

# Complexes of the Platinum Metals. Part 41.<sup>1</sup> Oxidative-substitution Reactions at Ruthenium(II) and Osmium(II) involving *N,N'*-Diphenylamidinate Ligands†

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Ruthenium(II) and osmium(II) complexes  $[\text{MCl}_2(\text{PPh}_3)_3]$  undergo oxidative-substitution reactions with *N,N'*-diphenylamidines  $\text{PhN}=\text{C}(\text{R})-\text{NPh}$  (R = H, Me, Et or Ph) under mild conditions to form the ruthenium(III) and osmium(III) products  $[\text{MCl}_2\{\text{PhN}=\text{C}(\text{R})=\text{NPh}\}(\text{PPh}_3)_2]$  (M = Ru; R = H or Ph; M = Os, R = H, Me or Ph). However, in contrast to other systems of this type, more prolonged reaction times lead to further substitution and/or oxidation steps which afford the ruthenium(III) complexes  $[\text{RuCl}\{\text{PhN}=\text{C}(\text{R})=\text{NPh}\}_2(\text{PPh}_3)]$  and the osmium(IV) species  $[\text{OsCl}_2\{\text{PhN}=\text{C}(\text{R})=\text{NPh}\}_2]$  (R = Me, Et or Ph). The crystal structure of *trans*- $[\text{OsCl}_2\{\text{PhN}=\text{C}(\text{Et})=\text{NPh}\}_2]$  has been determined.

Some years ago one of us (S. D. R.) reported that treatment of the halides  $[\text{MX}_2(\text{PPh}_3)_3]$  (M = Ru or Os; X = Cl or Br) with carboxylic acids  $\text{RCO}_2\text{H}$  (R = alkyl or aryl) in warm benzene under aerobic conditions gave the ruthenium(III) and osmium(III) complexes  $[\text{MX}_2(\text{O}_2\text{CR})(\text{PPh}_3)_2]$ .<sup>2</sup> We have subsequently shown that reactions of this type, to which we have applied the term 'oxidative substitution', can be extended to involve other weak organic acids. Thus under similar conditions 1,3-diaryltriazenes and  $\beta$ -diketones give the products  $[\text{MX}_2(\text{RN}=\text{N}=\text{NR})(\text{PPh}_3)_2]$ <sup>3</sup> and  $[\text{MX}_2(\beta\text{-dik})(\text{PPh}_3)_2]$ <sup>4</sup> respectively. We now find that *N,N'*-diarylamidines participate in similar reactions to yield oxidative-substitution products  $[\text{MX}_2\{\text{PhN}=\text{C}(\text{R})=\text{NPh}\}(\text{PPh}_3)_2]$  which in turn undergo further oxidations and/or substitutions to afford the ruthenium(III) and osmium(IV) complexes  $[\text{RuCl}\{\text{PhN}=\text{C}(\text{R})=\text{NPh}\}_2(\text{PPh}_3)]$  and  $[\text{OsCl}_2\{\text{PhN}=\text{C}(\text{R})=\text{NPh}\}_2]$  respectively. The X-ray crystal structure of one of the osmium(IV) products  $[\text{OsCl}_2\{\text{PhN}=\text{C}(\text{Et})=\text{NPh}\}_2]$  is reported.

## Experimental

The ruthenium and osmium complexes  $[\text{MCl}_2(\text{PPh}_3)_3]$ <sup>3,5</sup> and the amidines<sup>6,7</sup> were prepared by standard literature methods. Light petroleum used had a boiling range of 60–80 °C. Reactions were performed in vessels open to the atmosphere and heated on a water-bath. Infrared spectra were taken as Nujol mulls on a Perkin Elmer 983G spectrometer. Magnetic moments were measured using a Johnson Matthey magnetic susceptibility balance. Elemental analyses were performed by the microanalytical service at University College, London. Melting points were taken in sealed tubes under nitrogen.

*Dichloro(N,N'-diphenylformamidinato)bis(triphenylphosphine)ruthenium(III)*.—Dichlorotris(triphenylphosphine)ruthenium(II) (0.31 g, 0.32 mmol) was added to a solution of *N,N'*-diphenylformamidine (0.19 g, 0.97 mmol) in benzene (20 cm<sup>3</sup>). The mixture was heated at 70–80 °C for 4 h under aerobic conditions with occasional stirring then allowed to cool. Filtration afforded a green crystalline solid which was washed with benzene and light petroleum, then dried *in vacuo*. Yield

0.07 g (24%), m.p. 222–225 °C (Found: C, 67.25; H, 4.75; N, 2.8. Calc. for  $\text{C}_{49}\text{H}_{41}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}$ : C, 66.0; H, 4.65; N, 3.15%).

