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Synthesis and properties of ruthenium and palladium iodide complexes of phosphorus, arsenic and antimony ligands

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Abstract

Iodoruthenium(II) complexes *trans*-$[Ru(L\text{–}L)_2I_2]$ (L–L = $Ph_2PCH_2CH_2PPh_2$, *cis*-$Ph_2PCHCHPPh_2$, $Ph_2AsCH_2CH_2AsPh_2$, *o*-$C_6H_4(AsMe_2)_2$), *trans*-$[Ru(SbPh_3)_4I_2]$ and $[Ru(PPh_3)_3I_2]$ have been made by reaction of $[Ru(H_2O)_6][BF_4]_2$ with the ligand and NaI in aqueous ethanol. Oxidation with conc. HNO_3–HBF_4 yielded *trans*-$[Ru(L\text{–}L)_2I_2]BF_4$. The complexes were characterised by spectroscopy (IR, UV–Vis, ^{31}P NMR) and cyclic voltammetry, and their properties compared with chloro- and bromo- analogues. Unsuccessful attempts to prepare palladium(IV) iodo complexes $[Pd(L\text{–}L)_2I_2][BF_4]_2$ are described. The crystal structures of $[Ru(Ph_2AsCH_2CH_2AsPh_2)_2I_2]BF_4$ and $[Pd\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2][BF_4]_2$ are reported.

Keywords: Crystal structures; Ruthenium complexes; Palladium complexes; Iodide complexes; Stibine complexes; Arsine complexes; Phosphine complexes

1. Introduction

A large number of platinum metal phosphine and arsine complexes with chloride or bromide co-ligands are known, in many cases with relatively high oxidation states of the metal such as palladium(IV), osmium(IV) or iridium(IV) [1]. In these complexes the effect of changing chloride for bromide is often minimal [2,3]. However the combination of a high oxidation state metal centre and soft, polarisable iodide ligands seems unfavourable, and indeed relatively few iodo-analogues have been reported, and detailed characterisations are lacking. In attempts to explore if iodo complexes containing medium or higher oxidation states can be obtained, and if so whether their properties are significantly different from those with lighter halogens, we have recently investigated the systematic synthesis of various metal iodo complexes. Examples of iron(III) [4], nickel(III) [5] and osmium(III) and osmium-(IV) [6] complexes of types *trans*-$[M(L\text{–}L)_2I_2]^{n+}$ where L–L is a bidentate ligand have been characterised, and here we report on attempts to prepare the ruthenium(III) and palladium(IV) iodo complexes. The corresponding chloro- and bromo complexes were described previously [2,7].

2. Experimental

Physical measurements were made as described previously [3,6,7]. $[Ru(H_2O)_6][BF_4]_2$ was synthesised according to the method of Bernhard et al. [8].

2.1. Ruthenium(II) complexes

2.1.1. $[Ru(L\text{–}L)_2I_2]$ (L–L = $Ph_2AsCH_2CH_2AsPh_2$, o-$C_6H_4(AsMe_2)_2$, $Ph_2PCH_2CH_2PPh_2$, cis-$Ph_2PCH{=}CHPPh_2$)

To 50 cm^3 of a 0.13 M aqueous solution of $[Ru(H_2O)_6][BF_4]_2$ (0.65 mmol) was added 1.3 mmol of the ligand dissolved in ethanol (30 cm^3). The mixture was refluxed for 1.5 h under nitrogen and then allowed to cool, whereupon NaI (0.23 g, 1.5 mmol) was added to the clear solution and the mixture was reheated to boiling and stirred for 1 h. Upon cooling, a solid deposited from the solution. This was collected by filtration, washed with distilled water (2 × 15 cm^3) and diethyl ether (2 × 10 cm^3) and dried in vacuo. Yields: 30–40%.

Trans-$[Ru\{Ph_2AsCH_2CH_2AsPh_2\}_2I_2]$: *Anal.* Found: C, 46.4; H, 3.8. Calc. for $C_{52}H_{48}As_4I_2Ru$: C, 47.0; H, 3.6%.

Trans-$[Ru\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]$: *Anal.* Found: C, 25.8; H, 3.6. Calc. for $C_{20}H_{32}As_4I_2Ru$: C, 25.9; H, 3.5%.

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Trans-$[Ru(Ph_2PCH_2CH_2PPh_2)_2I_2]$: *Anal.* Found: C, 53.7; H, 4.8. Calc. for $C_{52}H_{48}I_2P_4Ru$: C, 54.2; H, 4.2%. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): 58.5 ppm.

Trans-$[Ru(Ph_2PCHCHPPh_2)_2I_2]$: *Anal.* Found: C, 54.8; H, 4.0. Calc. for $C_{52}H_{48}I_2P_4Ru$: C, 54.4; H, 3.8%. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): 63.0 ppm.

2.1.2. *Trans-$[Ru(SbPh_3)_4I_2]$ and $[Ru(PPh_3)_3I_2]$*

The complexes *trans*-$[Ru(SbPh_3)_4I_2]$ and $[Ru(PPh_3)_3I_2]$ were prepared similarly to the method described above, using 0.65 mmol of $[Ru(H_2O)_6][BF_4]_2$ and 3.2 mmol of the appropriate ligand.

Trans-$[Ru(SbPh_3)_4I_2]$: *Anal.* Found: C, 49.3; H, 3.6. Calc. for $C_{72}H_{60}I_2RuSb_4$: C, 48.9, H, 3.4%.

