Syntheses, Electrochemistry, and Spectroscopy of Dirhodium(II) Tetra-acetamidate and Tetrakis(trifluoroacetamide) Complexes with Axial Group 15* Substituents. The *X*-Ray Crystal Structures of $[Rh_2(CH_3CONH)_4(AsPh_3)_2]$ and $[Rh_2(CH_3CONH)_{4-n}(CH_3CO_2)_n(MPh_3)_2]$, M = As or Sb, $n \approx 1$†

Stephen P. Best, Peter Chandley, Robin J. H. Clark, and Simon McCarthy
Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ
Michael B. Hursthouse and Paul A. Bates
Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

The complexes $[Rh_2(CH_3CONH)_4(MPh_3)_2]$ and $[Rh_2(CF_3CONH)_4(MPh_3)_2]$, M = P, As, or Sb, have been synthesised, studied by electronic and Raman spectroscopy, and their electrochemical properties investigated. Single-crystal *X*-ray crystallographic studies of $[Rh_2(CH_3CONH)_4(AsPh_3)_2]$ (**1**) and $[Rh_2(CH_3CONH)_{4-n}(CH_3CO_2)_n(MPh_3)_2]$, M = As or Sb, $n \approx 1$ (**2**) and (**3**) respectively, have been carried out and, in each case, the structures are found to refine in the space group $P\bar{1}$ with one centrosymmetric molecule per unit cell. For (**2**) and (**3**) the acetate group randomly replaces acetamidate to give an effective symmetry of C_i. The dirhodium tetra-bridged cage has the typical, near D_{4h}, symmetry with axially co-ordinated Group 15 ligands and Rh–Rh bond lengths ranging from 2.471(2) to 2.461(2) Å. The Rh–As bond lengths are 2.540(2) and 2.553(4) Å for (**1**) and (**2**), respectively, and the Rh–Sb bond length is 2.699(3) Å for (**3**). The Rh–N and Rh–O bond lengths are significantly different from one another in (**1**) [2.014(6) *vs.* 2.077(6) Å]; it is inferred from this that, in the tetra-acetamidate, there is no scrambling of the arrangement of dimers within the crystal, and that each dimer has no two oxygen or nitrogen atoms *trans* to each other. The wavenumber of the rhodium–rhodium stretching mode [ν(RhRh)] has been identified from the resonance Raman spectra and found to be 273.5, 283.5, and 294 cm^{-1} for the phosphine, arsine, and stibine tetra-acetamidate complexes, respectively; ν(RhRh) is insensitive to trifluoroacetamidate for acetamidate substitution despite the fact that the oxidation potential differs by *ca.* 0.5 V for the differently bridged species. As far as the dirhodium fragment is concerned, the order of σ-donor ability of the bridging ligand is acetamide > acetate ≈ trifluoroacetamide, and of π-acceptor ability is acetamide ≈ trifluoroacetamide > acetate. The RhRh stretching frequency is more sensitive to the σ-donor than the π-acceptor properties of the axial ligand but to the π-acceptor rather than the σ-donor properties of the bridging ligand.

Research by Bear and co-workers[1,2] has suggested that the acetamidate ion is a better σ donor but poorer π acceptor than is any carboxylate ion. Thus $[Rh_2(CH_3CONH)_4]$ is expected to exhibit quantitatively different properties from $[Rh_2(CH_3CO_2)_4]$ with respect to the metal–metal and metal-to-axial ligand bonds. Furthermore the half-wave potential for oxidation of dirhodium tetra-acetamidate complexes is *ca.* 0.6 V more negative than that of the corresponding tetra-acetate complex. With the object of extending the electronic, vibrational, and structural information available on acetamidate complexes and of studying the implications of changing acetate to acetamidate in dinuclear rhodium complexes we have prepared the complexes $[Rh_2(CH_3CONH)_4(MPh_3)_2]$ and $[Rh_2(CF_3CONH)_4(MPh_3)_2]$, M = P, As, or Sb, the arsine and stibine complexes being prepared for the first time.

In this paper we report the synthesis, spectroscopy, and electrochemistry of the acetamidate and trifluoroacetamidate analogues of $[Rh_2(CH_3CO_2)_4L_2]$. *X*-Ray structure determinations of $[Rh_2(CH_3CONH)_4(AsPh_3)_2]$ and $[Rh_2(CH_3CONH)_{4-n}(CH_3CO_2)_n(MPh_3)_2]$, M = As or Sb, $n \approx 1$, are also presented. We discuss the influence of acetamidate for acetate substitution on the interaction between rhodium and the axial ligand, together with general features of the structures of the dirhodium tetra-acetamidate and tetra-acetate complexes.[3–5] The relationship between the Rh–Rh stretching frequency, ν(RhRh), and the Rh–Rh bond length is detailed. Finally we discuss the influence of the electronic properties of the axial and equatorial ligands on ν(RhRh).

Experimental

Preparation of the Complexes.—Dirhodium tetra-acetamidate was prepared by an adaptation of a previously reported method.[1] The complex $[Rh_2(CH_3CO_2)_4]$ (100 mg) was placed in an acetamide (8 g) melt at 120 °C *in vacuo* for 24 h. The excess of ligand and free ethanoic acid were then removed by sublimation *in vacuo*, and a further portion of acetamide added and the melt reaction repeated up to four times in order to complete the substitution of acetamidate for acetate. The crude product was then recrystallised from methanol. The purity of the product was checked either by ^1H n.m.r. spectroscopy or by electrochemical techniques.

The bis(triphenylphosphine) adduct was prepared by the dropwise addition of a saturated methanol solution of the ligand to a solution of dirhodium tetra-acetamidate in the same solvent. Pale brown crystals of the adduct were precipitated,

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* Refers to the 18-Group format of the Periodic Table; formerly Group 5A.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

isolated by filtration, and recrystallised from dichloromethane. The bis(triphenylarsine) and bis(triphenylstibine) adducts were prepared as orange and maroon crystals, respectively, by a similar procedure. The nitrogen analyses were erratic and could not be relied upon to provide a good measure of acetate/acetamidate substitution. Since the analytical figures for carbon and hydrogen are relatively insensitive to the extent of acetamidate for acetate exchange, the sample purity was established by ^{1}H n.m.r. spectroscopic, electrochemical, and *X*-ray techniques.