*Dichloro(N,N'-diphenylbenzamidinato)bis(triphenylphosphine)ruthenium(III)* was similarly prepared from *N,N'*-diphenylbenzamidine and was isolated as dark brown crystals (32%) which become dark green when powdered. M.p. 202–206 °C (Found: C, 67.75; H, 4.8; N, 2.85. Calc. for  $\text{C}_{55}\text{H}_{45}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}$ : C, 68.25; H, 4.7; N, 2.9%).

*Chlorobis(N,N'-diphenylacetamidinato)(triphenylphosphine)ruthenium(III)*.—Dichlorotris(triphenylphosphine)ruthenium(II) (1.05 g, 1.1 mmol) was added to a solution of *N,N'*-diphenylacetamidine (1.5 g, 7.17 mmol) in benzene (150 cm<sup>3</sup>). The mixture was heated at 70–80 °C for 8 h under aerobic conditions to give a green solution which was subsequently cooled and filtered. The filtrate was evaporated to dryness under reduced pressure and the residue crystallised from dichloromethane–methanol to yield large emerald-green crystals which were filtered off, washed successively with methanol and light petroleum, and then dried *in vacuo*. Yield 0.76 g (84%), m.p. 212–215 °C (Found: C, 66.8; H, 4.95; N, 6.75. Calc. for  $\text{C}_{46}\text{H}_{41}\text{ClN}_4\text{PRu}$ : C, 67.6; H, 5.05; N, 6.85%).

*Chlorobis(N,N'-diphenylpropionamidinato)(triphenylphosphine)ruthenium(III)*.—Dichlorotris(triphenylphosphine)ruthenium(II) (0.5 g, 0.52 mmol) was added to a solution of *N,N'*-diphenylpropionamidine (0.54 g, 2.4 mmol) in benzene (75 cm<sup>3</sup>). The mixture was heated at 70–80 °C for 1 h under aerobic conditions with occasional stirring, then allowed to cool. Filtration of the cooled solution to remove traces of black solid, followed by evaporation to dryness under reduced pressure and crystallisation of the residue from dichloromethane–methanol, yielded large dark green crystals which were filtered off, washed with methanol and light petroleum then dried *in vacuo*. Yield 0.24 g (54%), m.p. 228 °C (Found: C, 68.3; H, 5.4; N, 6.75. Calc. for  $\text{C}_{48}\text{H}_{45}\text{ClN}_4\text{PRu}$ : C, 68.2; H, 5.35; N, 6.65%).

*Chlorobis(N,N'-diphenylbenzamidinato)(triphenylphosphine)ruthenium(III)–Dichloromethane* (1/0.25).—Dichlorotris(triphenylphosphine)ruthenium(II) (0.4 g, 0.42 mmol) was added to a solution of *N,N'*-diphenylbenzamidine (1.13 g, 4.17 mmol) in benzene (75 cm<sup>3</sup>). The mixture was heated at 70–80 °C for 9 h under aerobic conditions with occasional stirring, then allowed to cool. Filtration of the cooled solution followed by evapor-

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

**Table 1** Atomic coordinates ( $\times 10^4$ ) for  $[\text{OsCl}_2\{\text{PhN}=\text{C}(\text{Et})=\text{NPh}\}_2]$ 

Atom	x	y	z
Os	0	0	0
Cl(1)	1013(1)	-1200(1)	-237(2)
N(1)	682(3)	149(3)	2689(5)
N(2)	110(2)	1474(4)	-1544(5)
C(1)	-400(3)	969(5)	-3095(6)
C(2)	-561(3)	1481(5)	-4881(6)
C(3)	-1213(5)	2539(7)	-5623(8)
C(4)	1187(3)	1125(5)	3833(6)
C(5)	1855(3)	843(6)	5400(6)
C(6)	2328(4)	1863(7)	6408(7)
C(7)	2157(4)	3158(7)	5896(8)
C(8)	1510(4)	3447(6)	4332(8)
C(9)	1022(3)	2436(5)	3304(7)
C(10)	595(3)	2622(5)	-1266(6)
C(11)	285(5)	3858(6)	-1598(11)
C(12)	787(7)	4941(6)	-1249(18)
C(13)	1581(6)	4813(7)	-562(12)
C(14)	1897(5)	3581(9)	-175(10)
C(15)	1408(4)	2480(7)	-519(9)

