarsine complexes bear considerable resemblance to that of the triphenylphosphine adduct (the electronic spectrum of which is included in Figure 1).

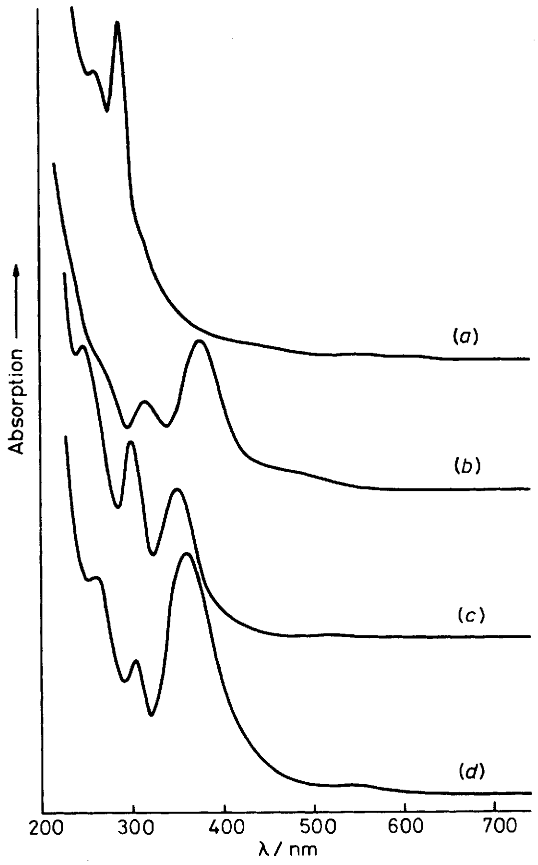

Figure 1. Electronic transmission spectra of the complexes $[Rh_2(O_2CMe)_4L_2]$, where L = $S(CH_2Ph)_2$ (*a*), PPh_3 (*b*), $AsPh_3$ (*c*), and $SbPh_3$ (*d*), recorded as KCl discs at *ca.* 14 K

The Raman spectra of the complexes have been recorded over a range of excitation line wavenumbers and will be reported on in detail elsewhere, together with the i.r. spectra of the complexes. Vibrations involving substantial metal–metal

Table 2. Fractional atomic co-ordinates (× 10^4)