The complexes $[Rh_2(CH_3CONH)_{4-n}(CH_3CO_2)_n(MPh_3)_2]$, M = P, As, or Sb, $n \approx 1$, were prepared by an analogous procedure although with incomplete substitution of the acetate. No purification procedures were employed to separate out the complexes with $n = 2$ or $n = 0$ which are expected to accompany the $n = 1$ complex. Electrochemical techniques and n.m.r. spectroscopy were used to establish that the sample was predominantly in the form indicated.

The analogous trifluoroacetamidate complexes were prepared by a similar procedure.[6] The greater acidity of trifluoroacetamidate with respect to acetamidate is apparently responsible for the faster rate of exchange of trifluoroacetamidate than acetamidate for acetate, this exchange being largely complete in a single melt reaction at 160 °C. In order to ensure that substitution was complete repeat reactions were carried out. Satisfactory analyses were obtained for each of the adducts (Found: C, 44.3; H, 2.65; N, 4.65. Calc. for $C_{44}H_{43}F_3N_4O_4P_2Rh_2$: C, 44.80; H, 2.90; N, 4.75. Found: C, 40.1; H, 2.40; N, 4.05. Calc. for $C_{44}H_{43}As_2F_3N_4O_4Rh_2$: C, 41.70; H, 2.70; N, 4.40. Found: C, 39.0; H, 2.60; N, 3.85. Calc. for $C_{44}H_{43}F_3N_4O_4Rh_2Sb_2$: C, 38.85; H, 2.50; N, 4.10%). The reported ^{19}F n.m.r. spectra of dirhodium tetrakis(trifluoroacetamidates) prepared by this procedure[6,7] indicate that only one of the three possible isomers is formed, *i.e.* the one with no two nitrogen or oxygen donor atoms *trans* to one another. This is the same isomer as that which occurs for the dirhodium tetra-acetamidate complexes.

Electrochemistry.—Voltammetric studies were carried out with a Metrohm E 506 potentiostat and an E 612 VA scanner. The working and auxiliary electrodes were constructed from high-purity platinum metal and a silver–silver ion electrode was used as the reference. The potential of the reference electrode was corrected by comparison with the ferrocene–ferrocenium couple. Solutions were prepared with freshly distilled dichloromethane (over P_2O_5) and tetrabutylammonium tetrafluoroborate (*ca.* 0.2 mol dm^{-3}) was used as the supporting electrolyte. For electrochemical studies of the triphenyl-phosphine, -arsine, and -stibine adducts it was necessary to add additional axial ligand to maintain the complex in the diaxially substituted form. Cyclic and a.c. voltammetry were used to confirm that the dirhodium tetra-acetamidate complex was not significantly contaminated by mixed acetate–acetamidate species. Since the oxidation potential of the complex $[Rh_2(CH_3CONH)_{4-n}(CH_3CO_2)_nL_2]$, $n = 0$—4, is raised by *ca.* 100 mV for each integral increase in *n*, the presence of a mixed acetate–acetamidate complex will be revealed by an electrochemical study. Typical voltammetric results for the dirhodium tetra-acetamidate species are shown in Figure 1; these demonstrate that the ratio $[Rh_2(CH_3CONH)_4]^{2+}/[Rh_2(CH_3CONH)_3(CH_3CO_2)]^{2+}$ is at least 15:1, a result which is supported by ^{1}H n.m.r. studies. The half-wave potential for the first oxidation of $[Rh_2(CH_3CONH)_4(PPh_3)_2]$ is −0.20 V (*vs.* ferrocene–ferrocenium), in exact agreement with a previous study,[1] the corresponding potentials for the arsine and stibine adducts being −0.09 and −0.05 V respectively. For the trifluoroacetamidate complexes only the triphenylphosphine adduct has a half-wave potential (+0.34 V) less positive than that of the free ligand.

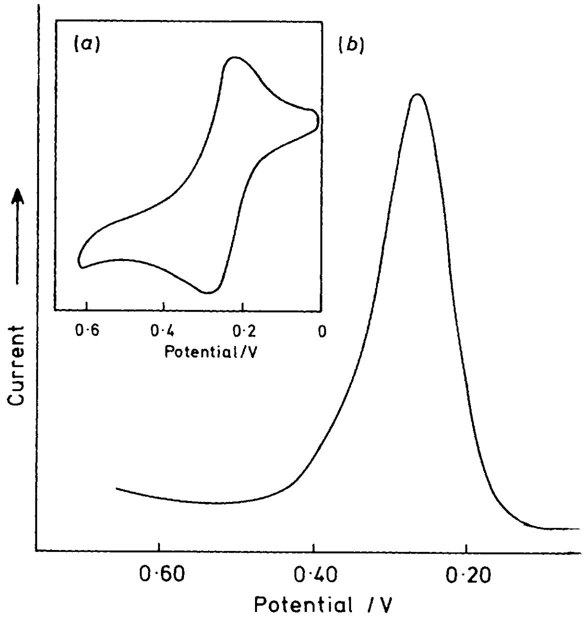

Figure 1. Cyclic voltammogram (*a*) and a.c. voltammogram (*b*) of $[Rh_2(CH_3CONH)_4(PPh_3)_2]$ + 0.1 mol dm^{-3} PPh_3 in CH_2Cl_2–0.2 mol dm^{-3} $[NBu^t_4][BF_4]$, using platinum working and counter electrodes and a Ag–AgCl reference electrode

Spectroscopy.—The electronic spectra of the complexes (*ca.* 2 × 10^{-3} mol dm^{-3} with 0.1 mol dm^{-3} added axial ligand) in dichloromethane were recorded on a Cary 2390 spectrometer.

Raman spectra were recorded on a Spex 14018/R6 spectrometer, the exciting radiation being provided by Coherent model I 18 UV and CR 3000 K lasers. Spectra were recorded either of pressed discs of the complexes (20:1 with KBr) at *ca.* 80 K or of solutions in dichloromethane. The spectrometer was calibrated by reference to the Rayleigh line in each case. Laser power was held at <20 mW to ensure that no sample degradation took place (excitation at 406.7 and 363.8 nm).