**Table 2** Selected bond lengths (Å) and angles (°) for  $[\text{OsCl}_2\{\text{PhN}=\text{C}(\text{Et})=\text{NPh}\}_2]^*$ 

Os-Cl(1)	2.321(2)	Os-N(1)	2.047(4)
Os-N(2)	2.037(4)	Os-N(1A)	2.047(4)
Os-Cl(1A)	2.321(2)	N(1)-C(1A)	1.347(7)
Os-N(2A)	2.037(4)	N(2)-C(10)	1.419(7)
N(1)-C(4)	1.402(6)	C(1)-N(1A)	1.346(7)
N(2)-C(1)	1.326(5)	C(4)-C(5)	1.381(6)
C(1)-C(2)	1.485(7)	C(5)-C(6)	1.372(8)
C(2)-C(3)	1.524(9)	C(7)-C(8)	1.363(8)
C(4)-C(9)	1.381(7)	C(10)-C(11)	1.347(8)
C(6)-C(7)	1.363(9)	C(11)-C(12)	1.379(12)
C(8)-C(9)	1.381(8)	C(13)-C(14)	1.348(11)
C(10)-C(15)	1.367(9)		
C(12)-C(13)	1.335(16)		
C(14)-C(15)	1.379(11)		
Cl(1)-Os-N(1)	90.1(1)	Cl(1)-Os-N(2)	90.5(1)
N(1)-Os-N(2)	117.4(1)	N(1)-Os-Cl(1A)	89.9(1)
Cl(1)-Os-Cl(1A)	180.0(1)	N(1)-Os-N(1A)	180.0(1)
N(2)-Os-Cl(1A)	89.5(1)	Cl(1)-Os-N(2A)	89.5(1)
Cl(1)-Os-N(1A)	89.9(1)	N(2)-Os-N(2A)	180.0(1)
N(2)-Os-N(1A)	62.6(1)	Cl(1A)-Os-N(2A)	90.5(1)
Cl(1A)-Os-N(1A)	90.1(1)	Os-N(1)-C(1A)	95.6(2)
N(1)-Os-N(2A)	62.6(1)	Os-N(2)-C(1)	96.7(3)
N(1A)-Os-N(2A)	117.4(1)	C(1)-N(2)-C(10)	126.8(4)
Os-N(1)-C(4)	134.9(3)	C(2)-C(1)-N(1A)	128.2(4)
C(4)-N(1)-C(1A)	129.0(4)	N(1)-C(4)-C(5)	123.8(4)
Os-N(2)-C(10)	136.2(3)	C(5)-C(4)-C(9)	118.7(4)
N(2)-C(1)-C(2)	126.5(5)	C(5)-C(6)-C(7)	121.5(5)
N(2)-C(1)-N(1A)	105.1(4)	C(7)-C(8)-C(9)	120.1(6)
C(1)-C(2)-C(3)	115.0(6)	N(2)-C(10)-C(11)	122.2(6)
N(1)-C(4)-C(9)	117.4(4)	C(11)-C(10)-C(15)	118.5(6)
C(4)-C(5)-C(6)	119.7(5)	C(11)-C(12)-C(13)	122.3(7)
C(6)-C(7)-C(8)	119.4(6)	C(13)-C(14)-C(15)	120.6(8)
C(4)-C(9)-C(8)	120.6(4)		
N(2)-C(10)-C(15)	119.1(5)		
C(10)-C(11)-C(12)	119.7(8)		
C(12)-C(13)-C(14)	118.3(8)		
C(10)-C(15)-C(14)	120.5(6)		

\* Atoms labelled A are generated by the symmetry operation  $-x, -y, -z$ .

ation under reduced pressure gave a green oil which was solidified by trituration under methanol. Crystallisation from dichloromethane-methanol gave dark green microcrystals which were filtered off, washed with methanol and light petroleum then dried *in vacuo*. Yield 0.08 g (20%), m.p. 205–207 °C (Found: C, 70.2; H, 4.9; Cl, 4.95; N, 5.7. Calc. for

$\text{C}_{36}\text{H}_{45}\text{ClN}_4\text{PRu}\cdot 0.25\text{CH}_2\text{Cl}_2$ : C, 70.2; H, 4.75; Cl, 5.5; N, 5.8%).