	x	*y*	*z*		*x*	*y*	*z*
(*a*) Complex (**1**)							
Rh(1)	515(0.5)	742(0.5)	790(0.5)	C(15)	−1 863(5)	4 222(3)	−371(6)
Sb(1)	1 652(0)	2 415(0)	2 592(0)	C(16)	−910(4)	3 495(3)	178(4)
O(1)	1 962(3)	735(2)	−349(3)	C(21)	2 123(4)	2 598(2)	5 126(3)
O(2)	−1 018(3)	639(1)	1 821(3)	C(22)	962(5)	2 238(3)	5 471(5)
O(3)	−1 319(3)	1 237(1)	−1 139(3)	C(23)	1 236(7)	2 304(3)	7 093(6)
O(4)	2 296(3)	134(2)	2 599(3)	C(24)	2 648(7)	2 714(3)	8 360(5)
C(1)	1 901(4)	65(2)	−1 392(4)	C(25)	3 772(7)	3 061(4)	8 026(5)
C(2)	2 985(7)	114(3)	−2 227(8)	C(26)	3 522(5)	3 016(3)	6 423(4)
C(3)	−2 325(4)	713(2)	−2 380(4)	C(31)	3 925(3)	2 913(2)	2 879(3)
C(4)	−3 663(6)	1 140(3)	−3 723(6)	C(32)	4 344(4)	3 809(3)	3 155(5)
C(11)	227(3)	3 553(2)	1 832(4)	C(33)	5 811(6)	4 077(4)	3 219(7)
C(12)	395(4)	4 351(2)	2 913(5)	C(34)	6 810(5)	3 439(4)	2 978(7)
C(13)	−573(5)	5 064(3)	2 330(6)	C(35)	6 411(5)	2 556(3)	2 689(6)
C(14)	−1 691(5)	4 990(3)	680(6)	C(36)	4 961(4)	2 273(3)	2 624(4)
(*b*) Complex (**2**)							
Rh(1)	120(0.5)	762(0.5)	886(0.5)	C(15)	3 131(5)	6 200(5)	4 257(4)
As(1)	206(0.5)	2 470(0.5)	2 694(0.5)	C(16)	2 388(4)	4 886(4)	4 073(3)
O(1)	2 172(2)	−126(2)	1 553(2)	C(21)	976(3)	1 878(3)	4 113(2)
O(2)	−1 062(2)	−823(2)	1 180(2)	C(22)	2 286(4)	1 091(4)	4 334(3)
O(3)	−1 914(2)	1 548(2)	90(2)	C(23)	2 872(5)	653(4)	5 335(3)
O(4)	1 279(2)	2 222(2)	462(2)	C(24)	2 145(5)	944(4)	6 107(3)
C(1)	1 503(3)	1 961(3)	−455(2)	C(25)	839(4)	1 697(4)	5 889(3)
C(2)	2 378(5)	3 098(4)	−684(4)	C(26)	267(4)	2 164(4)	4 905(3)
C(3)	−2 635(3)	1 045(3)	−923(2)	C(31)	−1 840(3)	3 079(3)	2 634(2)
C(4)	−4 205(4)	1 600(6)	−1 408(4)	C(32)	−2 119(4)	4 480(3)	2 986(3)
C(11)	1 334(3)	4 305(3)	3 040(2)	C(33)	−3 605(4)	4 855(4)	2 892(3)
C(12)	1 048(4)	5 053(4)	2 188(3)	C(34)	−4 809(4)	3 855(4)	2 457(3)
C(13)	1 788(5)	6 383(4)	2 397(5)	C(35)	−4 541(4)	2 461(5)	2 107(3)
C(14)	2 833(5)	6 947(4)	3 434(5)	C(36)	−3 068(4)	2 082(4)	2 182(3)
(*c*) Complex (**3**)							
Rh(1)	781(0.5)	5 211(1)	5 023(0.5)	C(13)	2 109(7)	10 226(11)	4 661(6)
S(1)	2 451(1)	5 761(2)	5 116(1)	C(14)	2 152(11)	11 422(14)	4 081(9)
O(1)	310(4)	7 382(6)	4 396(4)	C(15)	2 882(14)	11 456(17)	3 857(9)
O(2)	1 153(3)	2 999(6)	5 667(4)	C(16)	3 607(14)	10 265(23)	4 202(12)
O(3)	278(4)	4 150(6)	3 751(4)	C(17)	3 554(9)	9 065(15)	4 775(9)
O(4)	1 179(4)	6 261(6)	6 282(4)	C(21)	3 141(7)	4 491(12)	6 120(7)
C(1)	−548(6)	7 781(9)	4 161(5)	C(22)	4 202(6)	4 725(9)	6 488(6)
C(2)	−881(7)	9 344(10)	3 630(7)	C(23)	4 712(8)	5 419(13)	7 321(7)
C(3)	−579(6)	3 643(9)	3 378(5)	C(24)	5 693(10)	5 595(13)	7 664(10)
C(4)	−941(6)	2 917(10)	2 422(5)	C(25)	6 168(8)	5 075(19)	7 174(13)
C(11)	2 745(7)	7 759(10)	5 656(6)	C(26)	5 687(9)	4 408(19)	6 370(13)
C(12)	2 809(6)	9 034(9)	5 009(6)	C(27)	4 709(7)	4 206(14)	6 008(8)

stretching character usually give rise to strong Raman bands.[8] However, the assignment of Rh–Rh stretching frequencies in dirhodium tetracarboxylates has long been controversial,[9,10] one school of thought[11] favouring the range 351—288 cm^{-1}, another *ca.* 170 cm^{-1}.[12–15] We favour the former since (*a*) there are no strong bands in the Raman spectrum of the triphenylstibine complex below 275 cm^{-1} and (*b*) strong bands at 289, 298, and 306 cm^{-1} for the PPh$_3$, AsPh$_3$, and SbPh$_3$ complexes, respectively, are readily so attributed: they are in each case the strongest bands in the off-resonance Raman spectrum of each complex and they are in each case the first members of the longest progressions observed under resonance-Raman conditions. Moreover, their wavenumbers bear the expected reciprocal relationship to the Rh–Rh bond lengths (see below).