Crystallography.—The crystal structure of $[Rh_2(CH_3CONH)_4(AsPh_3)_2]$ (**1**) is isomorphous with those of $[Rh_2(CH_3CONH)_{4-n}(CH_3CO_2)_n(MPh_3)_2]$, M = As or Sb, (**2**) and (**3**). Unit-cell parameters and intensity data were obtained by following previously detailed procedures,[8] using a CAD4 diffractometer operating in the ω—2θ scan mode, with monochromated Mo-K_α radiation (λ = 0.710 69 Å). The reflection intensities for all structures were corrected for absorption, using the azimuthal-scan method.[9] The relevant experimental data are summarised in Table 1.

The structures were solved by the application of routine heavy-atom methods and refined by full-matrix least squares (SHELX 76).[10] The final refinement cycles included all methyl and phenyl hydrogen atoms in their calculated positions (C–H 0.96 Å, U = 0.10 Å^2). All non-hydrogen atoms for these structures were refined with anisotropic thermal parameters.

The assignments of nitrogen *vs.* oxygen in the acetamidate ligands were made after the location of all amide hydrogen atoms. Continuing unrestricted refinement moved these hydrogen atoms to chemically unacceptable positions. However, restraining the nitrogen-to-hydrogen bond lengths to a fixed value (N–H 0.96 Å) produced sensible Rh–N–H and C–N–H bond angles. The final isotropic thermal parameters for these

Table 1. Crystal data, details of intensity measurements, and structure refinement* for $[Rh_2(CH_3CONH)_4(AsPh_3)_2]$ (**1**), $[Rh_2(CH_3CONH)_{4-n}(CH_3CO_2)_n(AsPh_3)_2]$ (**2**), and $[Rh_2(CH_3CONH)_{4-n}(CH_3CO_2)_n(SbPh_3)_2]$ (**3**), $n \approx 1$

Complex	(**1**)	(**2**)	(**3**)
Formula	$C_{44}H_{46}As_2N_4O_4Rh_2$	$C_{44}H_{45}As_2N_3O_5Rh_2$	$C_{44}H_{45}N_3O_5Rh_2Sb_2$
M	1 050.53	1 051.52	1 145.19
a/Å	9.473(3)	9.518(1)	9.465(1)
b/Å	13.149(4)	13.165(2)	13.506(2)
c/Å	9.299(2)	9.247(1)	9.270(1)
α/°	110.07(2)	109.97(2)	108.86(1)
β/°	88.66(2)	89.04(1)	90.19(1)
γ/°	101.66(2)	101.57(1)	99.88(1)
U/Å^3	1 064.2(6)	1 065.2(3)	1 102.4(2)
D_c/g cm^{-3}	1.639	1.638	1.723
F(000)	526	526	562
Crystal size/mm	0.48 × 0.23 × 0.08	0.50 × 0.10 × 0.05	0.40 × 0.10 × 0.10
μ/cm^{-1}	23.5	23.5	19.9
Absorption correction (min., max.)	0.90, 1.00	0.96, 1.00	0.98, 1.00
Total no. of reflections	3 988	3 987	4 118
No. of unique reflections	3 723	3 728	3 853
No. of reflections used in the refinement $[F_o \geqslant 6\sigma(F_o)]$	2 782	2 199	2 908
Min. and max. height in final difference Fourier map, $\Delta\rho$/e Å^{-3}	−0.17, 0.41	−0.17, 0.41	−0.19, 0.46
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.001	0.003	0.001
Final R	0.025	0.028	0.027
Final R'	0.027	0.029	0.029

* Details common to all three complexes: crystal system, triclinic; space group $P\bar{1}$ (no. 2); $Z = 1$; θ range = 1.5—25.0°; hkl range −11 to 11, −15 to 15, 0 to 11; intensity variation <2%; number of parameters refined 267; maximum least-squares shift-to-error ratio 0.1; function minimised $\Sigma w(|F_o| - |F_c|)^2$.

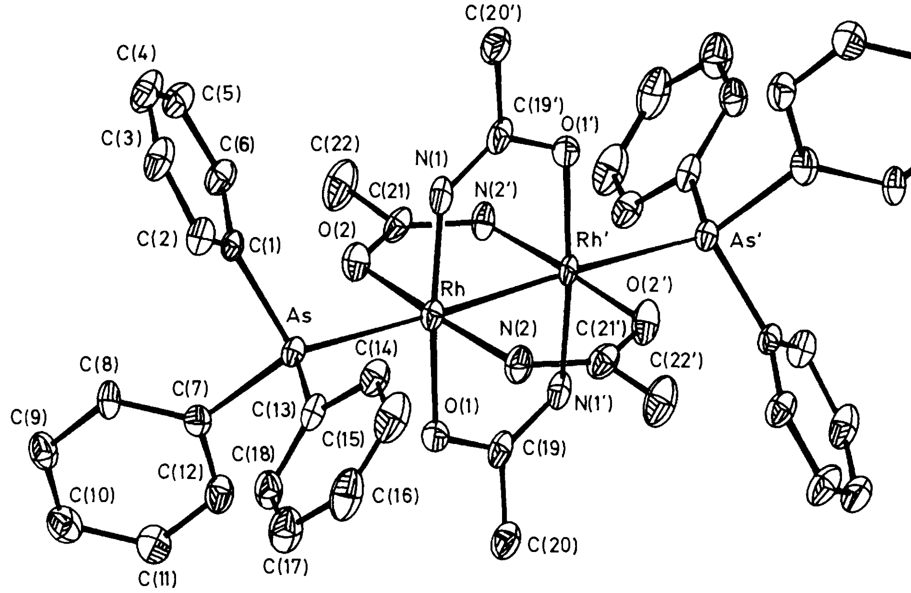

Figure 2. Molecular structure and atom labelling scheme of $[Rh_2(CH_3CONH)_4(AsPh_3)_2]$. For clarity the hydrogen atoms have been omitted and the thermal ellipsoids have been drawn at the 30% probability level

hydrogen atoms are reasonable [0.057(12)—0.117(4) Å^2], the higher values corresponding to hydrogen atoms on the expected mixed N/O sites where no allowance was made for reduced occupancy.

Atomic scattering factors and anomalous scattering parameters were taken from refs. 11 and 12, respectively. All computations were made on a DEC VAX-11/750 computer. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Description of the Structures.—The molecules $[Rh_2(CH_3CONH)_4(AsPh_3)_2]$ (**1**) and $[Rh_2(CH_3CONH)_{4-n}(CH_3CO_2)_n(MPh_3)_2]$, M = As (**2**) or Sb (**3**), $n \approx 1$, are effectively isostructural. Figure 2 shows the molecular structure and labelling scheme for (**1**). For (**2**) and (**3**) the same labelling scheme applies, although the extra oxygen atom from the acetate group randomly replaces one quarter of the NH groups and for (**3**), in addition, Sb replaces As. Positional parameters are presented in Table 2 and selected bond lengths and angles in Table 3.

