Binuclear Complexes of Ruthenium with Diphosphines and Bridging Benzene-1,2-diamide. X-Ray Crystal Structure of $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}\{\mu\text{-}(Ph_2P)_2CH_2\}(CO)_2(PPh_3)_2]\cdot C_6H_5Me$†

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The binuclear complex $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]$ **1** reacts with the diphosphines $(Ph_2P)_2X$ [X = C_2H_4 (dppe), *cis*-C_2H_2 (dppen), 1,2-C_6H_4 (dppbz), C_3H_6 (dppp) and C_4H_8 (dppb)], in boiling toluene, to give purple solutions from which the yellow compounds $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(PPh_3)(\text{diphosphine})]$ [dppe, **2**; dppen, **3**, dppbz, **4**; dppp, **5**; or dppb, **6** can be obtained after purification on an Al_2O_3 column and crystallization from toluene–hexane solutions. The reaction of **1** with $(Ph_2P)_2CH_2$ (dppm), in boiling toluene or xylene, affords $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(\mu\text{-dppm})(CO)_2(PPh_3)_2]$ **7** as the unique product. All these new complexes can be obtained in good yields by reaction of $[Ru\{1,2\text{-}(NH)_2C_6H_4\}(PPh_3)(\text{diphosphine})]$ with $[Ru(CO)_3(PPh_3)_2]$ in boiling mesitylene. Compound **1** also reacts with $[Ru\{1,2\text{-}(NH)_2C_6H_4\}(PPh_3)_3]$ or $[RuH_2(PPh_3)_4]$ in boiling xylene to give $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(PPh_3)_3]$ **8** which easily regenerates **1** by reaction with CO. An excess of diphosphine (except for dppm) in the reaction with **1** produced the mononuclear complexes $[Ru\{1,2\text{-}(NH)_2C_6H_4\}(CO)(\text{diphosphine})]$ and $[Ru(CO)_2(PPh_3)(\text{diphosphine})]$ and for the reaction with dppb the complexes $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(\text{dppb-}P)(\text{dppb-}PP')]$ **9**, $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(\mu\text{-dppb})(CO)_2(PPh_3)_2]$ **10**, $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_2(\text{dppb})_2]$ **11** and $[Ru(CO)_2(\text{dppb-}P)(\text{dppb-}PP')]$ **12** were also detected or isolated. All complexes have been characterized by elemental analysis and by IR and NMR spectroscopy. The structure of the toluene solvate of **7** has been determined by X-ray diffraction methods: monoclinic, space group $P2_1/n$, with $a = 18.563(8)$, $b = 21.066(9)$, $c = 17.936(7)$ Å, $\beta = 110.47(2)°$ and $Z = 4$. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.0524$ for 6679 observed reflections. The two Ru atoms are doubly bridged by the nitrogen atoms of the 1,2-diimine ligand with a short Ru–Ru separation, 2.562(1) Å, consistent with a metal–metal bond.

The synthesis of $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]$ **1** in good yield,[1] the first binuclear ruthenium(I) complex stabilized by benzene-1,2-diamide and having the shortest Ru–Ru distance [2.560(1)Å] reported for ruthenium(I) species, allowed studies of its reactivity towards Lewis acids.[2]

Binuclear complexes of transition metals have proved to be efficient catalysts,[3] particularly in processes involving small molecules[4] and carbon–carbon bonds,[5] and have been used to explain co-operative effects in catalytic reactions.[6] Some binuclear ruthenium(I) complexes are versatile catalysts.[7,8] Furthermore, metal complexes with polydentate phosphines have attracted interest in catalysis, asymmetric synthesis and organometallic stereochemistry.[9]

We decided to study the ligand-substitution reactions of complex **1**, in order to determine the effect on its $Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}$ framework, mainly using bis(diphenylphosphino) ligands, although other reactions such as substitution of CO and PPh_3 and reactivity towards bipyridine, cycloocta-1,3- and 1,5-diene were also investigated. Studies on binuclear and polymeric ruthenium(I) complexes have recently led to polymeric species where the bidentate ligands bridge dimeric units,[10] and the complex $[Ru_2(\mu\text{-L})_2(CO)_6]$ (HL = 3,5-dimethylpyrazole) reacts with acetonitrile and with pyridine to give two different types of monosubstituted products.[11]

Results and Discussion

Complexes $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(PPh_3)(\text{diphosphine})]$.—The reaction of $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]$ **1** with diphenylphosphines $(Ph_2P)_2X$ where X = C_2H_4 (dppe), C_2H_2 (dppen), C_6H_4 (dppbz), C_3H_6 (dppp) and C_4H_8 (dppb) in boiling toluene gives purple or red-brown solutions, which when chromatographed on an Al_2O_3 column give a yellow solution as a first fraction. From this solution, by addition of hexane, the yellow complexes $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(PPh_3)(\text{diphosphine})]$ **2**–**6** have been isolated as crystalline solids with variable amounts of toluene. Better yields can be obtained from $[Ru\{1,2\text{-}(NH)_2C_6H_4\}(PPh_3)(\text{diphosphine})]$ and $[Ru(CO)_3(PPh_3)_2]$ in boiling mesitylene, chromatographic separation in order to recover other reaction products being avoided as they were detected only in minor amounts. The IR spectra of the solids show bands between 3355 and 3342 cm^{-1} [ν(N–H)] and the solutions in toluene two strong bands at *ca.* 1972 and between 1917 and 1906 cm^{-1} [ν(C≡O)].

