Complexes of the Platinum Metals. Part 44.[1] Benzamidato and Toluamidato Derivatives of Ruthenium and Osmium†

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Benzamide reacts with [RuH$_2$(CO)(PPh$_3$)$_3$] and [RuH(Cl)(PPh$_3$)$_3$] or [RuCl$_2$(PPh$_3$)$_3$]–NEt$_3$ in boiling toluene to afford the amidato products [(Ph$_3$P)(OC)Ru{μ-NHC(O)C$_6$H$_4$}{μ-NHC(O)Ph}(μ-H)Ru(CO)(PPh$_3$)$_2$] **1a** and [Ru$_2$(μ-Cl)(μ-H){μ-NHC(O)Ph}$_2$(PPh$_3$)$_4$] **2a** respectively as orange or red air-stable crystals. Parallel reactions with *o*-, *m*- and *p*-toluamides yield analogous products **1b**–**1d** and **2b**–**2d**. Carbonylation of [Ru$_2$(μ-Cl)(μ-H){μ-NHC(O)Ph}$_2$(PPh$_3$)$_4$] in boiling toluene affords the dicarbonyl [Ru$_2$(μ-Cl)(μ-H){μ-NHC(O)Ph}$_2$(CO)$_2$(PPh$_3$)$_2$] **3**. Benzamide also reacts with [OsH$_2$(CO)(PPh$_3$)$_3$] to yield the bis(benzamidato) complex [Os{NHC(O)Ph}$_2$(CO)$_2$(PPh$_3$)$_2$] **4**. A crystallographic study of **1a** established a binuclear structure bridged by hydride, benzamidate(1−) and benzamidate(2−) ligands.

As a logical extension of our work on the reactions of diphenylamidines PhNC(R)NHPh[1] and carboxylic acids RCO$_2$H[2] with platinum-metal hydrides and related complexes we have now turned our attention to the behaviour of amides RC(O)NH$_2$ (R = aryl) and R$_F$C(O)NH$_2$ (R$_F$ = perfluoroalkyl or -aryl) with similar systems. The synthesis of transition-metal amide (RCONH$_2$)[3,4] and amidato (RCONH$^-$)[3,5] complexes has received a fair amount of attention over the years and has recently been the focus of renewed interest following the confirmation that 'platinblau' and related compounds of possible value as anti-tumour agents contain bridging RC(O)NH$^-$ ligands.[6] However, transition-metal-mediated cleavage of amide N–H bonds remains relatively uncommon. The best known examples are provided by the syntheses of binuclear ruthenium and rhodium amidato-bridged complexes [Ru$_2$(NHCOR)$_4$Cl][7] and [Rh$_2$(NHCOR)$_4$][8] (R = Me, CMe$_3$, CF$_3$ or aryl) from the corresponding carboxylates and free amides under vigorous conditions. More recently reactions of free amides with various molybdenum,[5] iron[9] and ruthenium[9,10] hydrides have afforded a small range of complexes containing monodentate, chelate or bridging amidate(1−) ligands. Some of our own work in this area, previously reported in a preliminary communication,[10] is now described in detail.

Experimental

Ruthenium and osmium complexes were prepared by literature methods;[11,12] amides were used as purchased. Reagent-grade organic solvents were dried over molecular sieves. Reactions were performed under nitrogen but products were worked up in open flasks. Elemental analyses were performed by the microanalytical service at University College, London. Melting points were taken in sealed tubes under nitrogen.

[(Ph$_3$P)(OC)Ru{μ-NHC(O)C$_6$H$_4$}{μ-NHC(O)Ph}(μ-H)-Ru(CO)(PPh$_3$)$_2$]·0.5CH$_2$Cl$_2$ **1a**.—Carbonyldihydridotris(triphenylphosphine)ruthenium (0.8 g, 0.87 mmol) and benzamide (0.42 g, 3.47 mmol) were heated under reflux in toluene (40 cm^3) for *ca.* 11 h. The reddish brown solution was cooled to ambient temperature, filtered and then concentrated under reduced pressure to leave an oil. Crystallisation of the oil from CH$_2$Cl$_2$–MeOH gave the product as orange crystals (0.34 g, 60%), m.p. 218–222 °C (decomp.) (Found: C, 63.8; H, 4.5; N, 2.1. Calc. for C$_{70}$H$_{57}$N$_2$O$_4$P$_3$Ru$_2$·0.5CH$_2$Cl$_2$: C, 63.8; H, 4.4; N, 2.1%). The crystals used for X-ray work were desolvated by a further drying cycle.