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

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) For $[Rh_2(CH_3CONH)_4(AsPh_3)_2]$							
Rh	774.9(3)	901.0(2)	101.4(3)	C(9)	1 681(4)	5 873(3)	845(5)
As	2 449.1(3)	2 691.2(2)	170.8(4)	C(10)	934(5)	6 088(3)	2 153(5)
O(1)	−141(3)	1 636(2)	2 146(3)	C(11)	644(5)	5 313(4)	2 869(5)
O(2)	−827(3)	1 200(2)	−1 098(3)	C(12)	1 080(4)	4 319(3)	2 260(4)
N(1)	1 515(3)	46(2)	−1 894(3)	C(13)	4 312(4)	3 056(3)	1 277(4)
N(2)	2 177(3)	481(2)	1 295(3)	C(14)	5 125(4)	2 245(3)	938(4)
C(1)	3 082(4)	2 649(3)	−1 866(4)	C(15)	6 459(5)	2 450(4)	1 677(5)
C(2)	4 512(4)	3 004(3)	−2 147(4)	C(16)	6 975(5)	3 463(4)	2 780(6)
C(3)	4 890(4)	2 928(3)	−3 614(4)	C(17)	6 180(5)	4 264(4)	3 143(5)
C(4)	3 875(5)	2 511(3)	−4 800(4)	C(18)	4 843(4)	4 072(3)	2 396(4)
C(5)	2 452(5)	2 153(3)	−4 538(4)	C(19)	−1 055(4)	1 005(3)	2 651(4)
C(6)	2 060(4)	2 210(3)	−3 078(4)	C(20)	−1 616(5)	1 528(3)	4 199(4)
C(7)	1 854(3)	4 102(3)	951(4)	C(21)	−1 963(4)	439(3)	−1 563(4)
C(8)	2 154(4)	4 885(3)	243(4)	C(22)	−3 089(5)	649(4)	−2 479(5)
(*b*) For $[Rh_2(CH_3CONH)_{4-n}(CH_3CO_2)_n(AsPh_3)_2]$, $n \approx 1$							
Rh	771.0(5)	900.1(4)	115.7(5)	C(9)	1 699(6)	5 864(5)	832(7)
As	2 454.5(6)	2 693.9(4)	196.7(6)	C(10)	931(7)	6 079(5)	2 132(8)
O(1)	−138(4)	1 607(3)	2 182(4)	C(11)	639(7)	5 314(6)	2 867(8)
O(2)	−847(4)	1 174(3)	−1 071(5)	C(12)	1 082(7)	4 307(5)	2 283(7)
N(1)	1 517(5)	65(4)	−1 901(5)	C(13)	4 306(6)	3 058(5)	1 312(6)
N(2)	2 212(5)	491(4)	1 300(5)	C(14)	5 095(6)	2 234(5)	991(7)
C(1)	3 081(5)	2 642(4)	−1 842(6)	C(15)	6 435(7)	2 443(6)	1 716(8)
C(2)	4 497(6)	2 993(5)	−2 127(7)	C(16)	6 950(7)	3 455(7)	2 807(8)
C(3)	4885(7)	2 915(5)	−3 607(7)	C(17)	6 180(7)	4 277(6)	3 155(8)
C(4)	3 866(7)	2 489(6)	−4 801(7)	C(18)	4 851(6)	4 079(5)	2 404(7)
C(5)	2 450(7)	2 137(6)	−4 549(7)	C(19)	−1 048(6)	972(5)	2 660(6)
C(6)	2 060(6)	2 196(5)	−3 067(6)	C(20)	−1 610(7)	1 476(5)	4 221(7)
C(7)	1 863(5)	4 099(4)	963(6)	C(21)	−1 989(6)	424(5)	−1 535(6)
C(8)	2 164(6)	4 891(5)	252(7)	C(22)	−3 138(7)	650(6)	−2 426(7)
(*c*) For $[Rh_2(CH_3CONH)_{4-n}(CH_3CO_2)_n(SbPh_3)_2]$, $n \approx 1$							
Rh	687.7(4)	890.8(2)	146.6(4)	C(9)	1 696(6)	6 014(4)	853(7)
Sb	2 343.8(3)	2 763.3(2)	296.9(3)	C(10)	1 020(6)	6 285(5)	2 160(7)
O(1)	−240(4)	1 495(2)	2 194(3)	C(11)	714(6)	5 603(5)	2 988(7)
O(2)	−989(4)	1 149(3)	−1 026(4)	C(12)	1 104(6)	4 596(5)	2 442(6)
N(1)	1 490(4)	164(3)	−1 857(4)	C(13)	4 417(5)	3 130(4)	1 447(5)
N(2)	2 218(4)	514(3)	1 310(4)	C(14)	5 227(6)	2 332(5)	1 136(6)
C(1)	3 046(5)	2 702(3)	−1 917(5)	C(15)	6 582(7)	2 525(6)	1 841(7)
C(2)	4 461(5)	3 070(4)	−2 150(5)	C(16)	7 113(6)	3 495(7)	2 889(8)
C(3)	4 889(6)	2 972(5)	−3 607(6)	C(17)	6 323(6)	4 293(6)	3 230(7)
C(4)	3 914(7)	2 507(5)	−4 841(6)	C(18)	4 965(5)	4 113(4)	2 505(6)
C(5)	2 511(6)	2 148(5)	−4 629(6)	C(19)	−1 101(5)	838(4)	2 635(5)
C(6)	2 077(5)	2 230(4)	−3 181(5)	C(20)	−1 696(7)	1 271(4)	4 172(6)
C(7)	1 802(5)	4 310(3)	1 103(5)	C(21)	−2 094(5)	401(4)	−1 507(5)
C(8)	2 084(5)	5 031(4)	305(6)	C(22)	−3 306(6)	599(5)	−2 375(6)