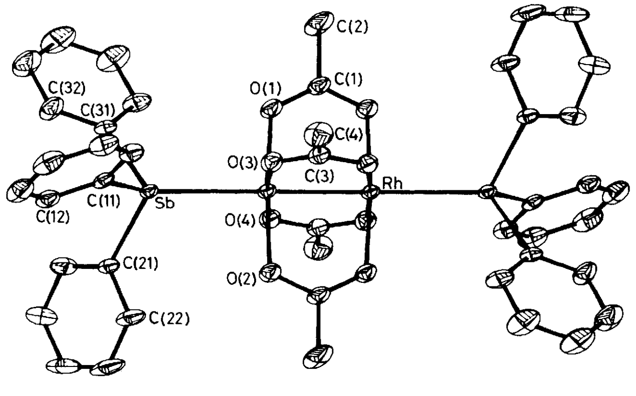

Figure 2. Crystal structure of [Rh$_2$(O$_2$CMe)$_4$(SbPh$_3$)$_2$], including the atom numbering scheme[16]

Description of the Structures.—Diagrams of each complex, showing the atom numbering schemes, are given in Figures 2—4.[16] Selected bond lengths and angles are listed in Table 3.

The common feature of each structure is the dirhodium tetra-acetate nucleus, which is nearly identical in the three structures, and closely similar to that found for a variety of other analogous adducts.[17] In particular, complexes (**1**), (**2**), and the analogous triphenylphosphine adduct[18] have closely similar structures, each possessing [as does (**3**)] a crystallo-

Table 3. Selected bond lengths (Å) and angles (°)

(*a*) Complex (**1**)

Rh(1)–Rh(1^{I})	2.421(4)	Rh(1^{I})–Rh(1)–Sb(1)	179.3(1)	Rh(1^{I})–Rh(1)–O(1)	87.4(2)
O(1)–Rh(1)	2.032(4)	Rh(1^{I})–Rh(1)–O(2)	87.6(2)	Rh(1^{I})–Rh(1)–O(3)	86.9(2)
O(3)–Rh(1)	2.036(4)	Rh(1^{I})–Rh(1)–O(4)	88.0(2)	O(1)–Rh(1)–Sb(1)	93.3(2)
C(1)–O(1)	1.259(4)	O(2)–Rh(1)–Sb(1)	91.7(2)	O(3)–Rh(1)–Sb(1)	93.1(2)
C(2)–C(1)	1.519(6)	O(4)–Rh(1)–Sb(1)	92.0(2)	O(2)–Rh(1)–O(1)	175.0(1)
C(3)–O(4^{I})	1.261(5)	O(3)–Rh(1)–O(1)	89.7(2)	O(4)–Rh(1)–O(1)	89.5(2)
C(11)–Sb(1)	2.130(4)	O(3)–Rh(1)–O(2)	90.1(2)	O(4)–Rh(1)–O(2)	90.4(2)
C(31)–Sb(1)	2.136(4)	O(4)–Rh(1)–O(3)	174.9(1)	C(1)–O(1)–Rh(1)	119.8(3)
Sb(1)–Rh(1)	2.732(4)	O(1)–C(1)–O(2^{I})	126.2(4)	C(2)–C(1)–O(1)	117.0(4)
O(2)–Rh(1)	2.046(4)	C(2)–C(1)–O(2^{I})	116.8(4)	Rh(1)–O(2)–C(1^{I})	119.0(4)
O(4)–Rh(1)	2.044(4)	C(3)–O(3)–Rh(1)	120.5(3)	O(3)–C(3)–O(4^{I})	125.7(4)
C(1)–O(2^{I})	1.256(5)	C(4)–C(3)–O(3)	116.7(4)	C(4)–C(3)–O(4^{I})	117.6(4)
C(3)–O(3)	1.257(4)	Rh(1)–O(4)–C(3^{I})	118.9(4)	C(11)–Sb(1)–Rh(1)	119.8(2)
C(4)–C(3)	1.505(7)	C(21)–Sb(1)–Rh(1)	116.4(2)	C(31)–Sb(1)–Rh(1)	117.9(2)
C(21)–Sb(1)	2.133(4)	C(21)–Sb(1)–C(11)	99.9(2)	C(31)–Sb(1)–C(11)	99.0(2)
		C(31)–Sb(1)–C(21)	100.1(2)	C(12)–C(11)–Sb(1)	123.2(3)
		C(16)–C(11)–Sb(1)	118.1(3)	C(22)–C(21)–Sb(1)	117.2(3)
		C(26)–C(21)–Sb(1)	123.8(3)	C(32)–C(31)–Sb(1)	123.7(3)
		C(36)–C(31)–Sb(1)	116.6(3)		