The following were similarly prepared using the appropriate amide and 16 h of reflux: [(Ph$_3$P)(OC)Ru{μ-NHC(O)C$_6$H$_3$-Me-*o*}{μ-NHC(O)C$_6$H$_4$Me-*o*}(μ-H)Ru(CO)(PPh$_3$)$_2$]·0.5CH$_2$Cl$_2$ **1b**, as yellowish orange microcrystals (50%), m.p. 190–193 °C (Found: C, 64.8; H, 4.6; N, 1.9. Calc. for C$_{72}$H$_{61}$N$_2$O$_4$P$_3$Ru$_2$·0.5CH$_2$Cl$_2$: C, 64.2; H, 4.6; N, 2.05%); [(Ph$_3$P)(OC)Ru{μ-NHC(O)C$_6$H$_3$Me-*m*}{μ-NHC(O)C$_6$H$_4$Me-*m*}(μ-H)Ru(CO)(PPh$_3$)$_2$]·0.5CH$_2$Cl$_2$ **1c**, as orange crystals (52%), m.p. 189–193 °C (Found: C, 63.7; H, 4.6; N, 1.8. Calc. for C$_{72}$H$_{61}$N$_2$O$_4$P$_3$Ru$_2$·0.5CH$_2$Cl$_2$: C, 64.2; H, 4.6; N, 2.05%); and [(Ph$_3$P)(OC)Ru{μ-NHC(O)C$_6$H$_3$Me-*p*}{μ-NHC(O)C$_6$H$_4$-Me-*p*}(μ-H)Ru(CO)(PPh$_3$)$_2$]·0.5CH$_2$Cl$_2$ **1d**, as dark orange crystals (53%), m.p. 222–226 °C (decomp.) (Found: C, 65.05; H, 4.8; N, 2.05. Calc. for C$_{72}$H$_{61}$N$_2$O$_4$P$_3$Ru$_2$·0.5CH$_2$Cl$_2$: C, 64.2; H, 4.6; N, 2.05%).

[Ru$_2$(μ-Cl)(μ-H){μ-NHC(O)Ph}$_2$(PPh$_3$)$_4$] **2a**.—*Method* (*a*). Dichlorotris(triphenylphosphine)ruthenium (0.9 g, 0.94 mmol), benzamide (0.52 g, 4.2 mmol) and triethylamine (3 cm^3) were heated under reflux in toluene (40 cm^3) for *ca.* 10 h. During the course of the reaction triethylamine (3 cm^3) was added every 3 h. The dark reddish brown solution was cooled to ambient temperature and then concentrated under reduced pressure to leave an oil. Crystallisation from CH$_2$Cl$_2$–MeOH afforded brick-red microcrystals (0.48 g, 67%), m.p. 215–220 °C (decomp.) (Found: C, 67.2; H, 4.8; N, 1.6. Calc. for C$_{86}$H$_{73}$ClN$_2$O$_2$P$_4$Ru$_2$: C, 67.6; H, 4.8; N, 1.8%).

Method (*b*). Chlorohydridotris(triphenylphosphine)ruthenium (0.8 g, 0.86 mmol) and benzamide (0.47 g, 3.9 mmol) were added to degassed toluene (40 cm^3) and the mixture heated under reflux for *ca.* 3.5 h. The dark reddish brown solution was cooled to ambient temperature, filtered and then concentrated

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

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Table 1 Infrared[a] and NMR[b] data