*Dichloro(N,N'-diphenylformamidinato)bis(triphenylphosphine)osmium(III)*.—Dichlorotris(triphenylphosphine)osmium(II) (0.5 g, 0.48 mmol) was added to a solution of *N,N'*-diphenylformamidine (0.43 g, 2.2 mmol) in benzene (75 cm<sup>3</sup>). The mixture was heated at 70–80 °C for 1 h under aerobic conditions with occasional stirring then allowed to cool. Filtration followed by evaporation under reduced pressure gave a green oil which was crystallised from dichloromethane-methanol to yield green microcrystals. These were filtered off, washed with methanol and light petroleum then dried *in vacuo*. Yield 0.08 g (20%), m.p. 250–254 °C (Found: C, 59.75; H, 4.2; N, 2.95. Calc. for  $\text{C}_{49}\text{H}_{41}\text{Cl}_2\text{N}_2\text{OsP}_2$ : C, 60.0; H, 4.2; N, 2.85%).

Similarly prepared were dichloro(*N,N'*-diphenylacetamidinato)bis(triphenylphosphine)osmium(III) from *N,N'*-diphenylacetamidine, isolated as dark green microcrystals (17%), m.p. 182 °C (Found: C, 60.25; H, 4.4; N, 2.8. Calc. for  $\text{C}_{50}\text{H}_{43}\text{Cl}_2\text{N}_2\text{P}_2\text{Os}$ : C, 60.35; H, 4.35; N, 2.8%), and dichloro(*N,N'*-diphenylbenzamidinato)bis(triphenylphosphine)osmium(III), from *N,N'*-diphenylbenzamidine, isolated as a dark green powder (24%), m.p. 203 °C (Found: C, 62.05; H, 4.35; N, 2.45. Calc. for  $\text{C}_{55}\text{H}_{45}\text{Cl}_2\text{N}_2\text{OsP}_2$ : C, 62.5; H, 4.3; N, 2.65%).

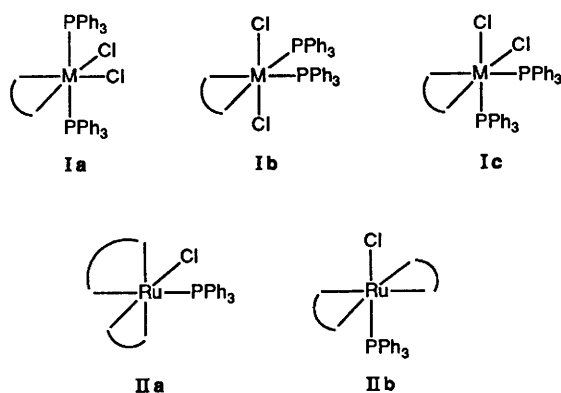
*Dichlorobis(N,N'-diphenylacetamidinato)osmium(IV)*.—Dichlorotris(triphenylphosphine)osmium(II) (1.13 g, 1.08 mmol) was added to a solution of *N,N'*-diphenylacetamidine (1.47 g, 7.02 mmol) in benzene (150 cm<sup>3</sup>). The mixture was heated at 70–80 °C for 8 h under aerobic conditions with occasional shaking, then cooled. Filtration followed by evaporation of the filtrate under reduced pressure gave a dark solid. Crystallisation from dichloromethane-methanol afforded dark purple microcrystals which were washed with methanol and light petroleum then dried *in vacuo*. Yield 0.23 g (31%), m.p. 278 °C (Found: C, 49.3; H, 3.7; N, 8.15. Calc. for  $\text{C}_{28}\text{H}_{26}\text{Cl}_2\text{N}_4\text{Os}$ : C, 49.5; H, 3.85; N, 8.25%).