The ^1H NMR spectra exhibit resonances expected for phenyl groups, for CH_3 (from toluene) and for hexane. The shifts due to NH were not assignable with accuracy, but the most interesting signals are those from the aromatic ring protons of the 1,2-

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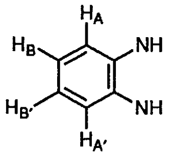
† μ-Benzene-1,2-diamido-κ*N*:κ*N'*-μ-bis(diphenylphosphino)methane-κ*P*:κ*P'*-bis[carbonyl(triphenylphosphine)ruthenium(I)](*Ru*–*Ru*)-toluene (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Proton and ^{31}P NMR spectral data for the binuclear ruthenium compounds[a]



	^1H[b]					^{31}P		
Compound	δ	$J(H_AH_B)$	$J(H_BH_{B'})$	$J(H_{A'}H_{B'})$	Assignment	δ	$J(PP)$/Hz	Assignment
2 $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(PPh_3)(dppe)]$	5.72(t)[c]		7.0		H_B	89.17(d)	16.0	PPh_3
	5.60(t)				$H_{B'}$	48.01(dd)		P_A
	5.53(d)	7.0			H_A	22.79(d)	73.3	P_B
	4.88(d)			7.0	$H_{A'}$			
3 $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(PPh_3)(dppen)]$	5.66(t)		7.3		H_B	91.00(d)	24.3	PPh_3
	5.47(d)	7.8			H_A	51.65(dd)		P_A
	5.45(t)				$H_{B'}$	23.52(d)	73.2	P_B
	4.69(d)			7.0	$H_{A'}$			
4 $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(PPh_3)(dppbz)]$	5.61(t)		7.1		H_B	85.38(d)	7.1	PPh_3
	5.49(t)				$H_{B'}$	46.81(dd)		P_A
	5.31(d)	6.5			H_A	24.04(d)	69.4	P_B
	4.93(d)			7.4	$H_{A'}$			
5 $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(PPh_3)(dppp)]$	5.44(d)	5.2			H_A	49.73(d)	13.0	PPh_3
	5.43(d)			5.2	$H_{A'}$	22.52(d)	74.0	P_B
	5.12(t)		3.5		H_B	20.65(dd)		P_A
	4.89(t)				$H_{B'}$			
6 $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(PPh_3)(dppb)]$	5.54(t)		7.3		H_B	62.48(s)		PPh_3
	5.31(t)				$H_{B'}$	25.67(d)		P_A
	5.10(d)	7.0			H_A	21.50(d)		P_B
	4.31(d)			7.1	$H_{A'}$			
8 $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(PPh_3)_3]$	5.61(t)		7.3		H_B	63.17(app.t)	3.2; 3.5	PPh_3
	5.34(t)				$H_{B'}$	30.25(dd)	3.6; 74.5	P_A
	4.90(d)	7.0			H_A	20.57(dd)	2.9; 74.5	P_B
	4.46(d)			7.2	$H_{A'}$			
9 $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(dppb\text{-}P)\text{-}(dppb\text{-}PP')]$	5.70(t)		7.3		H_B	62.97(s)		P_C
	5.44(t)				$H_{B'}$	25.67(d)	74.0	P_A
	5.24(d)	7.2			H_A	14.60(d)		P_B
	4.36(d)			7.2	$H_{A'}$	−15.32(s)		P_D
7 $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(\mu\text{-}dppm)(CO)_2\text{-}(PPh_3)_2]$	6.11(t)		7.5		H_B	43.79(s)		PPh_3
	5.87(d)	6.7			H_A	27.21(s)		dppm
	5.58(t)				$H_{B'}$			
	4.41(d)			7.2	$H_{A'}$			
10 $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(\mu\text{-}dppb)(CO)_2\text{-}(PPh_3)_2]$	5.72(t)		7.3		H_B	59.00(s)		PPh_3
	5.44(t)				$H_{B'}$	14.48(s)		dppb
	5.32(d)	7.1			H_A			
	4.30(d)			6.8	$H_{A'}$			
11 $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_2(dppb\text{-}PP')_2]$	5.37(m)				$H_B(=H_{B'})$	25.85(d)	74.5	P_A
	4.22(m)				$H_A(=H_{A'})$	14.70(d)		P_B

[a] In C_6D_6 solutions; s = singlet, d = doublet, t = triplet, and dd = doublet of doublets. [b] $J(H_AH_{B'})$, $J(H_AH_{A'})$ and $J(H_{A'}H_B)$ < 1 Hz and were not defined for these samples. Values in Hz. [c] When $J(H_AH_B)$, $J(H_BH_{B'})$ and $J(H_{A'}H_{B'})$ have similar values, the expected patterns for protons H_B and $H_{B'}$ (dd) appeared as triplets.

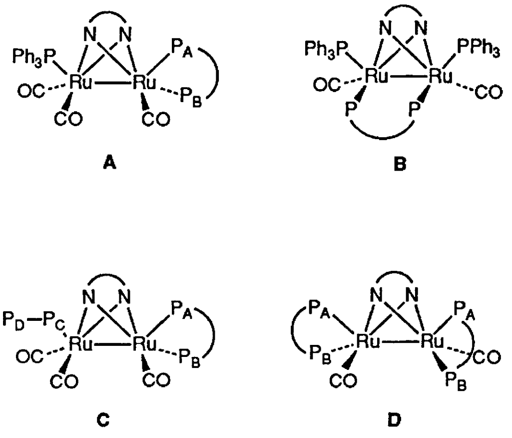


Fig. 1 Structures of the binuclear ruthenium complexes

$(NH)_2C_6H_4$ ligand. In all cases they appeared as a set of two apparent triplets and two doublets (for the dppp complex, two doublets and two doublets of doublets) between δ 5.72 and 4.31 (Table 1). These patterns are derived from the more symmetric starting compound which shows two multiplets at δ 5.30 and 4.90 (in C_6D_6 solution),[1] where there are equivalences between the 4- and 5- and between the 3- and 6-protons of the diimine aromatic ring, as confirmed by its X-ray structure: the molecule (C_{2v}) has a σ_v plane which contains the two ruthenium and the two phosphorus atoms. The J_{HH} values for the diimine ring protons are also consistent with their aromaticity,[12] suggesting that this ligand is present in its dianionic form $(NH)_2C_6H_4{}^{2-}$.