Complex	Infrared (cm^{-1}) ν(CO)	^1H NMR[c] δ(RuHRu)	^{31}P NMR[d] δ(PPh_3)
1a	1953, 1912	−11.43 (d of d of d, $^2J_{HP}$ 63.5, 27.5 and 22.7)	52.55 (d of d, J_{PP} 17 and 4) 50.08 (d of d, J_{PP} 40 and 4) 22.70 (d of d, J_{PP} 40 and 17)
1b	1954, 1897	−11.18 (d of d of d, $^2J_{HP}$ 63.8, 27.9 and 21.6)	51.61 (d, J_{PP} 18) 50.32 (d, J_{PP} 40) 22.77 (d of d, J_{PP} 40 and 18)
	[e] Masked	−11.48 (d of d of d, $^2J_{HP}$ 63.1, 25.4 and 21.1)	53.22 (d, J_{PP} 14) 47.24 (d, J_{PP} 35) 29.3 (d of d, J_{PP} 35 and 14)
1c	1954, 1912	−11.43 (d of d of d, $^2J_{HP}$ 64.4, 27.3 and 23.1)	52.49 (d of d, J_{PP} 17 and 4) 50.42 (d of d, J_{PP} 40 and 4) 23.53 (d of d, J_{PP} 40 and 17)
	[e] Masked	Masked	53.68 (d of d, J_{PP} 17 and 4) 47.60 (d of d, J_{PP} 40 and 4) 31.59 (d of d, J_{PP} 40 and 17)
1d	1952, 1902	−11.36 (d of d of d, $^2J_{HP}$ 63.9, 27.3 and 23.1)	52.34 (d of d, J_{PP} 17 and 4) 50.60 (d of d, J_{PP} 40 and 4) 23.56 (d of d, J_{PP} 40 and 17)
	[e] Masked	Masked	54.02 (d, $J_{PP} \approx 16$) 47.79 (d, $J_{PP} \approx 36$) 31.65 (d of d, $J_{PP} \approx 36$ and 16)
2a		−6.66 (t of t, $^2J_{HP}$ 50.5 and 17)	53.96 (d of d, $^2J_{PP'}$ 20, $^4J_{PP'}$ 14), 33.44 (d of d, $^2J_{PP'}$ 20, $^4J_{PP'}$ 14)
2b		−7.32 (t of t, $^2J_{HP}$ 49.3 and 16)	55.0 (d of d, $^2J_{PP'}$ 20, $^4J_{PP'}$ 14), 31.51 (d of d, $^2J_{PP'}$ 20, $^4J_{PP'}$ 14)
2c		−6.58 (t of t, $^2J_{HP}$ 50.6 and 17)	53.90 (d of d, $^2J_{PP'}$ 18.0, $^4J_{PP'}$ 15), 33.69 (d of d, $^2J_{PP'}$ 18.0, $^4J_{PP'}$ 15)
2d		−6.61 (t of t, $^2J_{HP}$ 50.5 and 16)	53.93 (d of d, $^2J_{PP'}$ 19, $^4J_{PP'}$ 14), 33.62 (d of d, $^2J_{PP'}$ 19, $^4J_{PP'}$ 14)
3	1959 and 1941	−1.95 (t, $^2J_{HP}$ 12)	58.63 (s)
4	2020 and 1945		1.40 (s)

[a] Nujol mulls. [b] Solvents: CD_2Cl_2, **1a**; $CDCl_3$, **1b**–**1d**, **3**, **4**; $C_6D_5CD_3$, **2a**–**2d**. *J* in Hz. [c] At 360 MHz, $SiMe_4$ as reference. [d] At 101.2 MHz, external 85% H_3PO_4 as reference. [e] Minor isomer.

under reduced pressure to leave an oil. Crystallisation from CH_2Cl_2–MeOH afforded the product as brick-red microcrystals (0.46 g, 71%).

The following were similarly prepared [method (*b*)] using the appropriate amide and different reaction times: $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)C_6H_4Me\text{-}o\}_2(PPh_3)_4]$ **2b**, after 3.5 h of reflux as brick-red microcrystals, contaminated with other products (see Discussion); $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)C_6H_4Me\text{-}m\}_2(PPh_3)_4]$ **2c**, after 3.5 h of reflux, as brick-red microcrystals (50%), m.p. 249–254 °C (decomp.) (Found: C, 66.7; H, 4.7; N, 1.7. Calc. for $C_{88}H_{77}ClN_2O_2P_4Ru_2$: C, 67.9; H, 5.0; N, 1.8%); and $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)C_6H_4Me\text{-}p\}_2(PPh_3)_4]$ **2d**, after 4 h of reflux, as brick-red microcrystals (55%), m.p. 262–266 °C (decomp.) (Found: C, 66.6; H, 5.0; N, 1.8. Calc. for $C_{88}H_{77}ClN_2O_2P_4Ru_2$: C, 67.9; H, 5.0; N, 1.8%).