(*b*) Complex (**2**)

Rh(1)–Rh(1^{I})	2.427(1)	Rh(1^{I})–Rh(1)–As(1)	175.9(1)	Rh(1^{I})–Rh(1)–O(1)	87.1(2)
O(1)–Rh(1)	2.032(4)	Rh(1^{I})–Rh(1)–O(2)	87.8(2)	Rh(1^{I})–Rh(1)–O(3)	87.3(2)
O(3)–Rh(1)	2.027(4)	Rh(1^{I})–Rh(1)–O(4)	87.6(2)	O(1)–Rh(1)–As(1)	92.4(2)
C(1)–O(1)	1.259(5)	O(2)–Rh(1)–As(1)	92.8(2)	O(3)–Rh(1)–As(1)	88.7(2)
C(2)–C(1)	1.494(6)	O(4)–Rh(1)–As(1)	96.5(2)	O(1)–Rh(1)–O(2)	174.9(1)
C(3)–O(4^{I})	1.259(5)	O(1)–Rh(1)–O(3)	90.1(2)	O(1)–Rh(1)–O(4)	88.9(2)
C(11)–As(1)	1.945(5)	O(3)–Rh(1)–O(2)	89.7(2)	O(2)–Rh(1)–O(4)	90.8(2)
C(31)–As(1)	1.949(5)	O(3)–Rh(1)–O(4)	174.8(1)	C(1)–O(1)–Rh(1)	120.5(3)
As(1)–Rh(1)	2.576(1)	O(1)–C(1)–O(2^{I})	125.6(3)	C(2)–C(1)–O(1)	116.4(4)
O(2)–Rh(1)	2.044(4)	C(2)–C(1)–O(2^{I})	118.1(4)	Rh(1)–O(2)–C(1^{I})	119.1(4)
O(4)–Rh(1)	2.047(4)	C(3)–O(3)–Rh(1)	120.0(4)	O(3)–C(3)–O(4^{I})	126.2(4)
C(1)–O(2^{I})	1.264(5)	C(4)–C(3)–O(3)	115.9(4)	C(4)–C(3)–O(4^{I})	117.9(4)
C(3)–O(3)	1.258(5)	Rh(1)–O(4)–C(3^{I})	118.7(4)	C(11)–As(1)–Rh(1)	116.8(2)
C(4)–C(3)	1.506(6)	C(21)–As(1)–Rh(1)	120.9(2)	C(31)–As(1)–Rh(1)	111.8(2)
C(21)–As(1)	1.938(5)	C(21)–As(1)–C(11)	101.6(2)	C(31)–As(1)–C(11)	100.6(2)
		C(31)–As(1)–C(21)	102.4(2)	C(12)–C(11)–As(1)	117.2(3)
		C(16)–C(11)–As(1)	123.7(4)	C(22)–C(21)–As(1)	118.3(3)
		C(26)–C(21)–As(1)	123.4(3)	C(32)–C(31)–As(1)	122.9(3)
		C(36)–C(31)–As(1)	118.4(3)		

(*c*) Complex (**3**)