$[Ru(PPh_3)_3I_2]$: *Anal.* Found: C, 56.3; H, 4.1. Calc. for $C_{54}H_{45}I_2P_3Ru$: C, 56.7; H, 3.9%.

2.1.3. *Cis-$[Ru(cis\text{-}Ph_2PCH{=}CHPPh_2)_2I_2]$*

To $[Ru(H_2O)_6][OTs]_2$ [8] (0.25 g, 0.3 mmol) in ethanol (40 cm^3) was added *cis*-$Ph_2PCHCHPPh_2$ (0.3 g, 0.75 mmol) and the mixture refluxed under nitrogen for 1.5 h. Sodium iodide (0.11 g, 0.65 mmol) was added and the mixture refluxed for a further 0.5 h. On cooling an orange solid separated, which was collected by filtration, washed with water (50 cm^3), and diethyl ether (2 × 15 cm^3) and dried in vacuo. Yield: 0.17 g, 50%. *Anal.* Found: C, 54.2; H, 4.0. Calc. for $C_{52}H_{44}I_2P_4Ru$: C, 54.4; H, 3.8%. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): +63.7(t), +38.0(t) ppm ($^2J(P\text{–}P) = 15$ Hz).

2.2. *Ruthenium(III) complexes*

Trans-$[Ru(L\text{–}L)_2I_2]BF_4$ were prepared by suspending the Ru(II) complexes (~0.05 g) in 5 cm^3 of 40% aq. HBF_4 at 0 °C and adding 1 cm^3 of conc. HNO_3 dropwise with vigorous stirring. The suspension was stirred for 5 min, the dark solid filtered off and washed with distilled water (5 cm^3) and diethyl ether (2 × 10 cm^3) and dried in vacuo. The complex *trans*-$[Ru(SbPh_3)_4I_2]BF_4$ was prepared in the same way.

Trans-$[Ru\{Ph_2AsCH_2CH_2AsPh_2\}_2I_2]BF_4$: *Anal.* Found: C, 44.5; H, 3.6. Calc. for $C_{52}H_{48}As_4BF_4I_2Ru$: C, 44.1; H, 3.4%.

Trans-$[Ru\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]BF_4$: *Anal.* Found: C, 24.0; H, 3.3. Calc. for $C_{20}H_{32}As_4BF_4I_2Ru$: C, 23.7; H, 3.2%.

Trans-$[Ru(Ph_2PCH_2CH_2PPh_2)_2I_2]BF_4$: *Anal.* Found: C, 50.0; H, 4.0. Calc. for $C_{52}H_{48}BF_4I_2P_4Ru$: C, 50.4; H, 3.9%.

Trans-$[Ru(Ph_2PCHCHPPh_2)_2I_2]BF_4$: *Anal.* Found: C, 50.8; H, 3.5. Calc. for $C_{52}H_{44}BF_4I_2P_4Ru$: C, 50.6; H, 3.6%.

Trans-$[Ru(SbPh_3)_4I_2]BF_4$: *Anal.* Found: C, 47.0; H, 3.3. Calc. for $C_{72}H_{60}BF_4I_2RuSb_4$: C, 46.6; H, 3.2%.

2.3. *Palladium(II) complexes*

$[Pd(L\text{–}L)_2I_2]$ (L–L = $o\text{-}C_6H_4(AsMe_2)_2$, $o\text{-}C_6H_4(PMe_2)_2$, $Me_2PCH_2CH_2PMe_2$) were prepared by stirring a mixture of $Na_2[PdCl_4]$ (0.85 mmol) and NaI (4.0 mmol) in water (20 cm^3) for 2 h under nitrogen. The ligand (1.7 mmol) in ethanol (30 cm^3) was added and the mixture stirred for a further 1 h. The precipitate was filtered off, washed with distilled water (2 × 25 cm^3) and diethyl ether (2 × 10 cm^3) and dried in vacuo. Yields: 40–50%. The crude solids could be recrystallised from CH_2Cl_2-diethyl ether mixtures.

Trans-$[Pd\{o\text{-}C_6H_4(PMe_2)_2\}_2I_2]$: *Anal.* Found: C, 31.5; H, 4.0. Calc. for $C_{20}H_{32}I_2P_4Pd$: C, 31.7; H, 4.2%.

Trans-$[Pd(Me_2PCH_2CH_2PMe_2)_2I_2]$: *Anal.* Found: C, 21.5; H, 5.0. Calc. for $C_{12}H_{32}I_2P_4Pd$: C, 21.8; H, 4.8%.

2.4. *Palladium(IV) complexes*

Attempts were made to generate complexes of the form *trans*-$[Pd(L\text{–}L)_2I_2][BF_4]_2$ by nitric acid oxidation of the recrystallised Pd(II) complexes in HBF_4 suspension at 0 °C, similar to the procedure used for the Ru(III) complexes. This resulted in the formation of a purple product that exhibited an absorbance in the UV–Vis region corresponding closely to that of free I_2.

The *trans*-$[Pd(L\text{–}L)_2Cl_2][BF_4]_2$ (L–L = $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$, $Me_2PCH_2CH_2PMe_2$) complexes were prepared by conc. HNO_3 oxidation of the Pd(II) chloro complexes suspended in HBF_4. They were identified by comparison of their spectroscopic properties, with those of the corresponding perchlorate salts [2].