$[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)Ph\}_2(CO)_2(PPh_3)_2]$ **3**.—Complex **2a** (0.13 g, 0.085 mmol) was dissolved in toluene (30 cm^3) and the solution heated under reflux under an atmosphere of CO for *ca.* 2 h. During this period the solution changed from orange to yellow. It was cooled to ambient temperature and then concentrated under reduced pressure to leave a yellow solid. Crystallisation from CH_2Cl_2–MeOH afforded the product as yellowish orange microcrystals (0.08 g, 90%), m.p. 281–285 °C (decomp.) (Found: C, 58.45; H, 4.10; N, 2.55. Calc. for $C_{52}H_{43}ClN_2O_4P_2Ru_2$: C, 58.95; H, 4.05; N, 2.65%).

$[Os\{NHC(O)Ph\}_2(CO)_2(PPh_3)_2]\cdot MeOH$ **4**.—Carbonyldihydridotris(triphenylphosphine)osmium (0.6 g, 0.59 mmol) and benzamide (0.34 g, 0.28 mmol) were heated under reflux in 2-methoxyethanol (40 cm^3) for *ca.* 72 h. The dark yellow-brown solution was cooled, filtered and then concentrated under reduced pressure to leave an oil. The first crystallisation from CH_2Cl_2–MeOH gave white microcrystals (0.14 g), identified as starting material $[OsH_2(CO)(PPh_3)_3]$. The filtrate from the above was concentrated and left to crystallise for several days, when the required product separated as pale yellow microcrystals (0.24 g, 40%), m.p. 252–254 °C (Found: C, 60.65; H, 4.10; N, 2.4. Calc. for $C_{52}H_{42}N_2O_4OsP_2\cdot CH_3OH$: C, 61.05; H, 4.4; N, 2.7%).

Crystallography.—Crystal data for complex **1a** have been published previously.[10] The molecular structure is shown in Fig. 1.

Results and Discussion

This paper extends our previous studies on the reactions of arylcarboxylic acids, RC(O)OH,[2] and 1,3-diarylamidines, RC(NR)NHR,[1] with selected ruthenium and osmium complexes to include similar reactions of the closely related arylamides $RC(O)NH_2$. However, although comparable reaction conditions were employed for all three series of ligands, the coordination chemistry of the arylamides is proving to be much richer than that of the carboxylic acids and amidines. In particular the arylamides show a marked preference for bridging rather than the chelate mode of bonding and have generated binuclear products of types not so far encountered with the other ligands.