Rh(1)–Rh(1^{II})	2.406(3)	Rh(1^{II})–Rh(1)–S(1)	177.6(2)	Rh(1^{II})–Rh(1)–O(1)	88.4(2)
O(1)–Rh(1)	2.030(7)	Rh(1^{II})–Rh(1)–O(2)	87.0(2)	Rh(1^{II})–Rh(1)–O(3)	87.8(2)
O(3)–Rh(1)	2.042(7)	Rh(1^{II})–Rh(1)–O(4)	87.9(2)	O(1)–Rh(1)–S(1)	90.6(2)
C(11)–S(1)	1.826(10)	O(2)–Rh(1)–S(1)	94.0(2)	O(3)–Rh(1)–S(1)	94.3(3)
C(1)–O(1)	1.255(9)	O(4)–Rh(1)–S(1)	90.0(3)	O(2)–Rh(1)–O(1)	175.3(2)
C(2)–C(1)	1.508(12)	O(3)–Rh(1)–O(1)	88.9(3)	O(4)–Rh(1)–O(1)	90.4(3)
C(3)–O(4^{II})	1.264(11)	O(3)–Rh(1)–O(2)	91.5(3)	O(4)–Rh(1)–O(2)	88.8(3)
S(1)–Rh(1)	2.561(5)	O(4)–Rh(1)–O(3)	175.7(2)	C(1)–O(1)–Rh(1)	119.2(6)
O(2)–Rh(1)	2.053(7)	O(1)–C(1)–O(2^{II})	126.0(6)	C(2)–C(1)–O(1)	117.0(8)
O(4)–Rh(1)	2.035(7)	C(1)–C(2)–O(2^{II})	117.1(8)	C(1^{II})–O(2)–Rh(1)	119.3(6)
C(21)–S(1)	1.831(11)	C(3)–O(3)–Rh(1)	119.0(6)	O(3)–C(3)–O(4^{II})	125.9(6)
C(1)–O(2^{II})	1.260(10)	C(4)–C(3)–O(3)	117.8(8)	C(3)–C(4)–O(4^{II})	116.3(8)
C(3)–O(3)	1.266(10)	C(3^{II})–O(4)–Rh(1)	119.4(6)	C(11)–S(1)–Rh(1)	103.1(4)
C(4)–C(3)	1.513(12)	C(21)–S(1)–Rh(1)	98.1(4)	C(21)–S(1)–C(11)	99.6(6)
		C(12)–C(11)–S(1)	112.3(7)	C(22)–C(21)–S(1)	113.4(7)

Symmetry operations relating designated atoms to reference atoms at *x*, *y*, *z*: I −*x*, −*y*, −*z*; II −*x*, 1.0 − *y*, 1.0 − *z*.

graphic centre of symmetry at the midpoint of the Rh–Rh axis. The averages of the chemically equivalent bond distances and interbond angles for the three complexes studied, and for the analogous triphenylphosphine complex,[18] are listed in Table 4.

The molecular packing is dominated by normal van der Waals interactions. In each structure the rhodium atoms are displaced by 0.08—0.09 Å from the plane formed by the four equatorial oxygen atoms towards the axial ligands. This feature is similar to that found for the analogous triphenylphosphine and triphenyl phosphite complexes,[18] for which the corresponding displacement is *ca.* 0.10 Å. The acetate groups are planar, and the dirhodium tetra-acetate moiety in each complex possesses essentially D_{4h} symmetry.

The Rh–Rh distance in the complexes $[Rh_2(O_2CMe)_4(MPh_3)_2]$ decreases in the order M = P > As ⩾ Sb [2.4505(2), 2.427(1), 2.421(4) Å], suggesting an increase in the

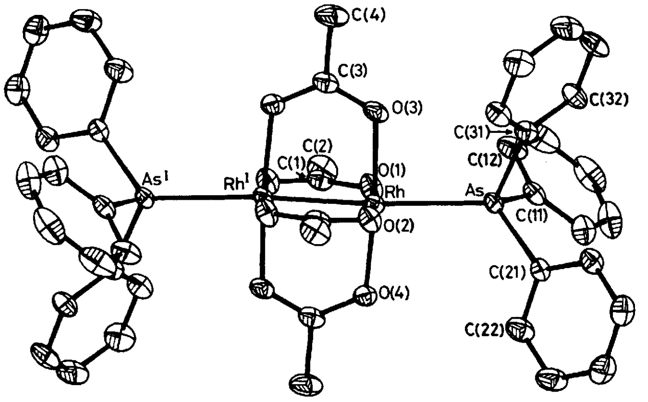

Figure 3. Crystal structure of $[Rh_2(O_2CMe)_4(AsPh_3)_2]$, including the atom numbering scheme[16]

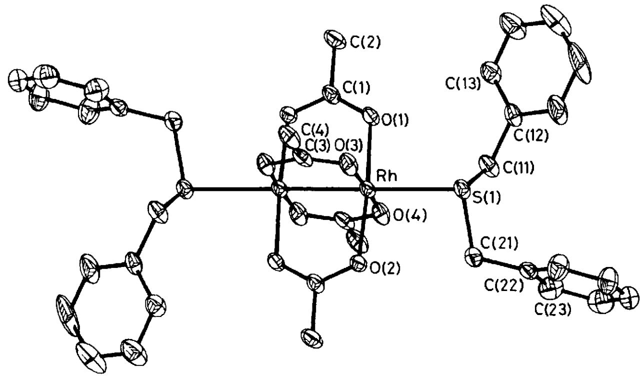

Figure 4. Crystal structure of $[Rh_2(O_2CMe)_4\{S(CH_2Ph)_2\}_2]$ including the atom numbering scheme[16]