Each molecule consists of a metal–metal bonded Rh_2 unit, surrounded by four acetamidate ligands, or three acetamidate and one acetate ligands. At the midpoint of the Rh_2 unit is a crystallographic centre of inversion; thus each rhodium atom is formally bound to a *cis* pair of amide nitrogen atoms. The axial co-ordination sites are taken up by either $AsPh_3$ (**1**) and (**2**) or $SbPh_3$ (**3**). The difference in axial ligand has a minimal effect on the Rh–Rh bond distance, this being 2.467(3) Å for (**2**) and 2.461(2) Å for (**3**). The Rh–Rh and Rh–As bond distances exhibit slight sensitivity to the exchange of one of the acetamidate ligands for acetate. Both bond length changes are in the same direction and of the magnitude expected on the basis of comparison with the structure of $[Rh_2(CH_3CO_2)_4(AsPh_3)_2]$.[3] The complete exchange of acetamidate for acetate leads to larger changes in the Rh–Rh distance (+0.044 Å) and rhodium-axial ligand distance (−0.036 Å). Complex (**3**) has Rh–Rh and Rh–Sb distances similar to those of $[Rh_2(PhCONH)_4(SbPh_3)_2]\cdot CH_2Cl_2$, for which the Rh–Sb and Rh–Rh distances are 2.681(1) and 2.463(1) Å, respectively[13] (Table 5).

A consideration of the bridging ligands reveals that for complex (**1**) the Rh–N bond length [average 2.014(6) Å] is distinctly shorter than the Rh–O bond length [average 2.077(6) Å] and that these values are in good agreement with the corresponding bond lengths in the recently reported structure of $[Rh_2(CH_3CONH)_4(H_2O)_2]\cdot 3H_2O$,[2] *viz*. Rh–N 2.008(2) Å and Rh–O 2.073(2) Å, in which the $[Rh_2(CH_3CONH)_4]$ unit is isostructural with that in (**1**). Notwithstanding the mixing of acetate and acetamidate in complexes (**2**) and (**3**), the Rh–N and Rh–O bond lengths are also distinctly different from one another averaging 2.023(8) (Rh–N) and 2.069(8) Å (Rh–O). These bond lengths are equal to those found for $[Rh_2(CH_3CONH)_3(CH_3CO_2)(Me_2SO)_2]\cdot 2H_2O$,[14] *viz*. Rh–N 2.023(2) and Rh–O 2.069(2) Å. The differences between the Rh–N and Rh–O bond lengths require that the molecules adopt the

Table 3. Selected bond lengths (Å) and angles (°) for $[Rh_2(CH_3CONH)_4(AsPh_3)_2]$ (**1**), $[Rh_2(CH_3CONH)_{4-n}(CH_3CO_2)_n(AsPh_3)_2]$ (**2**), and $[Rh_2(CH_3CONH)_{4-n}(CH_3CO_2)_n(SbPh_3)_2]$ (**3**)

	(1) (M = As)	(2) (M = As)	(3) (M = Sb)
Rh–Rh′	2.471(2)	2.467(3)	2.461(2)
M–Rh	2.540(2)	2.553(4)	2.699(3)
O(1)–Rh	2.075(4)	2.078(6)	2.072(5)
O(2)–Rh	2.079(4)	2.064(6)	2.061(5)
N(1)–Rh	2.007(5)	2.014(6)	2.019(6)
N(2)–Rh	2.021(5)	2.029(6)	2.030(5)
C(1)–M	1.959(5)	1.951(7)	2.140(6)
C(7)–M	1.941(5)	1.937(7)	2.132(6)
C(13)–M	1.951(5)	1.945(7)	2.132(6)
C(19)–O(1)	1.271(5)	1.262(7)	1.267(6)
C(21)–O(2)	1.279(5)	1.279(7)	1.287(6)
C(19′)–N(1)	1.303(5)	1.291(7)	1.298(6)
C(21′)–N(2)	1.293(5)	1.272(7)	1.292(6)
M–Rh–Rh′	176.4(1)	176.1(1)	175.2(1)
O(1)–Rh–Rh′	89.5(2)	89.0(2)	89.6(2)
O(2)–Rh–Rh′	89.3(2)	87.9(2)	88.6(2)
O(1)–Rh–M	93.9(2)	94.9(2)	95.0(2)
O(2)–Rh–M	91.2(2)	92.6(2)	92.9(2)
O(2)–Rh–O(1)	89.9(2)	90.0(3)	90.4(2)
N(1)–Rh–Rh′	84.6(2)	85.0(2)	85.0(2)
N(2)–Rh–Rh′	84.9(2)	86.1(2)	86.2(2)
N(1)–Rh–M	92.0(2)	91.1(2)	90.5(2)
N(2)–Rh–M	94.6(2)	93.4(2)	92.3(2)
N(1)–Rh–O(1)	174.1(1)	174.0(2)	174.5(1)
N(1)–Rh–O(2)	89.6(2)	89.7(3)	89.8(3)
N(2)–Rh–O(1)	88.7(2)	88.8(3)	88.6(2)
N(2)–Rh–O(2)	174.1(1)	174.0(2)	174.7(1)
N(2)–Rh–N(1)	91.3(2)	90.8(3)	90.7(3)
C(19)–O(1)–Rh	117.1(3)	117.3(4)	117.0(4)
C(21)–O(2)–Rh	117.3(3)	118.8(5)	118.6(4)
C(19′)–N(1)–Rh	125.2(3)	124.2(5)	123.9(4)
C(21′)–N(2)–Rh	124.7(3)	122.7(5)	122.6(4)
N(1′)–C(19)–O(1)	123.3(4)	124.3(6)	124.5(5)
N(2′)–C(21)–O(2)	123.7(4)	124.4(6)	124.0(5)
Rh–N(1)–HN(1)	118(2)	118(2)	118(2)
C(19′)–N(1)–HN(1)	115(3)	117(2)	119(1)
Rh–N(2)–HN(2)	122(3)	119(3)	118(2)
C(21′)–N(2)–HN(2)	112(3)	118(2)	119(2)

Key to symmetry operation: (′) $-x$, $-y$, $-z$.

structure shown in Figure 2 and that the packing of the molecules in the crystal is highly ordered. It is interesting that the bite angle of the acetamidate ligand is identical with that of the carboxylates, although the Rh–Rh bond distance is significantly (0.044 Å) longer for the former. In these structures the O–Rh–Rh angle is preserved near 90° (89.4°) at the expense of the N–Rh–Rh angle (84.8°). The observed shortening of the rhodium axial ligand bond on acetamidate for acetate substitution results from the stronger σ-donating properties of acetamidate (compared with acetate); this lowers the effective nuclear charge on the rhodium atoms and thereby facilitates stronger π donation from rhodium to the axial donor atom.