Reactions of Arylamides with $[RuH_2(CO)(PPh_3)_3]$.—The treatment of $[RuH_2(CO)(PPh_3)_3]$ with benzamide in boiling toluene, over a period of 11 h, affords a reddish brown solution from which, after evaporation and crystallisation (CH_2Cl_2–MeOH), an air-stable orange crystalline product **1a** can be isolated in good yield. The spectroscopic properties (Table 1) indicated that **1a** contains a bridging hydride ligand but, taken with the analytical data, did not provide sufficient information to determine the stoichiometry and structure. We therefore resorted to X-ray crystallography to resolve these points. The crystal structure of **1a** is shown in Fig. 1. The complex is indeed binuclear with a bridging hydride as anticipated; there are also two bridging benzamidate anions. The first of these is a conventional 1 – ligand co-ordinated through N- and O-donor atoms. However the second is a 2 – ligand bridging through the N atom alone and further bound to one ruthenium centre by cyclometallation through an *o*-carbon. Cyclometallated carboxylate(2 –),[13] amidinate(1 –)[14–16] and amidate(1 –)[14] ligands have previously been reported. A cyclometallated amidinate(2 –) complex has also been postulated.[17] However, to the best of our knowledge, the present complex provides the first examples of a cyclometallated amidate(2 –) ligand. The corresponding *o*-, *m*- and *p*-toluamides form a series of analogous complexes **1b**–**1d** all of which have been isolated and purified as air-stable orange crystals and characterised by means of analytical and spectroscopic data. The toluamide derivatives exist in two isomeric forms with very similar spectroscopic properties (Table 1). In almost every case the infrared [ν(CO)] and high-field ^1H NMR patterns of the minor isomer are partially obscured by those of the major isomer and cannot be accurately measured. However in each case the very distinctive ^{31}P-{^1H} NMR patterns of the isomer pairs are well resolved and clearly arise from species with closely allied structures. The apparent absence of isomers in the case of the benzamidate derivative **1a** suggests that the methyl groups of the toluamidate ligands are implicated in isomer formation. However inspection reveals that only the *m*-tolyl group gives scope for isomers arising from the location of the methyl group in the cyclometallated toluamidate(2 –) ligand. It therefore appears more probable that the isomers are differentiated by the relative orientations of the amidate-(1 –) and -(2 –) ligands (Fig. 2). By analogy with the structure established for the benzamidate derivative **1a** we suggest that the major isomer has the cyclometallated carbon and the nitrogen of the amidate(1 –) ligand bound to the same ruthenium atom. Given that aryl carboxylic acids[2] and *N*,*N*′-diarylamidines[1] react with $[RuH_2(CO)(PPh_3)_3]$ under similar conditions to afford simple chelates (HL) of the general form $[RuH(L)(CO)(PPh_3)_2]$ [L = RCO_2^- or $RNC(R)NR^-$ respectively] the formation of the binuclear cyclometallated products was unexpected. However, the outcome of the reaction can be rationalised in terms of equations (1)–(3).

$$[RuH_2(CO)(PPh_3)_3] + PhC(O)NH_2 \longrightarrow [Ru\{NHC(O)Ph\}H(CO)(PPh_3) + H_2]_3 \tag{1}$$

$$[Ru\{NHC(O)Ph\}H(CO)(PPh_3)_3] \longrightarrow [\overline{Ru\{NHC(O)C}_6H_4\}(CO)(PPh_3)_3] + H_2 \tag{2}$$

$$[Ru\{NHC(O)Ph\}H(CO)(PPh_3)_3] + [\overline{Ru\{NHC(O)C}_6H_4\}(CO)(PPh_3)_3] \longrightarrow [(Ph_3P)(OC)\overline{Ru\{\mu\text{-}NHC(O)C}_6H_4\}\text{-}\{\mu\text{-}NHC(O)Ph\}(\mu\text{-}H)Ru(CO)(PPh_3)_2] + 3\,PPh_3 \tag{3}$$

In particular, if we accept that C-metallation precedes bridge formation then the N-bridging mode adopted by the cyclometallated benzamidate(2 –) ligand can be attributed to its 'strapped back' position which prevents the amide oxygen from engaging the other ruthenium centre.