Table 4. Comparison of key bond lengths (Å) and angles (°) in the complexes $[Rh_2(O_2CMe)_4L_2]$

	L			
	PPh_3*	$AsPh_3$	$SbPh_3$	$S(CH_2Ph)_2$
Rh–Rh	2.4505(2)	2.427(1)	2.421(4)	2.406(3)
Rh–L	2.4771(5)	2.576(1)	2.732(4)	2.561(5)
Rh–O(av.)	2.045(4)	2.040(4)	2.040(4)	2.040(7)
C–O(av.)	1.260(3)	1.260(5)	1.258(5)	1.261(10)
$C–CH_3$(av.)	1.502(2)	1.500(6)	1.512(7)	1.511(12)
Rh–Rh–O(av.)	87.1(1)	87.5(2)	87.5(2)	87.8(2)
O–C–O(av.)	125.7(4)	125.9(3)	126.0(4)	126.0(6)
Rh–O–C(av.)	120.0(4)	119.6(3)	119.6(4)	119.2(6)

* Ref. 18.

Table 5. Rhodium–arsenic bond lengths (Å)

	Rh–As	Ref.
(*a*) Rh^{III}–As[a]		
$[RhCl_3\{o\text{-}C_6H_4(AsMe_2)(OMe)\}_2]$	2.333(5) 2.354(6)	24
$[RhCl_3\{o\text{-}C_6H_4(AsMe_2)(NMe_2)\}_2]$	2.342(4) 2.529(5)	25
$[Rh(CO_2)Cl\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$	2.397 2.406	26
$[RhCl(H_2O)(AsMe_3)_2\{C_4(CF_3)_4\}]$	2.436(2) 2.436(2)	27
$[RhCl_2(AsPh_3)_2(\eta\text{-}C_4H_7)]$	2.492(2) 2.494(2)	28
(*b*) Rh^I–As[b]		
$[Rh\{o\text{-}C_6H_4(AsMe_2)_2\}_2]Cl$	2.375 2.388	26
$[Rh\{S\text{-}o\text{-}(AsPh_2)C_6H_4CH(Me)NMe_2\}(C_7H_8)]ClO_4$	2.393(3) 2.400(3)	29
$[\{RhCl(CO)(Ph_2AsCH_2AsPh_2)\}_2]\cdot CH_2Cl_2$	2.399(1) 2.430(1)	30
$[\{RhCl(CO)(Ph_2AsCH_2AsPh_2)\}_2]$	2.404(1) 2.410(1)	31
$[RhO_2(AsMe_2Ph)_4]ClO_4$	2.418(4) 2.430(5) 2.440(6) 2.471(6)	32

[a] All complexes are octahedral. [b] All complexes are square planar except the last which is trigonal bipyramidal.

Rh–Rh bond strength in this order. This feature is related to the weaker ligating properties of the axial ligands in this order, as reflected (in part) by the substantial increase in Rh–M distance for heavier M (Table 4). It is noteworthy that the wavenumbers of the bands attributed to ν(RhRh) (see above) increase in the order $PPh_3 < AsPh_3 < SbPh_3$, *i.e.* in the opposite direction to the mass change, and also in the opposite direction to that of the Rh–Rh bond lengths, as expected on bond strength/bond length grounds. The Rh–Rh distance in the bis(dibenzyl sulphide) adduct [2.406(3) Å] is closely similar to that found for the other bis adducts of dirhodium tetra-acetate with sulphur-donor ligands, *viz.* 2.4020(3), 2.4024(7), 2.413(1), and 2.406(1) Å where the axial ligands are $PhCH_2SH$,[19] PhSH,[9] C_4H_4S,[20] and Me_2SO,[20] respectively.