Electronic and Raman Spectra.—The electronic spectra of dirhodium tetracarboxylates, tetra-acetamidates, and tetrakis(trifluoroacetamidates) are qualitatively similar to one another. They are characterised (Table 4) in the near-u.v. region (338—377 nm) by the appearance of an intense band which is thought to arise from a $\sigma(Rh\text{–}Rh) \longrightarrow \sigma^*(Rh\text{–}Rh)$ transition with some axial ligand character,[1] and a shoulder at 435—510 nm which increases in intensity as the axial ligand is changed from $SbPh_3$ to $AsPh_3$ to PPh_3. If the assignment of the band at *ca.* 350 nm is correct, then irradiation within the contour of that band should lead to resonance enhancement of certain Raman bands, in particular that assigned to ν(RhRh). For example, near-u.v. excitation of $[Rh_2(CH_3CO_2)_4(MPh_3)_2]$, M = P, As, or Sb, leads to Raman spectra in the region 50 to 700 cm^{-1} which are dominated by the band at *ca.* 300 cm^{-1} assigned to ν(RhRh).[4,5] Another band, at *ca.* 340 cm^{-1}, is assigned to ν(RhO), a normal mode which involves the motion of the acetate group against the dirhodium core. Isotopic studies have been carried out to identify the character of the normal modes for the dirhodium tetra-acetates.[4,5] For the acetamidates and trifluoroacetamidates, excitation within the contour of the band at *ca.* 350 nm generates spectra which are qualitatively similar to those of the acetates, although the choice of exciting line has a dramatic effect on the complexity of the spectra. In Figure 3(*a*) and (*b*) spectra of $[Rh_2(CF_3CONH)_4(PPh_3)_2]$ are shown, excited with radiation at (*a*) 406.7 and (*b*) 363.8 nm. The ν(RhRh) mode at 274 cm^{-1} is not easily assigned from spectra obtained with excitation at 406.7 nm, but it gives rise to the dominant band in the 363.8-nm spectrum. Since this mode transforms as the totally symmetric representation, the presence of overtones in the 363.8-nm spectrum indicates that enhancement of the Raman spectra occurs *via* the A-term mechanism.[15]

Table 4. Properties of dirhodium tetra-acetamidate complexes

L	Colour	$E_{\frac{1}{2}(ox)}{}^{a}$/V	$\lambda_{max.}{}^{b}$/nm	ν(Rh–Rh)[c]/ cm^{-1}	*r*(Rh–Rh)/ Å
$[Rh_2(CH_3CONH)_4L_2]$					
PPh_3	Light brown	−0.20	372s, 467vw	273.5	
$AsPh_3$	Orange			283.5	2.467
$SbPh_3$	Maroon	−0.09 −0.05	338s, 435vw 356s, 510vw	294	2.461
$[Rh_2(CF_3CONH)_4L_2]$					
PPh_3	Orange	+0.34	377s, 440w	274	
$AsPh_3$	Reddish orange	*d*	366s, 444vw	284	
$SbPh_3$	Maroon	*d*	375s, 444vw	295.5	

[a] *vs.* Ferrocene–ferrocenium. [b] The absorption coefficients of the band at *ca.* 370 nm are *ca.* 70 000 $dm^3\ mol^{-1}\ cm^{-1}$. [c] KBr disc (406 nm excitation), 80 K. [d] Ligand oxidises at more negative potentials than does the complex.

Raman spectra of $[Rh_2(CH_3CONH)_4(MPh_3)_2]$, M = P, As, or Sb, are shown in Figure 4, and of the corresponding trifluoroacetamidates in Figure 3. Both sets of spectra are dominated by a band at *ca.* 280 cm^{-1} which is sensitive to the identity of the axial ligand but not to trifluoroacetamidate for acetamidate exchange; this band is assigned to the ν(RhRh) mode. This assignment is supported by the observed depolarisation ratio of the band at 280 cm^{-1} at resonance (0.34, CH_2Cl_2 solvent), a result which confirms the axial nature of the resonant electronic transition.[15] The ν(RhRh) values bear the expected reciprocal relationship with the Rh–Rh bond distances in the complexes (Table 4). For the acetamidates somewhat weaker bands at *ca.* 347 cm^{-1} are assigned to modes which involve the motion of the acetamidate group against the dirhodium core. Since ν(RhO) depends on the mass of the bridging ligand,[4,5] the absence of analogous bands at *ca.* 347 cm^{-1} in the spectra of the trifluoroacetamidates is consistent with the above interpretation. The assignment of the weak bands between 300 and 350 cm^{-1} is uncertain, but the appearance of similar bands in the spectra of the carboxylates is significant. These bands are sensitive to ^{18}O and ^{2}H substitution (in the carboxylates), and to the replace-