The ^{31}P NMR spectra show three non-equivalent phosphorus atoms, with a set of two doublets and a doublet of doublets (except for the dppb complex where the coupling between PPh_3 and dppb is too weak and was not resolved) which can be assigned[13] to PPh_3 (the higher chemical shift) and to a diphosphine asymmetrically chelating one of the ruthenium atoms as in structure **A** (Fig. 1): the P_A atom is bonded to the

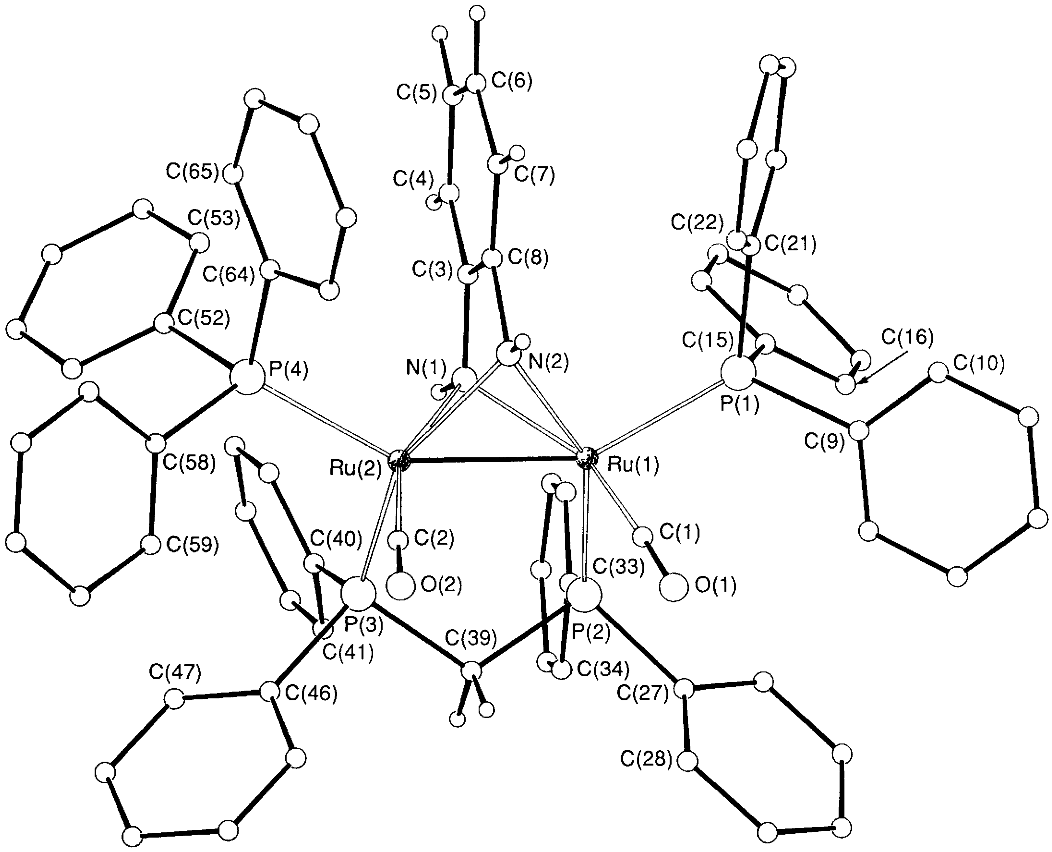


Fig. 2 View of the molecular structure of the complex $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(\mu\text{-dppm})(CO)_2(PPh_3)_2]$ **7** with the atomic numbering scheme

metal centre in the position formerly occupied by PPh_3, and the P_B atom is in that which corresponded to one CO in the starting compound. The coupling constant between PPh_3 and P_A or P_B is expected to be higher for P_A than for P_B (assuming that P_A is in an 'equivalent' position to PPh_3) as in $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]$ the angle P–Ru–Ru is larger than that of Ru–Ru–C. The PPh_3–P_B couplings are too weak in all these complexes and were not observed, and for the weakest chelating diphosphines (dppp and dppb) the chemical shifts for P_A and P_B differ by less than 5 ppm (for other diphosphines >22 ppm), which can be compared with a difference of *ca.* 10 ppm between two PPh_3 bonded to the same ruthenium atom in $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(PPh_3)_3]$ (see later).

The reactivity of compound **1** differs from that found for binuclear ruthenium complexes,[10] where the large *trans* influence of the metal–metal bond favours substitution reactions of a ligand, L, bonded with an L–Ru–Ru angle close to 180°. In compound **1** the P–Ru–Ru [151.3(1)°] and C–Ru–Ru [104.5(1)°] angles are far from that value and substitution reactions require more rigorous conditions (>100 °C).