2.5. *Palladium(II) polyiodide complexes*

$[Pd(L\text{–}L)_2][I_3]_2$ were prepared by refluxing together the *trans*-$[Pd(L\text{–}L)_2Cl_2][BF_4]_2$ complex (0.1 mmol) with $^nBu_4NI$ (0.5 mmol) in ethanol (10 cm^3) under nitrogen for 1 h. The resulting green–black precipitate was filtered off, washed with distilled water (2 × 10 cm^3) and diethyl ether (2 × 5 cm^3) and dried in vacuo. Yields: ~50% on Pd.

$[Pd\{o\text{-}C_6H_4(PMe_2)_2\}_2][I_3]_2$: *Anal.* Found: C, 20.5; H, 3.0. Calc. for $C_{20}H_{32}I_6P_4Pd$: C, 21.0; H, 2.8%.

$[Pd(Me_2PCH_2CH_2PMe_2)_2][I_3]_2$: *Anal.* Found: C, 12.7; H, 3.0. Calc. for $C_{12}H_{32}I_6P_4Pd$: C, 12.3; H, 2.7%.

$[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2][I_3]_2$: *Anal.* Found: C, 16.8; H, 2.2. Calc. for $C_{20}H_{32}As_4I_6Pd$: C, 16.7; H, 2.2%.

2.6. *Crystal structure determination*

2.6.1. *$[Ru(Ph_2AsCH_2CH_2AsPh_2)_2I_2]BF_4$*

Dark brown air-stable crystals were obtained by vapour diffusion from $MeCN/Et_2O$. Data were collected from a room temperature crystal using a Rigaku AFC7S diffractometer fitted with Mo Kα radiation and graphite monochromator. Cell dimensions were obtained from 20 reflections (2θ 15.0 to 23.0°). Data were corrected for absorption using ψ-scan data (3 reflections: transmission: 1.00 max.; 0.80 min.) and a small amount of decay (1.8% based on I). The systematic absences indicated the space group $P\bar{3}$ or $P3$ and the structure was solved in the former centrosymmetric space group using SHELXS86 [9]. Two of the three BF_4^- groups in the unit cell were not disordered (B(1)) but the disorder

Table 1

Crystal data and summary of the data collection and refinement procedures

Compound	$[Ru(Ph_2AsCH_2CH_2AsPh_2)_2I_2]BF_4$	$[Pd\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2][BF_4]_2$
Molecular formula	$C_{52}H_{48}As_4BF_4I_2Ru$	$C_{20}H_{32}B_2Cl_2F_8P_4Pd$
Molecular weight	1414.32	747.28
Crystal system	trigonal	monoclinic
Space group	$P\bar{3}$ (No. 147)	$P2_1/n$ (No. 14)
a (Å)	20.655(2)	7.585(1)
b (Å)	20.655(2)	17.595(2)
c (Å)	11.784(2)	11.035(1)
α (°)	90.0	90.0
β (°)	90.0	105.99(1)
γ (°)	120.0	90.0
V (Å^3)	4353.8(1.2)	1415.8(3)
T (K)	299	123
Density (calc.) (g cm^{-3})	1.624	1.753
Z	3	2
F(000) (e)	2049	748
Crystal size (mm)	0.25×0.15×0.15	0.25×0.08×0.06
Type data collection	ω–2θ	ω–2θ
Total no. observations	4231	3435
Total no. unique observations	2867 (0.050)	3201 (0.029)
Absorption correction	ψ-scan	none
No. refinement data	1230 ($F>4\sigma(F)$)	2180 ($I>2.5\sigma(I)$)
No. parameters	152	233
Weighting scheme (w^{-1})	$\sigma^2(F)+0.0005F^2$	$\sigma^2(F)$
λ (Mo Kα) (Å)	0.71069	0.71069
μ (cm^{-1})	36.0	11.4
Max. 2θ (°)	50	54
Max. shift/e.s.d.	0.04	0.00
R [a]	0.069	0.027
wR [b]	0.073	0.028

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $wR=[\Sigma w(F_o-F_c)^2/\Sigma wF_o{}^2]^{1/2}$.

in the third (B(2)) was satisfactorily modelled. However not surprisingly the atoms of the anion had large thermal parameters. Refinement was carried out using SHELX76 [10] with H atoms introduced in calculated positions (d(C–H) 0.95 Å) and anisotropic atoms for Ru, I and As atoms only. Crystal parameters, details of data collection and refinement and R values are given in Table 1 and atomic coordinates in Table 2.

2.6.2. $[Pd\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2][BF_4]_2$

Small yellow air-stable crystals were obtained by vapour diffusion from $MeCN/Et_2O$. Data were collected at −150(1) °C using a Rigaku AFC7R diffractometer fitted with Mo Kα X-radiation and graphite monochromator. Cell dimensions were obtained from 22 reflections ($22.3<2\theta<39.5°$). No absorption correction was applied; a small amount of decay (1.7% based on I) was observed and allowed for in the data reduction. The systematic absences established the space group as $P2_1/n$ (No. 14) and the structure was solved using SHELXS86 [9] to locate the heavy atoms. Hydrogen atoms were located in later electron-density maps and refinement was carried out using teXsan software [11] with anisotropic non-hydrogen atoms and isotropic H atoms. Unlike many $[BF_4]^-$ anions, in this compound it is not disordered. Crystal parameters, details of data collection and refinement and R values are given in Table 1 and atomic coordinates in Table 3.