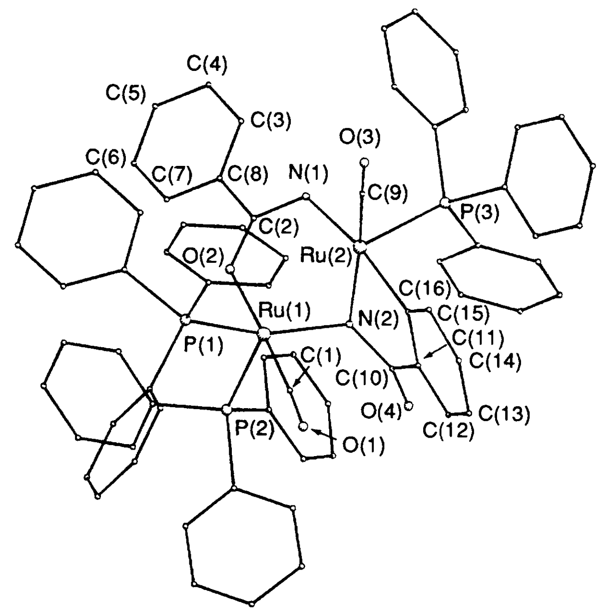


Fig. 1 Crystal structure of complex **1a**

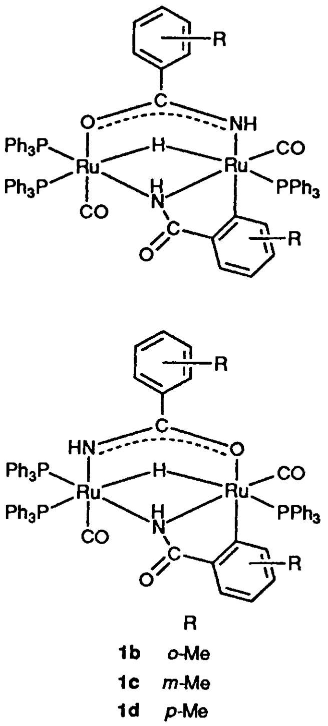


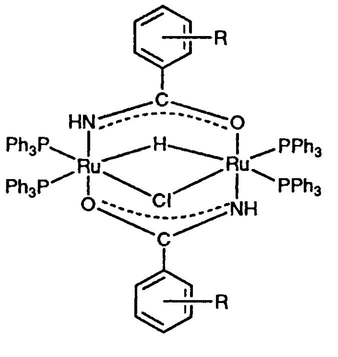
Fig. 2 Isomers of complexes **1b**–**1d**

Reaction of Arylamides with $[RuH(Cl)(PPh_3)_3]$.—Treatment of $[RuH(Cl)(PPh_3)_3]$ with benzamide in boiling toluene over a period of *ca.* 3.5 h affords a reddish brown solution from which after evaporation and crystallisation (CH_2Cl_2–MeOH) an air-stable brick-red product **2a** can be isolated in good yield. Analytical and spectroscopic data indicate that it has a quadruply bridged structure $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)Ph\}_2(PPh_3)_4]$ (Fig. 3) analogous to those previously established in our laboratories for the corresponding trifluoroacetamide[10] and succinimide[18] complexes by X-ray crystallography. Reaction of *o*-, *m*- and *p*-toluamides with $[RuH(Cl)(PPh_3)_3]$ yielded products analogous to that obtained with benzamide. The product obtained from *o*-toluamide gave good spectroscopic data (Table 1) but contained a small amount of impurity. Attempts to remove this by recrystallisation resulted in slow decomposition of the complex.

Reactions of Arylamides with $[RuCl_2(PPh_3)_3]$ *in the Presence of Triethylamine.*—These reactions, performed in refluxing toluene over a period of 10 h, gave products identical to those obtained from $[RuH(Cl)(PPh_3)_3]$.