Complexes $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(\mu\text{-diphosphine})(CO)_2(PPh_3)_2]$.—The reactions of $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]$ or $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(PPh_3)_3]$ with an excess of bis(diphenylphosphino)methane (dppm) in boiling toluene, or of $[Ru\{1,2\text{-}(NH)_2C_6H_4\}(PPh_3)(dppm)]$ with $[Ru(CO)_3(PPh_3)_2]$ in boiling mesitylene, afforded a brown solution from which $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(\mu\text{-dppm})(CO)_2(PPh_3)_2]$ **7** was the only compound isolable in good yield. Its IR spectrum shows bands at 3347w [ν(N–H)] and 1909vs and 1877w cm^{-1} [ν(C≡O)], accounting for the presence of diimine and, presumably, a dicarbonylic species as suggested by the lowering of ν(C≡O) relative to the starting and the binuclear tricarbonyl complexes.

The ^1H NMR spectrum shows, between δ 6.11 and 4.41, the pattern of two triplets and two doublets, expected for the aromatic protons of a asymmetrically bonded diimine (Table 1), and as found for compounds **2**–**6**. The $^{31}P\text{-}\{^1H\}$ NMR spectrum has two singlets, that at lower field (δ 43.79) being assignable to the equivalent phosphorus atoms of PPh_3 ligands (one on each ruthenium) and that at δ 27.21 to a bridging dppm, within the range of values found for binuclear dppm-bridged complexes.[14] The phosphorus atoms occupy the positions of two *syn*-CO in the starting compound **1**, where the expected couplings between both types of phosphorus were not observed under the experimental conditions, and the structure **B** is proposed (Fig. 1).

When an excess of 1,4-bis(diphenylphosphino)butane (dppb) was refluxed with $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]$ in toluene, chromatography gave first a yellow fraction which after solvent evaporation and washing with hot hexane gave a solid mixture (low yield). One of the species contained therein showed a ^1H NMR spectrum assignable to the asymmetrical diimine protons and a set of two singlets in the $^{31}P\text{-}\{^1H\}$ NMR spectrum without, as in the dppm-bridged complex, couplings between PPh_3 and dppb. The structure **B** in Fig. 1 is consistent with the properties of this complex.

X-Ray Structure of $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(\mu\text{-dppm})(CO)_2(PPh_3)_2]$ **7**.—The structure of complex **7** is shown in Fig. 2; selected bond and angles are given in Table 2. The two Ru atoms are doubly bridged by two nitrogen atoms from the 1,2-diimine ligand [Ru(1)–N(1) 2.186(7) and Ru(2)–N(1) 2.195(6), Ru(1)–N(2) 2.159(7) and Ru(2)–N(2) 2.128(6) Å] in the $\mu,\eta^2(\perp)$ fashion as in compound **1**, and the dppm also bridges both metal atoms through the two phosphorus atoms [Ru(1)–P(2) 2.289(2) and Ru(2)–P(3) 2.277(2) Å]. The Ru_2N_2 framework is in a butterfly arrangement with the two 'wing' bridges almost perpendicular one to other, the dihedral angle being 87.6(2)°. The dppm bridge [showing an 'envelope' conformation with the C(39) displaced by 0.685(7) Å from the mean plane through the two metal and two phosphorus atoms] is almost perpendicular to the $Ru_2N(1)$ bridge and almost coplanar with the $Ru_2N(2)$

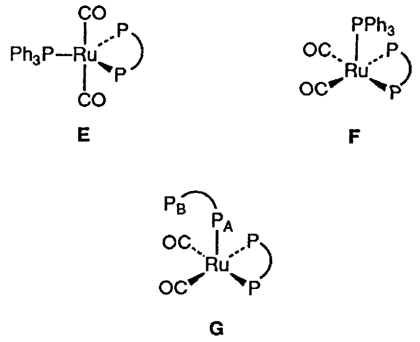
Table 2 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for compound **7**

Ru(1)–Ru(2)	2.562(1)	C(2)–O(2)	1.14(1)
Ru(1)–N(1)	2.186(7)	P(1)–C(9)	1.860(9)
Ru(1)–N(2)	2.159(7)	P(1)–C(15)	1.824(8)
Ru(2)–N(1)	2.195(6)	P(1)–C(21)	1.846(8)
Ru(2)–N(2)	2.128(6)	P(2)–C(27)	1.825(9)
Ru(1)–C(1)	1.832(8)	P(2)–C(33)	1.839(7)
Ru(2)–C(2)	1.843(8)	P(2)–C(39)	1.860(8)
Ru(1)–P(1)	2.372(2)	P(3)–C(39)	1.841(9)
Ru(1)–P(2)	2.289(2)	P(3)–C(40)	1.835(7)
Ru(2)–P(3)	2.277(2)	P(3)–C(46)	1.834(8)
Ru(2)–P(4)	2.374(3)	P(4)–C(52)	1.831(8)
N(1)–C(3)	1.41(1)	P(4)–C(58)	1.843(9)
N(2)–C(8)	1.43(1)	P(4)–C(64)	1.836(8)
C(1)–O(1)	1.16(1)		
Ru(2)–Ru(1)–N(1)	54.4(2)	P(4)–Ru(2)–N(1)	107.3(2)
Ru(2)–Ru(1)–N(2)	52.8(2)	P(4)–Ru(2)–P(3)	108.8(1)
Ru(2)–Ru(1)–C(1)	101.5(3)	P(3)–Ru(2)–C(2)	90.8(3)
N(2)–Ru(1)–C(1)	97.9(3)	P(3)–Ru(2)–N(2)	149.0(2)
N(1)–Ru(1)–C(1)	155.9(3)	P(3)–Ru(2)–N(1)	92.2(2)
N(1)–Ru(1)–N(2)	67.7(3)	Ru(1)–Ru(2)–P(3)	95.3(1)
P(1)–Ru(1)–C(1)	95.2(2)	Ru(1)–Ru(2)–P(4)	150.8(1)
P(1)–Ru(1)–N(2)	103.1(2)	Ru(1)–N(1)–Ru(2)	71.6(2)
P(1)–Ru(1)–N(1)	106.7(2)	Ru(1)–N(1)–C(3)	110.4(5)
P(1)–Ru(1)–P(2)	105.3(1)	Ru(2)–N(1)–C(3)	109.4(5)
P(2)–Ru(1)–C(1)	88.5(3)	Ru(1)–N(2)–Ru(2)	73.4(2)
P(2)–Ru(1)–N(2)	150.2(2)	Ru(1)–N(2)–C(8)	110.9(5)
P(2)–Ru(1)–N(1)	95.2(2)	Ru(2)–N(2)–C(8)	110.2(5)
Ru(2)–Ru(1)–P(2)	97.4(1)	Ru(1)–C(1)–O(1)	176.9(7)
Ru(2)–Ru(1)–P(1)	152.1(1)	Ru(2)–C(2)–O(2)	176.5(7)
Ru(1)–Ru(2)–N(1)	54.0(2)	N(1)–C(3)–C(8)	110.9(7)
Ru(1)–Ru(2)–N(2)	53.9(2)	N(1)–C(3)–C(4)	130.5(9)
Ru(1)–Ru(2)–C(2)	103.1(3)	C(4)–C(3)–C(8)	118.6(9)
N(2)–Ru(2)–C(2)	98.8(3)	C(3)–C(8)–C(7)	121.7(9)
N(1)–Ru(2)–C(2)	157.1(3)	N(2)–C(8)–C(7)	127.5(8)
N(1)–Ru(2)–N(2)	68.1(3)	N(2)–C(8)–C(3)	110.8(7)
P(4)–Ru(2)–C(2)	93.2(3)	P(2)–C(39)–P(3)	112.0(4)
P(4)–Ru(2)–N(2)	100.2(2)		