3. Results and discussion

3.1. Ruthenium(II) complexes

Reported syntheses of $[Ru(L\text{–}L)_2I_2]$ (L–L = diphosphine or diarsine) complexes have used exchange between the $[Ru(L\text{–}L)_2Cl_2]$ and alkali iodide in refluxing alcohols [12,13]. Even after several days exchange is incomplete and the diiodide products were separated in poor yield chromatographically. Our results fully support the difficulty of halide metathesis in these inert $t_{2g}{}^6$ complexes. For example, after refluxing $[Ru(cis\text{-}Ph_2PCH{=}CHPPh_2)_2Cl_2]$ with a large excess of LiI in ethanol for 2 days, the ^{31}P NMR spectrum of the product revealed several species to be present, with about 50% of the dichloride unchanged, and less than 30% converted to the diiodide. In view of these results, we believe that literature claims for the synthesis of similar iodoruthenium complexes by metathesis, without further purification and in the absence of good evidence of purity such as iodine analysis or appropriate spectroscopic data, should be viewed with some scepticism. In related studies of the osmium ana-

Table 2
Atomic coordinates for $[Ru(Ph_2AsCH_2CH_2AsPh_2)_2I_2]BF_4$

Atom	*x*	*y*	*z*
Ru	0.5000	0.0000	0.0000
I	0.4650(1)	0.0568(1)	0.1721(2)
As(1)	0.6132(2)	0.1254(2)	−0.0288(3)
As(2)	0.4432(2)	0.0550(2)	−0.1296(3)
C(1)	0.5812(19)	0.1946(19)	−0.0732(28)
C(2)	0.5070(22)	0.1608(21)	−0.1140(35)
C(11)	0.6781(17)	0.1807(17)	0.0959(26)
C(12)	0.7376(18)	0.1720(19)	0.1198(29)
C(13)	0.7823(23)	0.2036(21)	0.2233(32)
C(14)	0.7547(22)	0.2384(21)	0.2903(33)
C(15)	0.6960(21)	0.2470(20)	0.2757(32)
C(16)	0.6537(20)	0.2161(19)	0.1738(31)
C(21)	0.6811(15)	0.1348(16)	−0.1469(23)
C(22)	0.6901(19)	0.1759(18)	−0.2408(29)
C(23)	0.7381(20)	0.1886(20)	−0.3335(33)
C(24)	0.7733(19)	0.1509(20)	−0.3108(31)
C(25)	0.7727(23)	0.1051(22)	−0.2201(34)
C(26)	0.7210(19)	0.0966(18)	−0.1377(29)
C(31)	0.3449(17)	0.0472(16)	−0.1024(26)
C(32)	0.3366(23)	0.0813(20)	−0.0118(32)
C(33)	0.2641(23)	0.0694(21)	0.0098(36)
C(34)	0.2121(26)	0.0329(23)	−0.0606(37)
C(35)	0.2239(28)	0.0032(24)	−0.1509(40)
C(36)	0.2901(20)	0.0088(18)	−0.1781(31)
C(41)	0.4326(16)	0.0297(18)	−0.2910(25)
C(42)	0.3980(18)	−0.0386(20)	−0.3289(29)
C(43)	0.3868(22)	−0.0615(26)	−0.4393(37)
C(44)	0.4115(26)	0.0001(30)	−0.5058(46)
C(45)	0.4517(24)	0.0701(28)	−0.4812(45)
C(46)	0.4695(22)	0.0901(24)	−0.3656(34)
B(1)	0.3333	0.6667	0.4566(158)
F(1)	0.3333	0.6667	0.3011(30)
F(2)	0.3852(18)	0.7289(18)	0.4488(32)
B(2) [a]	0.0000	0.0000	0.0246(284)
F(3) [a]	0.0000	0.0000	0.0246(284)
F(4) [a]	0.0636(38)	0.0152(41)	0.1296(56)

[a] Disordered BF_4^- anion.

Table 3
Atomic coordinates and isotropic thermal parameters (Å^2) of $[Pd\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2][BF_4]_2$

Atom	*x*	*y*	*z*	B_{eq}
Pd	0.0000	0.0000	0.0000	0.843(6)
Cl	−0.21557(10)	−0.00328(5)	0.11226(7)	1.43(1)
P(1)	0.1263(1)	0.11768(5)	0.08564(8)	1.08(2)
P(2)	0.2310(1)	−0.05315(5)	0.16844(8)	1.17(2)
F(1)	0.0265(3)	0.2195(1)	0.4999(2)	2.96(5)
F(2)	0.1255(3)	0.0979(1)	0.5006(2)	2.51(5)
F(3)	0.2317(3)	0.1735(1)	0.6731(2)	3.09(5)
F(4)	0.3175(3)	0.1962(1)	0.4958(2)	3.46(6)
C(1)	0.0081(5)	0.1622(2)	0.1878(3)	1.52(7)
C(2)	0.1495(5)	0.1887(2)	−0.0264(4)	1.66(8)
C(3)	0.1570(6)	−0.0882(2)	0.2999(4)	2.09(8)
C(4)	0.3625(5)	−0.1286(2)	0.1238(4)	1.92(8)
C(5)	0.3522(4)	0.0970(2)	0.1866(3)	1.18(6)
C(6)	0.4823(5)	0.1541(2)	0.2306(3)	1.56(7)
C(7)	0.6461(5)	0.1375(2)	0.3182(3)	1.78(7)
C(8)	0.6830(5)	0.0639(2)	0.3645(3)	1.74(7)
C(9)	0.5567(4)	0.0070(2)	0.3207(3)	1.52(7)
C(10)	0.3923(4)	0.0225(2)	0.2308(3)	1.12(6)
B	0.1756(6)	0.1714(2)	0.5428(4)	1.64(8)