Table 2 Selected bond lengths (Å) and angles (°) for complex **1a**

Ru(2) ··· Ru(1)	2.842(4)	C(8)–C(2)	1.508(16)	P(1)–Ru(1)	2.329(5)	N(1)–C(2)	1.318(14)
P(2)–Ru(1)	2.395(5)	C(9)–O(3)	1.153(14)	C(1)–Ru(1)	1.825(13)	C(10)–N(2)	1.385(16)
O(2)–Ru(1)	2.128(10)	O(4)–C(10)	1.233(14)	N(2)–Ru(1)	2.178(11)	C(11)–C(10)	1.483(18)
P(3)–Ru(2)	2.293(5)	C(12)–C(11)	1.394(21)	N(1)–Ru(2)	2.142(12)	C(16)–C(11)	1.402(15)
C(9)–Ru(2)	1.815(12)	C(13)–C(12)	1.380(22)	N(2)–Ru(2)	2.127(9)	C(14)–C(13)	1.398(19)
C(16)–Ru(2)	2.056(15)	C(15)–C(14)	1.403(22)	C(2)–O(2)	1.273(14)	C(16)–C(15)	1.409(18)
C(1)–O(1)	1.150(16)						
P(1)–Ru(1)–Ru(2)	115.1(2)	P(2)–Ru(1)–Ru(2)	139.3(1)	C(136)–P(1)–Ru(1)	113.5(3)	C(226)–P(2)–Ru(1)	114.6(4)
P(2)–Ru(1)–P(1)	104.6(2)	C(1)–Ru(1)–Ru(2)	99.8(4)	C(216)–P(2)–Ru(1)	120.9(3)	C(236)–P(2)–Ru(1)	112.2(4)
C(1)–Ru(1)–P(1)	83.9(4)	C(1)–Ru(1)–P(2)	92.9(4)	C(316)–P(3)–Ru(2)	113.8(4)	C(326)–P(3)–Ru(2)	116.0(4)
O(2)–Ru(1)–Ru(2)	82.2(3)	O(2)–Ru(1)–P(1)	95.0(3)	O(1)–C(1)–Ru(1)	176.3(9)	C(336)–P(3)–Ru(2)	115.7(4)
O(2)–Ru(1)–P(2)	85.8(3)	O(2)–Ru(1)–C(1)	178.0(4)	C(8)–C(2)–O(2)	116.5(10)	C(2)–O(2)–Ru(1)	126.6(8)
N(2)–Ru(1)–Ru(2)	47.9(2)	N(2)–Ru(1)–P(1)	162.9(2)	N(1)–C(2)–C(8)	119.3(10)	N(1)–C(2)–O(2)	124.2(11)
N(2)–Ru(1)–P(2)	92.5(3)	N(2)–Ru(1)–C(1)	96.8(5)	C(7)–C(8)–C(2)	119.2(9)	C(3)–C(8)–C(2)	120.7(8)
N(2)–Ru(1)–O(2)	84.7(4)	P(3)–Ru(2)–Ru(1)	150.1(1)	O(3)–C(9)–Ru(2)	176.0(12)	C(2)–N(1)–Ru(2)	123.9(9)
N(1)–Ru(2)–Ru(1)	82.9(3)	N(1)–Ru(2)–P(3)	90.4(4)	C(10)–N(2)–Ru(1)	116.4(9)	Ru(2)–N(2)–Ru(1)	82.6(4)
C(9)–Ru(2)–Ru(1)	120.1(5)	C(9)–Ru(2)–P(3)	89.7(5)	O(4)–C(10)–N(2)	123.0(12)	C(10)–N(2)–Ru(2)	111.8(7)
C(9)–Ru(2)–N(1)	100.2(5)	N(2)–Ru(2)–Ru(1)	49.5(2)	C(11)–C(10)–O(4)	123.5(12)	C(11)–C(10)–N(2)	113.4(10)
N(2)–Ru(2)–P(3)	101.4(4)	N(2)–Ru(2)–N(1)	87.5(4)	C(16)–C(11)–C(10)	116.8(12)	C(12)–C(11)–C(10)	120.9(11)
N(2)–Ru(2)–C(9)	166.5(5)	C(16)–Ru(2)–Ru(1)	88.4(4)	C(13)–C(12)–C(11)	120.7(12)	C(16)–C(11)–C(12)	122.2(12)
C(16)–Ru(2)–P(3)	92.7(4)	C(16)–Ru(2)–N(1)	167.4(3)	C(15)–C(14)–C(13)	122.0(14)	C(14)–C(13)–C(12)	118.0(15)
C(16)–Ru(2)–C(9)	92.0(6)	C(16)–Ru(2)–N(2)	80.0(5)	C(11)–C(16)–Ru(2)	113.2(9)	C(16)–C(15)–C(14)	119.9(11)
C(116)–P(1)–Ru(1)	117.8(4)	C(126)–P(1)–Ru(1)	116.6(4)	C(15)–C(16)–C(11)	117.2(12)	C(15)–C(16)–Ru(2)	129.5(9)