Table 3 31-Phosphorus NMR spectral data for mononuclear ruthenium compounds*

Compound	δ	*J*(PP)/Hz	Assignment
[Ru{1,2-$(NH)_2C_6H_4$}(CO)(dppb)]	52.52(s)		
[$Ru(CO)_2(PPh_3)$(dppe)]	69.70(d)	83.2	dppe
	56.13(t)		PPh_2
[$Ru(CO)_2(PPh_3)$(dppen)]	76.50(d)	88.1	dppen
	56.47(t)		PPh_3
[$Ru(CO)_2(PPh_3)$(dppbz)]	72.98(d)	85.0	dppbz
	55.60(t)		PPh_3
[$Ru(CO)_2(PPh_3)$(dppp)]	44.89(t)	74.5	PPh_3
	27.37(d)		dppp
[$Ru(CO)_2(PPh_3)$(dppb)]	54.62(t)	80.3	PPh_3
	40.06(d)		dppb
[$Ru(CO)_2$(dppb-*P*)(dppb-*PP′*)] **12**	45.19(t)	80.5	P_A
	39.84(d)		dppb-*PP′*
	−15.09(s)		P_B

* Solvent: C_6D_6–toluene.



E **F** **G**

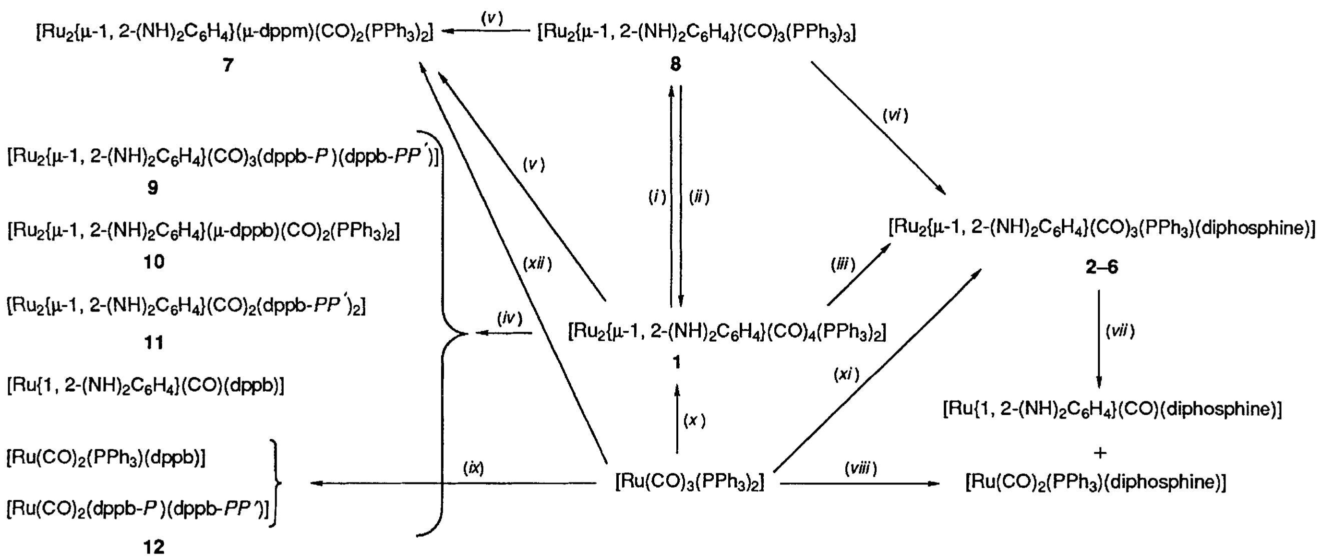
Fig. 3 Structures of the mononuclear ruthenium complexes