logues [8], we found it best to avoid chloride containing reagents altogether and introduced the osmium as $[OsI_6]^{2-}$ either preformed or generated in situ from OsO_4/HI. Identification of a suitable ruthenium precursor was more difficult. Hexaiodoruthenate ions $[RuI_6]^{n-}$ are not well characterised [1,14], and ruthenium tetraoxide violently oxidises HI and many organic materials. Moreover we found that reaction of $K[RuO_4]$ with aqueous ROH/HI and the appropriate ligand always precipitated a black insoluble ligand-free ruthenium species which from its properties was identified as impure RuI_3 [14].

The method finally adopted was to generate $[Ru(H_2O)_6][BF_4]_2$ from lead reduction of RuO_4 in aq. HBF_4 [8], and then react this sequentially with the appropriate ligand and with NaI in aq ethanol. The complexes *trans*-$[Ru(L\text{–}L)_2I_2]$ (L–L = $o\text{-}C_6H_4(AsMe_2)_2$, $Ph_2AsCH_2CH_2AsPh_2$, $Ph_2PCH{=}CHPPh_2$, $Ph_2PCH_2CH_2PPh_2$), *trans*-$[Ru(SbPh_3)_4I_2]$ and $[Ru(PPh_3)_3I_2]$ were obtained in good yield (Table 4). The diphosphine complexes were also obtainable by reaction of $[Ru(PPh_3)_3I_2]$ with 2 equiv. of the diphosphine in hexane. The reaction of $[Ru(H_2O)_6][OTs]_2$ (OTs = tosylate) [8,15] with *cis*-$Ph_2PCH{=}CHPPh_2$ and NaI in ethanol yielded a yellow powder, identified by analysis and ^{31}P NMR spectroscopy as *cis*-$[Ru(Ph_2PCH{=}CHPPh_2)_2I_2]$. It seems likely that an intermediate with a coordinated bidentate OTs^- ligand sets up the *cis* stereochemistry in this case (cf. Ref. [15]).

The dark purple $[Ru(PPh_3)_3I_2]$, the iodine analogue of the much studied $[Ru(PPh_3)_3Cl_2]$ [16], is reasonably stable in the solid state when pure and dry, but is unstable in solution, rapidly turning green and then yellow, due to oxidation of the phosphine ligands. The $^{31}P\{^1H\}$ NMR spectrum in CH_2Cl_2 at 300 K consists of a broad resonance at +55 ppm ($w^{1/2}$ = 180 Hz), with a small peak at −6 ppm due to free PPh_3. Samples often show a small peak at +28 ppm due to $OPPh_3$ formed by air-oxidation. On cooling the solution, the major resonance first broadens, then < ~250 K splits and < ~230 K two resonances are present at +90 and +37.5 ppm (ratio 1:2). These sharpen on further cooling but even at 180 K no P–P coupling was clearly resolved. This behaviour is qualitatively similar to that of the chloride [17], and is consistent with a square-pyramidal geometry with apical PPh_3 at low temperatures, which undergoes fast intramolecular apical–basal phosphine exchange on warming (the free PPh_3 resonance is unchanged over the temperature range showing dissociative phosphine exchange is slow). The spectroscopic properties of the *trans*-$[Ru(L\text{–}L)_2I_2]$ complexes (Table 4) are typical of Ru(II)–t_{2g}^6 metal centres in local D_{4h} symmetry [7].

Cyclic voltammetric (CV) studies of the *trans*-$[Ru(L\text{–}L)_2I_2]$ complexes revealed reversible 1*e* oxidations (Table 5), and chemically the oxidation to Ru(III) was

Table 4
Ruthenium(II) and ruthenium(III) compounds

Compound	Colour	UV–Vis E_{max} (10^3 cm^{-1}) (ϵ_{mol}/dm^3 mol^{-1} cm^{-1}) [a]
trans-$[Ru(Ph_2AsCH_2CH_2AsPh_2)_2I_2]$	pink	34.6(sh), 30.3(1755), 25.0(sh), 19.2(475)
trans-$[Ru\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]$	brown	35.6(1560), 27.1(700), 23.6(500)
$[Ru(PPh_3)_3I_2]$	purple	33.8, 25.5, 20.5(sh), 18.1 [b]
trans-$[Ru(Ph_2PCH_2CH_2PPh_2)_2I_2]$	yellow	32.2(sh), 27.1(930), 22.1(470)
trans-$[Ru(Ph_2PCHCHPPh_2)_2I_2]$	yellow–orange	33.8(2290), 24.5(350), 20.4(230)
trans-$[Ru(SbPh_3)_4I_2]$	grey–green	30.0, 27.4, 27.1(sh), 21.7, 17.5 [b]
cis-$[Ru(Ph_2PCHCHPPh_2)_2I_2]$	orange	33.3(sh), 24.4(530)
trans-$[Ru(Ph_2AsCH_2CH_2AsPh_2)_2I_2]BF_4$	green	31.7(sh), 26.9(3690), 20.5(sh), 17.8(sh), 12.3(sh), 10.0(2930), 9.1(sh)
trans-$[Ru\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]BF_4$	dark brown	29.2(sh), 22.9(sh), 19.8(780), 12.7(sh), 10.6(1600), 8.6(sh)
trans-$[Ru(Ph_2PCH_2CH_2PPh_2)_2I_2]BF_4$	dark brown	28.1(sh), 20.2(4000), 10.1(sh), 9.1(1000)
trans-$[Ru(Ph_2PCHCHPPh_2)_2I_2]BF_4$	brown	30.0(sh), 26.9(sh), 20.3(1040), 11.3(370), 8.8(2360)
trans-$[Ru(SbPh_3)_4I_2]BF_4$	dark brown	32.6(12400), 26.1(9040), 23.9(sh), 18.7(sh), 11.9(920), 8.9(1450), 7.9(sh)

[a] CH_2Cl_2 solution except [b].
[b] Diffuse reflectance diluted with MgO.