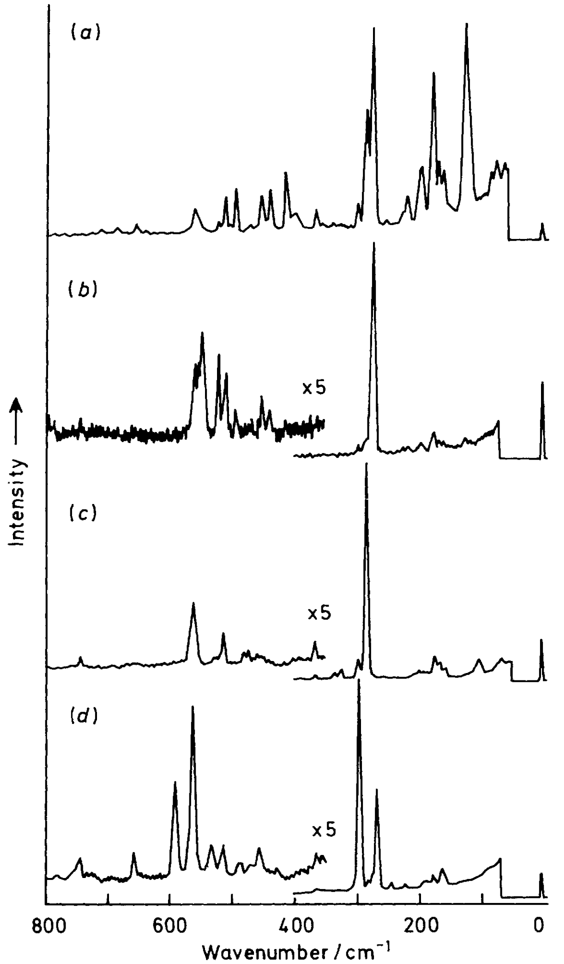

Figure 3. Resonance Raman spectra of $[Rh_2(CF_3CONH)_4(MPh_3)_2]$ as KBr discs at 80 K: (*a*) M = P, λ_0 = 406.7 nm, spectral bandpass (s.b.p.) = 3.0 cm^{-1}; (*b*) M = P, λ_0 = 363.8 nm, s.b.p. = 2.6 cm^{-1}; (*c*) M = As, λ_0 = 406.7 nm, s.b.p. = 3.0 cm^{-1}; (*d*) M = Sb, λ_0 = 406.7 nm, s.b.p. = 3.0 cm^{-1}. In each case the incident laser power was less than 15 mW at the sample

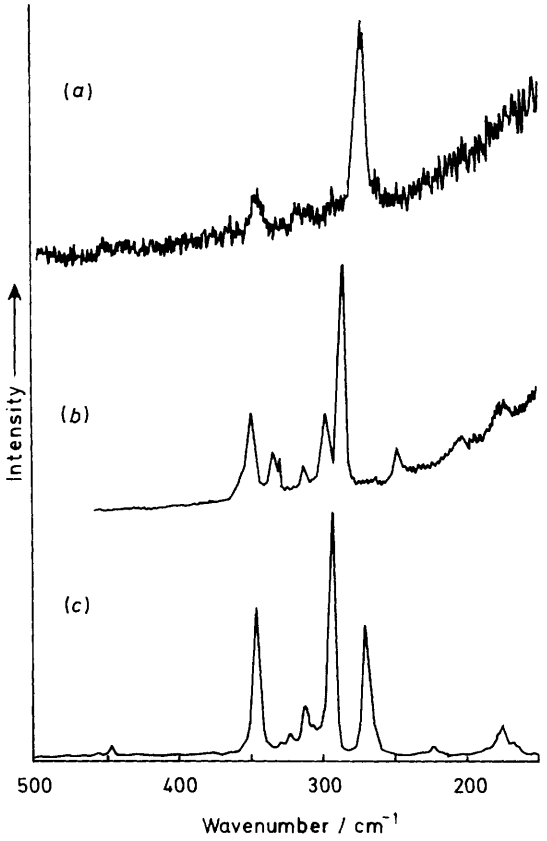

Figure 4. Resonance Raman spectra of $[Rh_2(CH_3CONH)_4(MPh_3)_2]$ as KBr discs at 80 K: (*a*) M = P, λ_0 = 363.8 nm, s.b.p. = 2.6 cm^{-1}; (*b*) M = As, λ_0 = 406.7 nm, s.b.p. = 3.0 cm^{-1}; (*c*) M = Sb, λ_0 = 406.7 nm, s.b.p. = 3.0 cm^{-1}. In each case the incident laser power was less than 15 mW at the sample

ment of acetate by acetamidate, and are thus assigned to lower-symmetry modes involving the motion of the bridging group. Bands at *ca.* 297 cm^{-1} (arsine derivative) and 267 cm^{-1} (stibine derivative) are assigned to fundamentals of the axial ligand.[5,16] On the basis of the depolarisation ratio (0.75) and high wavenumber it is unlikely that the Rh–As or Rh–Sb stretching modes give rise to these bands.

General Discussion.—The PPh_3, $AsPh_3$, and $SbPh_3$ axial ligands can influence the Rh–Rh bond by σ donation, by π acceptance, or by both. σ Donation has the effect of adding electron density to orbitals which are σ antibonding with respect to the dirhodium entity. π Acceptance results in the removal of electron density from the dirhodium core by overlap between full d_{xz},d_{yz} rhodium and empty orbitals on the Group 15 donor atom.† The d_{xz} and d_{yz} rhodium orbitals form the π and π^* orbitals of the dirhodium entity. Since the π^*-RhRh orbital is expected to interact the more strongly with the Group 15 atom's acceptor orbitals, the net effect of π acceptance by the axial ligand is to strengthen the Rh–Rh bond. Both the σ-donor and the π-acceptor properties of the ligands are expected to increase in the order $SbPh_3 < AsPh_3 < PPh_3$, based on the effectiveness of overlap of the appropriate donor and acceptor orbitals, and therefore the balance between σ and π effects will lead to the observed changes in the Rh–Rh bond lengths and stretching frequencies with changes of the axial ligand. For the dirhodium tetra-acetates, -acetamidates, and -trifluoroacetamidates, ν(RhRh) increases in the order $PPh_3 < AsPh_3 < SbPh_3$, *i.e.* in that expected on the basis of the σ-donating properties of the ligand, but not on that expected on the basis of their π-acceptor properties. Thus, in so far as the dirhodium entity is concerned, it is the σ interactions with the axial ligand which dominate the changes in the strength of the Rh–Rh bond.

The electrochemical properties of the dirhodium complexes are a measure of their electron richness. For the dirhodium tetra-acetamidates the oxidation potential decreases as the axial ligand becomes more strongly σ donating, *viz.* $SbPh_3 < AsPh_3 < PPh_3$, allied to which is a corresponding decrease of ν(RhRh). It is important to explore the relationship between the electron richness, determined electrochemically, and ν(RhRh) with changes to the bridging ligand. By changing the latter from acetate to acetamidate the dirhodium entity becomes more electron rich (by *ca.* 0.6 V) and the Rh–Rh bond becomes weaker [lower ν(RhRh) by *ca.* 13 cm^{-1}, longer Rh–Rh bond lengths by *ca.* 0.04 Å]. However, when the bridging ligand is trifluoroacetamidate the complex exhibits the electrochemical

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† The π-acceptor orbitals on the phosphorus atoms may be *d*, P–C σ^*, or an admixture of each. See D. S. Marynick, *J. Am. Chem. Soc.*, 1984, **106**, 4064; A. G. Orpen and N. G. Connelly, *J. Chem. Soc., Chem. Commun.*, 1985, 1310.