one [dihedral angles 90.0(2) and 2.4(1) respectively]. The very short Ru–Ru distance of 2.562(1) Å suggests a metal–metal bond, comparable to that found in the starting compound. The severely distorted octahedral co-ordination around each Ru atom is completed by a carbon from a carbonyl group. [Ru(1)–C(1) 1.832(8) and Ru(2)–C(2) 1.843(8) Å] and by a phosphorus atom from a PPh_3 ligand [Ru(1)–P(1) 2.372(2) and Ru(2)–P(4) 2.374(3) Å]. The distortion of the octahedral co-ordination is evidenced especially by the P(1)–Ru(1)–Ru(2) and P(4)–Ru(2)–Ru(1) angles, 152.1(1) and 150.8(1)°, by the N–Ru(1)–Ru(2) and N–Ru(2)–Ru(1) angles, in the range 52.8(2)–54.4(2)°, and by the N(1)–Ru(1)–N(2) and N(1)–Ru(2)–N(2) angles, 67.7(3) and 68.1(3)°, differing significantly from the theoretical 180 and 90°, respectively. The complex as a whole displays an approximate C_s symmetry with the mirror plane containing the 1,2-diimine ligand and perpendicular to the Ru–Ru bond. The carbonyl groups and the phosphorus atoms of the dppm ligand are *trans* to the N(1) and N(2) atoms, respectively, whereas the PPh_3 ligands are *trans* to the Ru–Ru bond. The large *trans* effect of the Ru–Ru bond is evidenced by the longer Ru(1)–P(1) and Ru(2)–P(4) bonds with respect to Ru(1)–P(2) and Ru(2)–P(3) which are *trans* to the N(2) atom. The larger *trans* effect of the carbonyl ligand with respect to the P atom is responsible for the longer Ru(1)–N(1) and Ru(2)–N(1) distances with respect to Ru(1)–N(2) and Ru(2)–N(2). The Ru–Ru separation is shorter than in most binuclear diruthenium(I) complexes with bridging ligands, in the range 2.639(1)–2.759(4) Å.[15] Both the distortions in the octahedral arrangement and in the rather short Ru–Ru separation must be caused by the strain imposed by the 1,2-diimine ligand, which nevertheless remains strictly planar. This strain also determines very narrow Ru(1)–N(1)–Ru(2) and Ru(1)–N(2)–Ru(2) angles, 71.6(2) and 73.4(2)° respectively, and N(1)–C(3)–C(8) and N(2)–C(8)–C(3), 110.9(7) and 110.8(7)°. Comparable short values of the $Ru^I–Ru^I$ separation have been found in the complex [Ru_2{μ-1,2-$(NH)_2C_6H_4$}$(CO)_4(PPh_3)_2$] **1**, 2.560(1) Å (this value refers to the more accurate structure determination of the two crystalline forms),[1] and in [Ru_2(μ-$C_{10}H_8N_2$)$(CO)_4(PPh_3)_2$], 2.58(1) Å,[16] and [Ru_2(μ-$C_{10}H_8N_2$)$(CO)_4${$P(OPh)_3$}$_2$], 2.571(1) Å,[15] with the rigid naphthalene-1,8-diamide ligand. It is noteworthy that the N(1)···N(2) separation in the two ligands is practically the same, 2.421(8) Å, with a remarkable strain in **7**, and 2.53(1) Å without strain in [Ru_2(μ-$C_{10}H_8N_2$)$(CO)_4${$P(OPh)_3$}$_2$].[15]

Cleavage of the Ru–Ru *Bond: Formation of the Mononuclear Complexes* [Ru{1,2-$(NH)_2C_6H_4$}(CO)(diphosphine)] *and* [$Ru(CO)_2(PPh_3)$(diphosphine)].—In all reactions of [Ru_2{μ-1,2-$(NH)_2C_6H_4$}$(CO)_4(PPh_3)_2$] with bis(diphenylphosphino) ligands in refluxing toluene an excess of diphosphine was required in order to complete the reaction (1). However the

$$[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_4(PPh_3)_2] + \text{diphosphine} \longrightarrow [Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(PPh_3)(\text{diphosphine})] + PPh_3 + CO \quad (1)$$

excess of diphosphine also affected the binuclear complexes (except for dppm) obtained, easily detected by the appearance of red-purple species which were also detected (in lower yields) with a **1**: diphosphine ratio > 1:1 indicating that more than a single reaction was taking place and thus always requiring a separation process (chromatography) to isolate the compounds **2**–**6**, as yellow solutions and leaving purple materials which were easily eluted with tetrahydrofuran (thf) or CH_2Cl_2. The



Scheme 1 Reagents and conditions: (*i*) $[Ru\{1,2\text{-}(NH)_2C_6H_4\}(PPh_3)_3]$ or $[RuH_2(PPh_3)_4]$–xylene, heat; (*ii*) CO–toluene; (*iii*) dppe (1 : 2), dppen (1 : 1.75), dppbz (1 : 1.5), dppp (1 : 1.5) or dppb (1 : 1)–toluene, heat; (*iv*) dppb (1 : 3)–toluene, heat; (*v*) dppm–toluene, heat; (*vi*), any diphosphine (1 : 1)–toluene, heat; (*vii*) dppe, dppen, dppbz or dppp (1 : 2)–toluene, heat; (*viii*) dppe, dppen, dppbz or dppp (1 : 1)–toluene, heat; (*ix*) dppb (1 : 2)–toluene, heat; (*x*) $[Ru\{1,2\text{-}(NH)_2C_6H_4\}(PPh_3)_3]$ or $[Ru\{1,2\text{-}(NH)_2C_6H_4\}(CO)(PPh_3)_2]$–mesitylene, heat; (*xi*) $[Ru\{1,2\text{-}(NH)_2C_6H_4\}(PPh_3)(diphosphine)]$–mesitylene, heat; (*xii*) $[Ru\{1,2\text{-}(NH)_2C_6H_4\}(PPh_3)(dppm)]$–mesitylene, heat