Table 5
Electrochemical data ($E_c°$/V vs. SCE)

Compound	Ru^{II}–Ru^{III} [a,b]	ΔE_p (mV)	Ru^{III}–Ru^{IV} [a,c]
trans-$[Ru(Ph_2AsCH_2CH_2AsPh_2)_2I_2]BF_4$	+0.61	90	+1.62
trans-$[Ru\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]BF_4$	+0.60	100	+1.47
trans-$[Ru(Ph_2PCH_2CH_2PPh_2)_2I_2]BF_4$	+0.55	90	+1.53
trans-$[Ru(Ph_2PCHCHPPh_2)_2I_2]BF_4$	+0.62	90	+1.68
trans-$[Ru(SbPh_3)_4I_2]BF_4$	+0.71	90	+1.30

[a] Similar data were obtained starting with the Ru(II) analogues, but due to their better solubility, the data reported above were obtained from the Ru(III) complexes.
[b] CH_2Cl_2 solution containing 0.1 mol dm^{-3} $N^nBu_4BF_4$.
[c] Irreversible couple.

effected with conc. HNO_3 in the presence of aq. HBF_4. In contrast the *cis*-$[Ru(Ph_2PCHCHPPh_2)_2I_2]$ was not oxidised by conc. HNO_3, and CV results in CH_2Cl_2 showed only an irreversible oxidation at highly positive potential (~ 1.53 V). The *trans*-$[Ru(L–L)_2I_2]BF_4$ complexes are green or brown in colour, with the UV–Vis spectra dominated by $L \rightarrow Ru$ charge transfer transitions. The spectral profiles are similar to those of Os(III) analogues [6] and Ru(III) chloro- and bromo complexes [7], with the maxima of the main features shifted progressively to low energy with change in the halide as illustrated in Fig. 1. We have proposed elsewhere assignments for the spectra of Ru(III) [7] and Os(III) [6,18] complexes in D_{4h} ligand fields, and those of the present complexes follow by analogy. It is notable that the lower energy features, which we assign to $\sigma(P,As,Sb) \rightarrow t_{2g}(Ru)$ and $\pi(I) \rightarrow t_{2g}(Ru)$ are in the near-IR rather than the visible region, and as a result the complexes appear less intensely coloured than their analogues with lighter halides.

The osmium(III) complexes *trans*-$[Os(L–L)_2I_2]BF_4$ showed reversible 1*e* oxidations in their cyclic voltammograms, and *trans*-$[Os\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2][ClO_4]_2$ was isolated by chemical oxidation and fully characterised [6]. In contrast the CVs obtained from the ruthenium complexes show only completely irreversible oxidations at highly positive potentials, probably indicative of transient formation of very unstable Ru(IV) complexes. Even in the chloride and bromide systems [7] the Ru(IV) complexes proved to be too unstable to isolate.

3.1.1. Structure of *trans*-$[Ru(Ph_2AsCH_2CH_2AsPh_2)_2I_2]BF_4$

The structure consists of discrete centrosymmetric cations and disordered BF_4^- anions in the rather unexpected trigonal space group $P\bar{3}$. The cation is shown in Fig. 2 and selected bond lengths are given in Table 6. The crystal quality is not high, however the structure confirms the identity of the complex inferred above from spectroscopic data, the stereochemistry at the ruthenium atom, and establishes the first example of a Ru–I bond distance. The Ru–I bond distance (2.619(2) Å) may be compared with Ru^{III}–Cl (2.38 (av.) Å [19]) in $[Ru(MeSeCH_2CH_2SeMe)Cl_4]^-$ and Ru^{III}–Br (2.455(1) Å [7]) in $[Ru\{o\text{-}C_6F_4(AsMe_2)_2\}_2Br_2]^+$. The diarsine ligand has been characterised several times by X-ray crystallography and occurs as a monodentate, bridging and bidentate chelating ligand with the latter found in the present compound. The As–C–C–As residue is nearly planar (torsion angle −2°) and it makes an angle of 24.7° to the plane containing the $RuAs_4$ group. The arsine ligand bond lengths and angles are unexceptional.