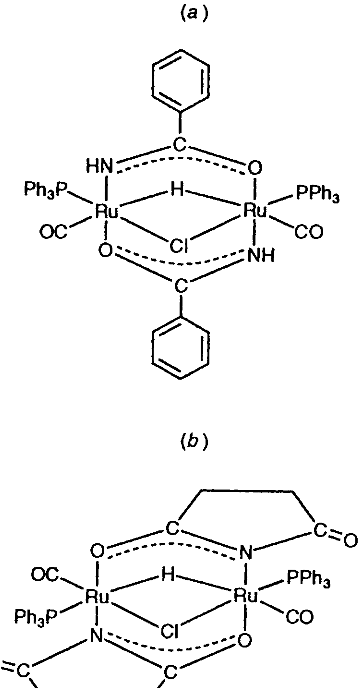


	R
2a	H
2b	*o*-Me
2c	*m*-Me
2d	*p*-Me

Fig. 3 Structure of complexes **2a**–**2d**

Carbonylation of $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)Ph\}_2(PPh_3)_4]$ **2a**.—Carbonylation of complex **2a** in refluxing toluene over a period of *ca*. 2 h afforded a yellow solution from which the orange crystalline dicarbonyl product $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)Ph\}_2(CO)_2(PPh_3)_2]$ **3** was isolated in excellent yield. The spectroscopic data for this product (Table 1) clearly confirm the presence of a bridging hydride ligand *cis* to two equivalent phosphines and, taken with the analytical results, establish the *cis*-dicarbonyl structure [Fig. 4(*a*)]. This result contrasts sharply with that observed for carbonylation of the related succinimide complex[18] $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}C_4H_4NO_2)_2(CO)(PPh_3)_3]$ which yields a dicarbonyl derivative $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}C_4H_4NO_2)_2(CO)_2(PPh_3)_2]$ containing carbonyl ligands in mutually *trans* sites [Fig. 4(*b*)].

The differences in stereochemistry displayed by the two dicarbonyls can be rationalised in terms of the synthetic routes employed. The benzamide derivative obtained by carbonylation of the hydride-bridged species $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)Ph\}_2(PPh_3)_4]$ reflects the *trans*-directing sequence H > Cl and consequently has both carbonyl ligands *trans* to the bridging hydride ligand. In contrast the succinimide derivative is prepared from a hydride-bridged precursor which already contains one carbonyl ligand located *trans* to chloride which probably entered the co-ordination sphere of ruthenium prior to the hydride ligand. This complex on further carbonylation substitutes a phosphine *trans* to hydride to give the observed overall *trans*-carbonyl stereochemistry.


(*a*)

(*b*)

Fig. 4 Structures adopted by complex **3**(*a*) and its succinimide analogue (*b*)

Reaction of Benzamide with $[OsH_2(CO)(PPh_3)_3]$.—In marked contrast to its ruthenium analogue, $[OsH_2(CO)(PPh_3)_3]$ reacts with benzamide in boiling benzene to form a simple mononuclear amido complex $[Os\{NHC(O)Ph\}_2(CO)_2(PPh_3)_2]$ **4**. In this reaction N-metallation clearly takes precedence over C-metallation and the amide presumably serves as the source of the second carbonyl ligand. The infrared spectrum establishes the *cis* orientation of the carbonyl ligands [ν(C=O) 1945 and 2020 cm^{-1}]. The $^{31}P\text{-}\{^1H\}$ NMR spectrum [δ(P) 1.40] is consistent with a *trans* orientation of the phosphine ligands and thus confirms the expected *cis*-carbonyl *trans*-phosphine stereochemistry.

Crystal Structure of Complex **1a**.—The molecular structure of compound **1a** is given in Fig. 1, selected bond lengths and angles in Table 2. The molecules each contain two octahedrally co-ordinated ruthenium(II) centres linked by bridging hydride, benzamidate(1−) and benzamidate(2−) ligands. The hydride ligand was not located crystallographically, but its presence and position was readily inferred from spectroscopic data (Table 1). The bridging benzamidate(2−) ligand is bound to both ruthenium centres through the amide nitrogen and further co-ordinated to Ru(2) *via* cyclometallation of the phenyl ring at an *o*-carbon position. The co-ordination sphere of Ru(2) is completed by a carbonyl and a triphenylphosphine, and that of Ru(1) by a carbonyl and two triphenylphosphine ligands. The co-ordination about each ruthenium centre deviates significantly from regular octahedral geometry. Bond angles subtended at ruthenium by adjacent ligands range from 83.9(4) to 104.6(2)° for Ru(1) and 80.0(5) to 101.4(4)° for Ru(2). These distortions are not unexpected given the disparate structures of the bridging groups and the additional constraints imposed by the cyclometallated benzamidate(2−) ligand. Ruthenium–ligand bond distances are inside the ranges expected for P, N, C and O donors bound to octahedral ruthenium(II) centres.

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