same purple products were obtained, in good yields, from $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(PPh_3)(diphosphine)]$ and diphosphine in boiling toluene, giving solutions from which, on crystallization, white or pale coloured solids were recovered. Their IR spectra show two bands in the ν(C≡O) region (between 1920 and 1840 cm^{-1}), with no bands assignable to ν(N–H), and their $^{31}P\text{-}\{^1H\}$ NMR spectra have one doublet and one triplet (Table 3) suggesting the presence of the compounds $[Ru(CO)_2(PPh_3)(diphosphine)]$. This is consistent with a structure closer to **E** than to **F** (Fig. 3) where C–Ru–C angles $\ll 180°$ would satisfy the spectral properties observed. Some of these dicarbonyl compounds were also prepared from $[Ru(CO)_3(PPh_3)_2]$ and the corresponding diphosphine.

In the residual solutions, after crystallization of the former compounds, the purple complexes $[Ru\{1,2\text{-}(NH)_2C_6H_4\}(CO)(diphosphine)]$ were detected [ν(C≡O) evidence], but not isolated in order to be analysed as the same products were previously characterized from reactions of $[Ru\{1,2\text{-}(NH)_2C_6H_4\}(CO)(PPh_3)_2]$ and diphosphines.[17] So the complete reaction between compound **1** and a diphosphine can be expressed in equation (2):

$$\begin{aligned}&[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_4(PPh_3)_2] + \text{diphosphine} \longrightarrow \\ &\quad [Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(PPh_3)(\text{diphosphine})] + \\ &\quad [Ru\{1,2\text{-}(NH)_2C_6H_4\}(CO)(\text{diphosphine})] + \\ &\quad [Ru(CO)_2(PPh_3)(\text{diphosphine})] + PPh_3 + CO \qquad (2)\end{aligned}$$

It was found (from NMR spectra of reaction solutions) that cleavage of the Ru–Ru and $Ru(N)_2$ bonds, and further addition of one diphosphine to the less co-ordinated Ru atom was easier with the diphosphines that, like dppe, dppen and dppbz, can lead to more stable chelates (five-atom rings) than does dppp or dppb (six- or seven-atom ring). An excess of dppm in the reaction with **1** did not produce any chelated complex and the products of cleavage of the binuclear structure were not detected, which is consistent with the fact that a more substituted binuclear ruthenium complex (with less than three CO ligands) is unstable, leading to its fragmentation, when these phosphines are used, unless the new ligand is able to bridge both Ru atoms. This suggestion was confirmed when the complex $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(\mu\text{-dppb})(CO)_2(PPh_3)_2]$ **10** was detected as one of the reaction products between **1** and dppb, as this phosphine has less chelating and greater bridging properties than the others, except for dppm.

Complexes $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_3(dppb\text{-}P)(dppb\text{-}PP')]$ **9** *and* $[Ru(CO)_2(dppb\text{-}P)(dppb\text{-}PP')]$ **12**.—When analysing the ^1H and ^{31}P NMR spectra of the first chromatographic fraction from the reaction between the compound **1** and dppb, similar patterns to those for complex **6**, but with slighly different chemical shifts, and with an additional singlet at δ −15.32 in the $^{31}P\text{-}\{^1H\}$ NMR spectrum, were found. The low amount of the substance responsible was increased with increasing dppb: compound **1** ratio. The IR spectrum only showed bands for ν(N–H) and ν(C≡O) as previously found for complex **6**. The results are consistent with structure **C** (Fig. 1), differing from **6** only in that the PPh_3 is replaced by one dppb ligand co-ordinated to one Ru by one P atom, favoured by a medium tendency to chelation, and with one free P atom [$\delta(^{31}P)$ −15.32].

The dppb-*P* co-ordination mode is also observed in one of the pale products obtained in a second chromatographic fraction: the $^{31}P\text{-}\{^1H\}$ NMR spectrum with signals at δ 45.19 (t), 39.84 (d) and −15.09(s) the lack of ν(N–H) and ν(C≡O) bands in the same positions as found for $[Ru(CO)_2(PPh_3)(dppb)]$ suggests a structure like **G** (Fig. 3) for the complex $[Ru(CO)_2(dppb\text{-}P)(dppb\text{-}PP')]$. The relation between reaction products is shown in Scheme 1.

Complex $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_2(dppb\text{-}PP')_2]$ **11**.—One of the complexes from the reaction of **1** with an excess of dppb is the binuclear dicarbonyl $[Ru_2\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}(CO)_2(dppb)_2]$, which was not isolated in a pure form always being contaminated with complex **9**. The ^1H and ^{31}P NMR spectra show clear sets of signals consistent with structure **D** (Fig. 1): two multiplets at δ 5.37 and 4.22, assignable to the diimine-ring protons, evidence the equivalencies $H_A = H_{A'}$ and $H_B = H_{B'}$ (C_2); and two doublets (^{31}P, δ 25.85 and 14.70) indicating the presence of two types of non-equivalent phosphorus atoms. So, this new complex (structure **D**, Fig. 1) can be considered as resulting from the substitution of the two PPh_3 and two *anti*-CO for two dppb ligands in the starting compound.