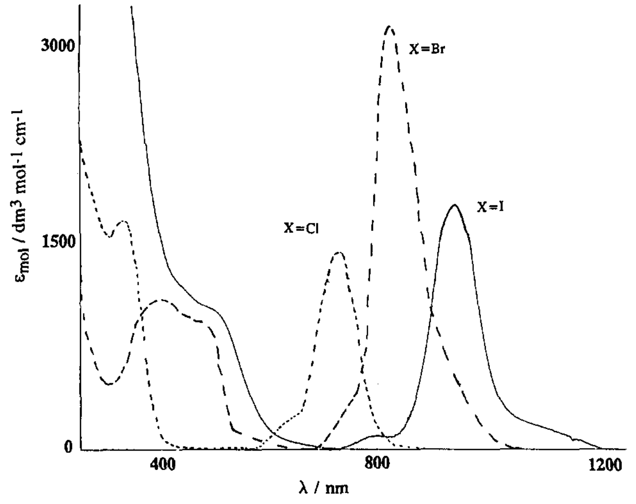

Fig. 1. UV–Vis spectra of *trans*-[Ru{o-$C_6H_4(AsMe_2)_2$}$_2X_2$][BF_4] (X = Cl, Br or I) in CH_2Cl_2 solution.

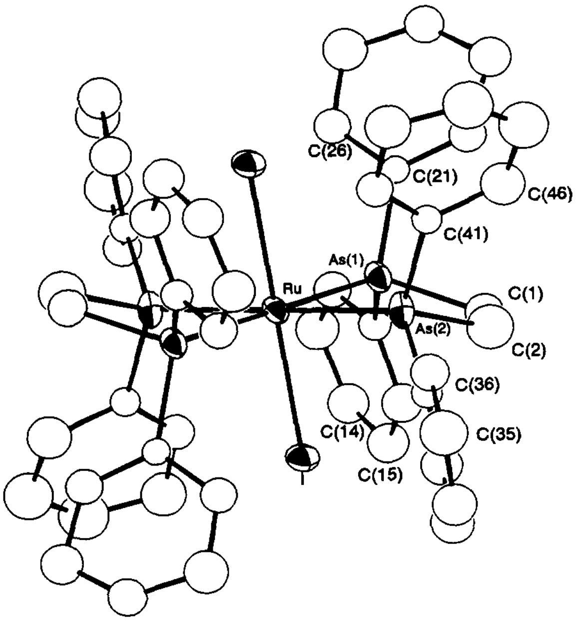

Fig. 2. Cation in [Ru($Ph_2AsCH_2CH_2AsPh_2$)$_2I_2$]BF_4 showing the atom labelling scheme. Thermal ellipsoids are drawn at the 20% probability level and no H atoms are shown.

3.2. Palladium complexes

Previous studies have shown [20] that palladium(II) complexes such as [Pd{o-$C_6H_4(AsMe_2)_2$}$_2$]I_2 react with molecular iodine to form the palladium(II) polyiodide, [Pd{o-$C_6H_4(AsMe_2)_2$}$_2$][I_3]$_2$. Similar metal(II) polyiodides are formed from diiodine and corresponding platinum(II) and nickel(II) [21,22] complexes. However nitric acid oxidation of [Pt{o-$C_6H_4(AsMe_2)_2$}$_2$]I_2 and [Ni{o-$C_6H_4(AsMe_2)_2$}$_2$]I_2 yield respectively the platinum(IV) [Pt{o-$C_6H_4(AsMe_2)_2$}$_2I_2$][ClO_4]$_2$ [22] and nickel(III) [Ni{o-$C_6H_4(AsMe_2)_2$}$_2I_2$]BF_4 [5] complexes. Hence the reaction of nitric acid with the palladium(II) iodocomplexes [Pd(L–L)$_2$]I_2, (L–L = o-$C_6H_4(PMe_2)_2$, o-$C_6H_4(AsMe_2)_2$, $Me_2PCH_2CH_2PMe_2$) was explored. However under a variety of conditions, including reaction of the solid palladium complex with conc. HNO_3, or of a suspension of the palladium complexes in 70% $HClO_4$ or 40% HBF_4 with conc. HNO_3 at various temperatures between ambient and −20 °C, the reactions resulted in liberation of diiodine and sometimes polyiodide formation, rather than oxidation of the metal centre. The reactions of the [Pd(L–L)$_2$]Cl_2 with HNO_3 in aq. HBF_4 solution readily generated the known [2] Pd(IV) complexes (Table 7), and the structure of one example is described below. The reaction of these Pd(IV) chloro complexes in MeCN solution with N^nBu_4I led to rapid precipitation of green–black solids, identified as palladium(II) polyiodides [Pd(L–L)$_2$][I_3]$_2$ by analysis and spectroscopic data, (cf. Ref. [20]). Unfortunately these compounds are poorly soluble in MeCN or chlorinated solvents and decomposed by others with loss of iodine, and attempts to grow cystals for an X-ray study have been unsuccesful.

3.2.1. Structure of trans-[Pd(o-$C_6H_4(PMe_2)_2$)$_2Cl_2$][BF_4]$_2$

The structure consists of discrete centrosymmetric cations (Fig. 3) and selected molecular parameters are shown in Table 8. The structure may be compared with that of the diarsine analogue [Pd(o-$C_6H_4(AsMe_2)_2$)$_2Cl_2$][ClO_4]$_2$ [2] which has an identical Pd–Cl distance. The diphosphine ligand geometry is very similar to that found in [Ni{o-$C_6H_4(PMe_2)_2$}$_2$]I_{10} [21]. This complex represents a valu-

Table 6
Selected bond lengths (Å) and angles (°) for [Ru($Ph_2AsCH_2CH_2AsPh_2$)$_2I_2$]BF_4