Similarly prepared were dichlorobis(*N,N'*-diphenylpropionamidinato)osmium(IV), using *N,N'*-diphenylpropionamidine, isolated as dark green microcrystals (30%), m.p. 238 °C (Found: C, 51.0; H, 4.05; N, 7.8. Calc. for  $\text{C}_{30}\text{H}_{30}\text{Cl}_2\text{N}_4\text{Os}$ : C, 50.9; H, 4.25; N, 7.9%), and dichlorobis(*N,N'*-diphenylbenzamidinato)osmium(IV), using *N,N'*-diphenylbenzamidine, isolated as dark green microcrystals (28%), m.p. 280 °C (Found: C, 56.9; H, 3.3; N, 6.85. Calc. for  $\text{C}_{38}\text{H}_{30}\text{Cl}_2\text{N}_4\text{Os}$ : C, 56.8; H, 3.75; N, 6.95%).

*Crystallography for*  $[\text{OsCl}_2\{\text{PhNC}(\text{Et})\text{NPh}\}_2]$ .—*Crystal data*.  $\text{C}_{30}\text{H}_{30}\text{Cl}_2\text{N}_4\text{Os}$ ,  $M = 707.700$ , monoclinic, space group  $P2_1/a$ ,  $a = 18.628(5)$ ,  $b = 10.049(2)$ ,  $c = 8.395(2)$  Å,  $\beta = 116.32(2)^\circ$ ,  $U = 1409 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.67 \text{ g cm}^{-3}$ ,  $F(000) 696$ ,  $\mu(\text{Mo-K}\alpha) = 47.5 \text{ cm}^{-1}$ .

*Data collection*. A dark green single crystal of approximate size  $0.40 \times 0.40 \times 0.25$  mm was mounted on a glass fibre. All geometric and intensity data were taken from this sample using an automated four-circle diffractometer (Nicolet R3 mV) equipped with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 30 reflections taken from a rotation photograph and centred by the diffractometer. The  $\omega$ - $2\theta$  technique was used to measure 2704 reflections (2471 unique) in the range  $5 < 2\theta < 50^\circ$ . Three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarisation effects, and empirically for absorption. The 1915 unique data with  $I > 3.0\sigma(I)$  were used to solve and refine the structure in the monoclinic space group  $P2_1/a$ .

*Structure solution*. The structure was solved by Patterson methods and developed by using alternating cycles of least-squares refinement and Fourier difference synthesis. The

**Table 3** Magnetic and far-infrared data

Complex	R	$\mu_{\text{eff}}$	$\nu(\text{M}-\text{Cl})/\text{cm}^{-1}$
[RuCl <sub>2</sub> {PhN=C(R)NPh}(PPh <sub>3</sub> ) <sub>2</sub> ]	H	1.62	308 [318 (sh)]
	Ph	1.74	310 [305 (sh)]
[RuCl{PhN=C(R)NPh} <sub>2</sub> (PPh <sub>3</sub> )]	Me	1.84	268 [263 (sh)]
	Et	1.91	274w [264 (sh)]
	Ph	1.76	304 [309 (sh)]
[OsCl <sub>2</sub> {PhN=C(R)NPh}(PPh <sub>3</sub> ) <sub>2</sub> ]	H	1.78	298 [303 (sh)]
	Me	2.09	298 [313 (sh)]
	Ph	3.59	310
[OsCl <sub>2</sub> {PhN=C(R)NPh} <sub>2</sub> ]	Me	0.78	324
	Et	0.83	321
	Ph	0.31	324

**Table 4** Proton and <sup>13</sup>C-<sup>1</sup>H NMR spectral data ( $\delta$ ,  $J$  in Hz) for paramagnetic osmium(IV) complexes *trans*-[OsCl<sub>2</sub>{PhN=C(R)NPh}<sub>2</sub>]

R	<sup>1</sup> H: $\delta$ (t, <sup>3</sup> J <sub>HH</sub> , CH <sub>2</sub> CH <sub>3</sub> ), 6.68 (t), 7.10 (d) and 8.50 (d of d) (all <sup>3</sup> J <sub>HH</sub> ca. 8, Ph), 11.96 (q, <sup>3</sup> J <sub>HH</sub> 7.5, CH <sub>2</sub> CH <sub>3</sub> ) <sup>13</sup> C- <sup>1</sup> H: -12.5 (CH <sub>2</sub> CH <sub>3</sub> ), 60.70 (CH <sub>2</sub> CH <sub>3</sub> ), 128.4, 129.0, 129.4 and 155.0 (Ph), 183.2 (NCN)
Et	<sup>1</sup> H: 6.55 (t, <sup>3</sup> J <sub>HH</sub> 7.5), 6.90 (d, <sup>3</sup> J <sub>HH</sub> 8.5) and ca. 8.20–8.25 (m)* (NPh), 6.68 (t, <sup>3</sup> J <sub>HH</sub> 7.5), 6.82 (d, <sup>3</sup> J <sub>HH</sub> 8.0) and ca. 8.20–8.25 (m)* (CPh) <sup>13</sup> C- <sup>1</sup> H: 94.8, 127.5, 128.5, 133.1, 136.4, 150.2 and 157.1 (NPh, CPh), 186.0 (NCN)