The Rh–Sb distance [2.732(4) Å] is the longest (by 0.13 Å) rhodium-to-donor-atom bond length known for a bis adduct of dirhodium tetra-acetate. It is much longer than the Rh–Sb bond length [2.553(3) Å][21] in the octahedral complex $[Rh(H_2dmg)_2Cl(SbPh_3)]$, where H_2dmg = dimethylglyoxime, or that [2.585(1) Å][22] in $[RhCl(SbPh_3)_2\{C_4(CF_3)_4\}]\cdot CH_2Cl_2$. This suggests little if any π contribution to the Rh–Sb bonds in complex (1), *cf.* the similar conclusion regarding the Rh–P bonds in $[Rh_2(O_2CMe)_4(PPh_3)_2]$.[18] The long Rh–Sb bond length also indicates a strong *trans* influence in the Rh–Rh bond. It is noteworthy that the Rh–Sb bond length in $[Rh_2(O_2CMe)_4(SbPh_3)_2]$ is closely similar to one of the two distinct Rh–Sb bond lengths [2.712(1) and 2.922(1) Å] found for the cluster complex ion $[Rh_{12}Sb(CO)_{27}]^{3-}$. This ion forms a distorted icosahedron with the twelve rhodium atoms located at the vertices and the antimony atom encapsulated at the centre of the polyhedron.[23]

The strong *trans* influence for the Rh–Rh bond is also reflected in the very long Rh–As bond in the triphenylarsine complex. This bond is not only much longer than all other known Rh^{III}–As bonds (range 2.333—2.494 Å),[24–28] as expected (though to a lesser extent) on oxidation-state grounds, but also and more surprisingly, much longer than all other known Rh^I–As bonds (range 2.375—2.471 Å),[26,29–32] *cf.* Table 5. Indeed the inductive and steric effects of the other ligands present, and the geometry and co-ordination number of the rhodium atom, seem to be more important than its formal oxidation state in determining the Rh–As bond length.

The Rh–S distance [2.561(5) Å] in the bis(dibenzyl sulphide) adduct is slightly longer than that found for other bis adducts of dirhodium tetra-acetate with sulphur-donor ligands, *viz.* 2.551(2), 2.548(1), 2.517(1), and 2.451(2) Å where the axial ligands are $PhCH_2SH$,[19] PhSH,[9] C_4H_4S,[20] and Me_2SO,[20] respectively.

The Rh–Rh–Sb linkage is virtually linear [179.3(1)°] whereas the Rh–Rh–S and Rh–Rh–As linkages deviate slightly from linearity [177.6(2) and 175.9(1)°, respectively]. The average C–Sb–C angle [99.7(2)°] in the triphenylstibine complex is 3.5° less and the average C–As–C angle [101.5(2)°] in the triphenylarsine complex is 1.7° less than the average C–P–C angle [103.2(2)°] of the co-ordinated phosphines in the analogous triphenylphosphine complex. The average Rh–Sb–C angle [118.0(2)°] is *ca.* 3° greater and the average Rh–As–C angle (*ca.* 116.5°) is *ca.* 1.5° greater than the average Rh–P–C angle (*ca.* 115°) in the triphenylphosphine analogue. These features presumably reflect the greater energy separation between the valence *s* and *p* orbitals of antimony and arsenic as compared with phosphorus. The C–Sb–C angle in the present complex in also significantly smaller than that [102.3(7)°] in $[\mathrm{RhCl(SbPh_3)_2\{C_4(CF_3)_4\}]\cdot CH_2Cl_2}$.[22]

It is also noteworthy that the average C–As–C angle in the triphenylarsine complex [101.5(2)°] is slightly greater than that for free triphenylarsine [100.1(4)°],[33] consistent with valence shell electron pair repulsion theory predictions that bond pair–bond pair repulsions are smaller than lone pair–bond pair repulsions. However, there is no significant difference between the average As–C bond length in the complex [1.944(5) Å] and in the free ligand [1.957(8) Å]. By contrast, the C–P–C angle in free triphenylphosphine [103.0(2)°][34] is identical with that in the dirhodium complex, presumably owing to a cancellation of the effect described above and that caused by steric interactions between the phenyl and acetate groups (these being greater in the triphenylphosphine than in the triphenylarsine case owing to the fact that the rhodium-to-axial-atom bond length is 0.1 Å shorter for the former). There are no crystallographic data for free triphenylstibine and so the comparison between the free and co-ordinated ligand is not possible in this case.

The Rh–S–C angles in the dibenzyl sulphide complex are 98.1(4) and 103.1(4)°.

Conclusions

The present synthetic and structural work further demonstrates the great ability of the dirhodium tetra-acetate nucleus to co-ordinate axially to a wide variety of ligands. In particular, it allows the close structural comparison of PPh_3, $AsPh_3$, and $SbPh_3$ when co-ordinated axially to this virtually invariant moiety.

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