Ru–As(1)	2.498(3)	Ru–I	2.619(2)
Ru–As(2)	2.516(3)	As(1)...As(2)	3.278
As–C	1.91(4)–1.98(3)	C–C (phenyl)	1.26(5)–1.47(4)
		C(1)–C(2)	1.42(4)
I–Ru–As(1)	88.0(1)	As(1)–Ru–As(2)	81.7(1)
I–Ru–As(2)	88.4(1)		
Ru–As(1)–C(1)	108(1)	Ru–As(2)–C(2)	104(1)
Ru–As(1)–C(11)	121.5(9)	Ru–As(2)–C(31)	123.7(8)
Ru–As(1)–C(21)	117.5(9)	Ru–As(2)–C(41)	119.0(9)
C(1)–As(1)–C(11)	99(1)	C(2)–As(2)–C(31)	100(2)
C(1)–As(1)–C(21)	103(1)	C(2)–As(2)–C(41)	109(2)
C(11)–As(1)–C(21)	104(1)	C(31)–As(2)–C(41)	99(1)
C(1)–C(2)–As(2)	124(3)	C(2)–C(1)–As(1)	115(3)

Table 7
Palladium compounds

Compound	Colour	UV-Vis E_{max} (10^3 cm^{-1}) (ϵ_{mol}/dm^3 mol^{-1} cm^{-1}) [a]	$^{31}P\{^1H\}$ NMR (ppm) [b]
$Pd\{o\text{-}C_6H_4(PMe_2)_2\}_2I_2$	yellow	32.3(2680), 25.7(300)	+31.5
$[Pd\{o\text{-}C_6H_4(PMe_2)_2\}_2][I_3]_2$	dark green	34.2(18000), 27.8(8500)	+37.0
$Pd(Me_2PCH_2CH_2PMe_2)_2I_2$	yellow	35.8(5700), 27.4(340)	+38.9
$[Pd(Me_2PCH_2CH_2PMe_2)_2][I_3]_2$	dark green	34.5(11400), 27.8(6200)	+42.5
$Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2$	red–orange	36.0(sh), 32.8(sh), 24.7(2800)	
$[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2][I_3]_2$	dark green	34.5(11600), 27.8(5450)	
$[Pd\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2][BF_4]_2$	orange	34.4(8350), 23.8(360)	+64.0
$[Pd(Me_2PCH_2CH_2PMe_2)_2Cl_2][BF_4]_2$	brown	35.7(6340), 23.4(1540)	+66.5
$[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][BF_4]_2$	orange–brown	30.6(sh), 22.2(sh)	

[a] Measured in freshly prepared CH_3CN solution.
[b] In MeCN relative to 85% H_3PO_4.

Table 8
Selected bond lengths (Å) and angles (°) for $[Pd\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2][BF_4]_2$

Pd–P(1)	2.366(1)	Pd–Cl	2.308(1)
Pd–P(2)	2.368(1)		
P(1)–C(1)	1.802(4)	P(2)–C(3)	1.803(4)
P(1)–C(2)	1.799(4)	P(2)–C(4)	1.808(4)
P(1)–C(5)	1.805(3)	P(2)–C(10)	1.810(3)
C(5)–C(6)	1.398(4)	C(8)–C(9)	1.378(5)
C(6)–C(7)	1.380(5)	C(9)–C(10)	1.390(4)
C(7)–C(8)	1.391(5)	C(10)–C(5)	1.403(4)
		C–H	0.88(3)–1.04(4)
Cl–Pd–P(1)	94.37(3)	P(1)–Pd–P(2)	84.34(3)
Cl–Pd–P(2)	92.83(3)		
Pd–P(1)–C(1)	114.5(1)	Pd–P(2)–C(3)	116.1(1)
Pd–P(1)–C(2)	116.0(1)	Pd–P(2)–C(4)	114.9(1)
Pd–P(1)–C(5)	106.3(1)	Pd–P(2)–C(10)	106.5(1)
C(1)–P(1)–C(2)	106.7(2)	C(3)–P(2)–C(4)	106.6(2)
C(1)–P(1)–C(5)	104.6(2)	C(3)–P(2)–C(10)	105.8(2)
C(2)–P(1)–C(5)	108.0(2)	C(4)–P(2)–C(10)	106.1(2)
C(10)–C(5)–P(1)	118.8(2)	C(5)–C(10)–P(2)	119.7(2)

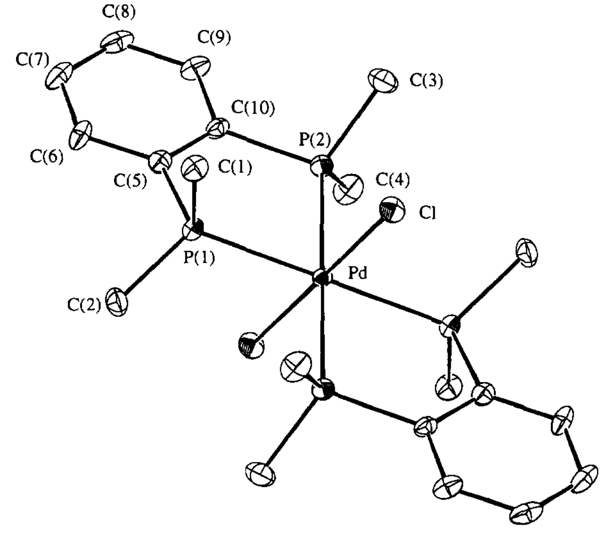

Fig. 3. Cation in $[Pd\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2][BF_4]_2$ showing the atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level and no H atoms are shown.

able addition to the small number of crystallographically characterised Pd^{IV} compounds [1].

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