\* Overlapping patterns of sharp lines.

molecule sits on the inversion centre at the origin. The non-hydrogen atoms were refined anisotropically while hydrogens were placed in idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter ( $U = 0.08 \text{ \AA}^2$ ). The final cycle of least-squares refinement included 169 parameters for 1915 variables and did not shift any parameter by more than 0.001 times its standard deviation. The residuals were  $R = 0.0265$ ,  $R' = 0.0275$  (weighting scheme:  $w^{-1} = \delta^2 F + 0.000 15 F^2$ ) and the final Fourier difference map was featureless with no peaks greater than  $0.77 \text{ e \AA}^{-3}$ . Structure solution used the SHELXTL PLUS program package<sup>8</sup> on a micro Vax II computer. Atomic positional parameters are given in Table 1, selected bond lengths and angles in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

## Results and Discussion

Previously reported examples of 'oxidative substitution' involving ruthenium(II) and osmium(II) complexes [MCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] afford a single product type of the general form MCl<sub>2</sub>(chelate)-

(PPh<sub>3</sub>)<sub>2</sub> (chelate = carboxylate,  $\beta$ -diketonate or 1,3-diaryltriazene)<sup>2–4</sup> for which the *trans*-phosphine isomer **Ia**<sup>9–12</sup> appears to be more common than the *trans*-halide isomer **Ib**.<sup>12</sup> The third possible isomer **Ic** is unknown. In many cases the products are of low solubility and deposit from the reaction solutions in high yield. We now find that related reactions involving *N,N'*-diphenylamidines PhN=C(R)–NPh follow a more complex pathway leading to at least two additional product types, the ruthenium(III) species RuCl(chelate)<sub>2</sub>(PPh<sub>3</sub>) and the osmium(IV) derivatives OsCl<sub>2</sub>(chelate)<sub>2</sub>. The courses of individual reactions show a significant dependence upon the nature of the groups R on the amidinate ligands. Furthermore the products rarely deposit spontaneously from the reaction solutions and are usually obtained in only modest yield on work-up.

The addition of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] to aerobic solutions of amidines PhN=C(R)–NPh in warm benzene followed by heating at 70–80 °C for 1–9 h affords dark solutions from which the products [RuCl<sub>2</sub>{PhN=C(R)NPh}(PPh<sub>3</sub>)<sub>2</sub>] (R = H or Ph) or [RuCl{PhN=C(R)NPh}<sub>2</sub>(PPh<sub>3</sub>)] (R = Me, Et or Ph) can be obtained in modest yields. In one instance a further product [RuCl{PhN=C(Et)NPh}<sub>2</sub>] was obtained and gave good analytical figures. However this synthesis cannot reliably be repeated. The complexes [RuCl<sub>2</sub>{PhN=C(R)NPh}(PPh<sub>3</sub>)<sub>2</sub>] are isolated as dark green, air-stable, crystalline solids with magnetic moments in the range 1.6–1.8 consistent with their formulation as octahedral, low-spin ruthenium(III) species. In the absence of X-ray crystallographic evidence it is not possible to distinguish unambiguously between the three possible isomeric forms **Ia–Ic**. However it seems probable that the *trans*-phosphine geometry **Ia** is adopted in each case. Infrared spectra which each show a partially resolved pair of  $\nu(\text{Ru}-\text{Cl})$  absorptions at ca. 310 cm<sup>-1</sup> are consistent with this conclusion.

The bis(chelate) products [RuCl{PhN=C(R)NPh}<sub>2</sub>(PPh<sub>3</sub>)] (R = Me, Et or Ph) are also isolated as dark green crystals with magnetic moments (ca. 1.75–1.95) typical of low-spin ruthenium(III). The paramagnetic nature of the products precludes structure determination by NMR spectroscopy and all attempts to grow crystals suitable for X-ray work failed. We are therefore unable to differentiate between the *cis* and *trans* geometrical isomers **IIa** and **IIb**.