Table 5. Vibrational and structural information on related dirhodium tetra-acetate and tetra-acetamidate complexes with two axial substituents (L)

Complex	ν(Rh–Rh)/cm^{-1}	*r*(Rh–Rh)/Å	*r*(Rh–L)/Å	Ref.
$[Rh_2(CH_3CO_2)_4(PPh_3)_2]$	289.3	2.450	2.477	4, *a*
$[Rh_2(CH_3CO_2)_4(AsPh_3)_2]$	297	2.427	2.576	3, 4
$[Rh_2(CH_3CO_2)_4(SbPh_3)_2]$	307	2.421	2.732	3, 4
$[Rh_2(CH_3CO_2)_4(H_2O)_2]$	*ca.* 340	2.386	2.310	*b*
$[Rh_2(CH_3CO_2)_4(py)_2]$		2.396	2.227	*c*
$[Rh_2(CH_3CO_2)_4(Me_2SO)_2]$		2.406	2.451	*d*
$[Rh_2(CH_3CONH)_4(PPh_3)_2]$	273.5			*e*
$[Rh_2(CH_3CONH)_4(AsPh_3)_2]$	283.5	2.471	2.540	*e*
$[Rh_2(CH_3CONH)_4(SbPh_3)_2]$	294	2.47	2.69	*e*, *f*
$[Rh_2(PhCONH)_4(SbPh_3)_2]{\cdot}CH_2Cl_2$		2.463	2.681	13
$[Rh_2(CH_3CONH)_4(H_2O)_2]$		2.415	2.352	2
$[Rh_2(CF_3CONH)_4(py)_2]$		2.472	2.26 2.31	*g*
$[Rh_2(PhCONH)_4(py)_2]$		2.437	2.227	13
$[Rh_2(CH_3CONH)_4(Me_2SO)_2]$		2.452	2.414	*h*
$[Rh_2(CH_3CONPh)_4(Me_2SO)_2]$		2.448	2.606 2.566	*h*

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properties of the acetates with the Rh–Rh bond strength found for the acetamidates. We explain this apparent anomaly by considering the particular orbitals involved and the σ-donating and π-accepting properties of the bridging ligand. σ Donation by the bridging ligand will lead to the donation of electron density to rhodium $d_{x^2-y^2}$ orbitals (which form both δ and δ* molecular orbitals of the dirhodium entity) whereas π acceptance by the bridging ligand will remove electron density from d_{xy} orbitals (the symmetry of the π*-acceptor orbital is such that electron density can be removed only from the δ-bonding orbital of the dirhodium entity). Consequently σ donation will have little effect on the Rh–Rh bond strength, since bonding and antibonding combinations will be involved to a similar extent, but π acceptance by empty antibonding orbitals of the ligand will take electron density from the δ-bonding orbital of the dirhodium entity and thereby weaken the Rh–Rh bond. The replacement of acetate by acetamidate therefore requires both greater σ donation and greater π acceptance on the part of the bridging ligand in order to account for the electrochemical, Raman, and *X*-ray results. For the dirhodium complexes studied here acetamidate is a better π acceptor than acetate, contrary to the proposal of Ahsan *et al.*[2] The insensitivity of the Rh–Rh bond strength to replacement of acetamidate by trifluoroacetamidate is explained by the influence of the CF_3 group on the σ-donor rather than by the π-acceptor properties of the ligand. Therefore the resulting dirhodium tetrakis(trifluoroacetamidate) complexes are less electron-rich than the corresponding acetamidates, but have Rh–Rh bonds of similar strengths.

The rhodium–axial ligand bond length is sensitive to acetate–acetamidate exchange, being shorter for the acetamidate complexes. This variation in bonding can be explained in terms either of the *trans* influence (which increases the shorter the Rh–Rh bond) or through changes in the Rh to axial ligand interaction as a result of changes in the size of the rhodium *d* orbitals with change in the effective nuclear charge. We can exclude the *trans* influence as the major cause of these bond length changes because the Rh–py (pyridine) bond length is insensitive to a 0.077 Å change in the Rh–Rh bond length for the complexes $[Rh_2(CH_3CO_2)_4(py)_2]$ and $[Rh_2(CF_3CONH)_4(py)_2]$ (Table 5).

Since the influence of the axial ligand on the Rh–Rh bond strength is a result of the balance between the σ- and π-bonding interactions of the axial ligand with rhodium, it would be expected that the effect of changing the axial ligand from PPh_3 to $AsPh_3$ or $SbPh_3$ would depend on the electronic properties of the dirhodium fragment, which are altered by changing the bridging group from acetate to acetamidate to trifluoroacetamidate. For the dirhodium tetra-acetate, tetra-acetamidate, and tetrakis(trifluoroacetamidate) complexes, ν(RhRh) increases by 9 ± 1 cm^{-1} on substitution of PPh_3 by $AsPh_3$ and by a further 10.5 ± 1 cm^{-1} on substitution by $SbPh_3$. The similarity of the changes in ν(RhRh) with change of axial ligand for the three series of complexes suggests that the relative importance of the σ and π bonding between rhodium and the axial ligand is insensitive to the σ and π properties of the bridging ligand; alternatively since the changes of the bridging ligand do not significantly influence the σ-acceptor properties of the dirhodium entity then changes in its π interaction with the axial ligand have a negligible influence on that Rh–Rh bond strength, due to approximately equal influence on the δ and δ* Rh–Rh orbitals.

Conclusions

Electrochemical, vibrational, and structural data on dirhodium tetra-acetate, tetra-acetamidate, and tetrakis(trifluoroacetamidate) complexes have been drawn together in order to establish the influence of the bridging and the axial ligand on the dirhodium fragment. It is concluded that acetamidate is both a better σ donor and a better π acceptor of electron density than acetate, and that trifluoroacetamidate is a poorer σ donor but an approximately equal π acceptor than acetamidate. From the key vibrational and structural data in Table 5 on a series of dirhodium complexes, it is evident that the increment in the Rh–Rh distance on changing tetra-acetate to tetra-acetamidate is typically *ca.* 0.04 Å, associated with a decrement in ν(RhRh) of *ca.* 15 cm^{-1}. It is important to recognise that the Rh–Rh bond length is *not* solely determined by the optimum bite angle of the ligand, but also by the net Rh–Rh bonding.

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