The corresponding reactions of [OsCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] with aerobic solutions of amidines in warm benzene also gave dark solutions from which two series of products, the osmium(III) species [OsCl<sub>2</sub>{PhN=C(R)NPh}(PPh<sub>3</sub>)<sub>2</sub>] and the osmium(IV) derivatives [OsCl<sub>2</sub>{PhN=C(R)NPh}<sub>2</sub>], could be isolated in modest yields. The complexes [OsCl<sub>2</sub>{PhN=C(R)NPh}(PPh<sub>3</sub>)<sub>2</sub>] (R = H, Me or Ph) are obtained as paramagnetic dark green microcrystalline solids. With one exception (R = Ph) the magnetic moments are in the range ca. 1.7–2.1 and are consistent with low-spin osmium(III). The far-infrared data (Table 3) are compatible with a *cis*-dichloride stereochemistry **Ia** in at least two of the three examples characterised. The osmium systems have not afforded any products of the general form [OsCl{PhN=C(R)NPh}<sub>2</sub>(PPh<sub>3</sub>)] analogous to those observed for ruthenium. However, they have furnished instead green crystalline, phosphine-free osmium(IV) complexes [OsCl<sub>2</sub>{PhN=C(R)NPh}<sub>2</sub>] (R = Me, Et or Ph). In one instance (R = Me) the crystals display a purple colour in the massive state but turn green on crushing. The magnetic moments (0.3–0.85) recorded for the complexes are much lower than the 'spin-only' value for a low-spin d<sup>4</sup> ion but are comparable with those previously reported for some osmium(IV) ethylenediamine complexes.<sup>13</sup> The <sup>1</sup>H and <sup>13</sup>C-<sup>1</sup>H NMR spectra (Table 4) are broad (R = Me) or show substantial paramagnetic 'Knight' shifts (R = Et or Ph) as expected for low-spin d<sup>4</sup> osmium(IV) species.<sup>14</sup> Complete loss of phosphine from platinum metal complexes under mild conditions is relatively rare. Moreover, the osmium(IV) products obtained provide the first examples of amidinate ligands bound to a high (>3+)-oxidation-state d-block metal centre. Therefore the X-ray

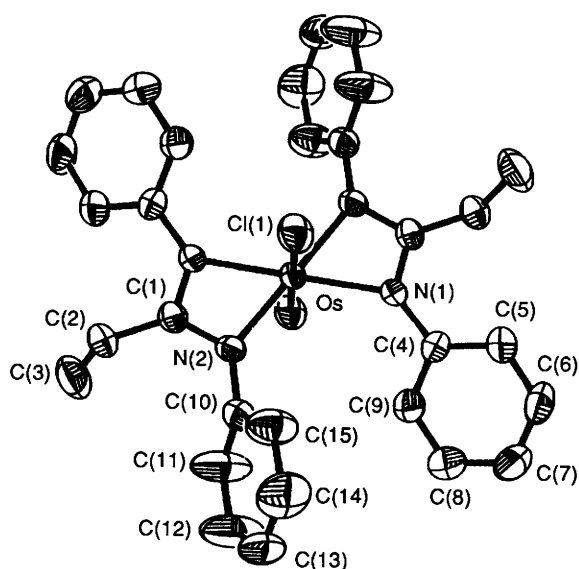


Fig. 1 Molecular structure of *trans*-[OsCl<sub>2</sub>{PhN---C(Et)---NPh}<sub>2</sub>]

crystal structure of one example [OsCl<sub>2</sub>{PhN---C(Et)---NPh}<sub>2</sub>] has been determined.

The molecular structure is shown in Fig. 1, and bond lengths and angles are given in Table 2. The complex has distorted-octahedral stereochemistry with *trans*-chloride ligands (Cl–Os–Cl 180° by crystal symmetry). The angles subtended by the amidinate ligands at the osmium centre [62.6(1)°] reflect the narrow bite of the chelate and are very similar to those recently found for the ruthenium(III) and rhodium(III) tris(acetamidinato) complexes [average N–Ru–N

62.7(3), N–Rh–N 62.8(3)°].<sup>15</sup> The Os–Cl and Os–N bonds which average 2.321(2) and 2.042(4) Å respectively are typical of octahedral osmium(IV).

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