The nature of this new complex also explains the versatility of the dppb as ligand. As previously stated, the stability of a dicarbonyldiruthenium complex towards diphosphines is rather low, related to the Ru–Ru bond cleavage, and if it exists, where others cannot, it must be assumed again that the stability of the Ru–dppb-*PP′* bonds is not enough to cleave other interactions to form mononuclear complexes.

Other Reactions.—As the compound $[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]$ has proved to be readily substituted by diphosphines, we tried other reactions with bidentate N- or C-co-ordinating ligands, like 2,2′-bipyridine, cycloocta-1,3- and 1,5-diene, in boiling mesitylene, but the starting compound was recovered unchanged.

The reactivity of compound **1** is summarized in Scheme 1.

Experimental

Reactions were carried out under nitrogen using Schlenk techniques. Solvents were freshly distilled under nitrogen; toluene, xylene, mesitylene, thf, and hexane were dried by refluxing over sodium or sodium–benzophenone.

Microanalytical data (C, H and N) were obtained with a Perkin-Elmer 240-B elemental analyser. Infrared spectra were measured as Nujol mulls (KBr discs) or solutions (CaF_2 discs) using Perkin-Elmer 298 and 1720-XFT spectrometers, ^1H and ^{31}P NMR spectra on a Bruker AC-300 (data relative to $SiMe_4$ and 85% external H_3PO_4).

The compounds $[Ru\{1,2-(NH)_2C_6H_4\}(PPh_3)_3]$,[18] $[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]\cdot C_6H_5Me$,[1] $[RuH_2(PPh_3)_4]$,[19] $[Ru(CO)_3(PPh_3)_2]$,[20] and $[Ru\{1,2-(NH)_2C_6H_4\}(PPh_3)$(diphosphine)$]$[17] were prepared by published procedures. All other products were used as supplied. Unless stated otherwise, Al_2O_3 (activity II) was used in chromatographic separations.

$[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(CO)_3(PPh_3)(dppe)]$ **2**.—The compound $[Ru\{\mu-1,2-(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]\cdot C_6H_5Me$ (50 mg, 0.048 mmol) and $Ph_2P(CH_2)_2PPh_2$ (30 mg, 0.096 mmol) were boiled for 1 h in toluene (3 cm^3) to give a purple solution, which was chromatographed. The first yellow fraction, eluted with toluene, was collected and its volume reduced to *ca.* 1 cm^3; after adding hexane (8 cm^3) and leaving for 1 d at room temperature, a yellow crystalline solid was collected, washed with hexane and dried *in vacuo*. Yield 30 mg (60%) (Found: C, 62.30; H, 4.80; N, 2.50. $C_{60}H_{53}N_2O_3P_3Ru_2$ requires C, 62.95; H, 4.65; N, 2.45%). IR: ν(NH) 3355w (Nujol mull); ν(CO) 1972s and 1912vs cm^{-1} (toluene).

$[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(CO)_3(PPh_3)(dppen)]$ **3**.—The compound $[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]\cdot C_6H_5Me$ (50 mg, 0.048 mmol) and *cis*-$Ph_2PCH{=}CHPPh_2$ (33 mg, 0.084 mmol) were refluxed in toluene (2.5 cm^3) for 1 h. The purple solution was chromatographed and the first yellow fraction eluted with toluene. The volume of this fraction was reduced to *ca.* 3 cm^3 and hexane (6 cm^3) added. After 2 d at −20 °C the yellow solid obtained was washed with hexane and vacuum dried. Yield 25 mg (50%) (Found: C, 63.90; H, 4.70; N, 2.30. $C_{60}H_{51}N_2O_3P_3Ru_2$ requires C, 63.05; H, 4.45; N, 2.45%). IR: ν(NH) 3354w (Nujol mull); ν(CO) 1973vs and 1917vs cm^{-1} (toluene).

$[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(CO)_3(PPh_3)(dppbz)]$ **4**.—The compound $[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]\cdot C_6H_5Me$ (40 mg, 0.038 mmol) and 1,2-$(Ph_2P)_2C_6H_4$ (26 mg, 0.058 mmol) were boiled for 1 h in toluene (2.5 cm^3). The yellow fraction obtained chromatographically on Al_2O_3(activity IV) by eluting with toluene was reduced in volume to 2 cm^3; hexane (5 cm^3) was added and, after 3 d at room temperature, a yellow-orange crystalline solid was collected, washed with hexane and dried *in vacuo*. Yield 25 mg (60%) (Found: C, 64.10; H, 4.60; N, 2.25. $C_{64}H_{53}N_2O_3P_3Ru_2$ requires C, 64.45; H, 4.45; N, 2.35%). IR: ν(NH) 3355w (Nujol mull); ν(CO) 1972vs and 1913vs cm^{-1} (toluene).

$[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(CO)_3(PPh_3)(dppp)]$ **5**.—The compound $[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]\cdot C_6H_5Me$ (50 mg, 0.048 mmol) and $Ph_2P(CH_2)_3PPh_2$ (30 mg, 0.072 mmol) were boiled in toluene (2.5 cm^3) for 1 h. The purple solution was chromatographed and the first yellow fraction, extracted with toluene (its volume reduced to *ca.* 2 cm^3), was mixed with hexane (5 cm^3) and kept at −20 °C for 2 d. The yellow crystalline solid was collected, washed with cold hexane and dried *in vacuo*. Yield 30 mg (60%) (Found: C, 62.90; H, 4.90; N, 2.50. $C_{61}H_{55}N_2O_3P_3Ru_2$ requires C, 63.20; H, 4.75; N, 2.40%). IR: ν(NH) 3345w (Nujol mull); ν(CO) 1972s and 1906vs cm^{-1} (toluene).

$[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(CO)_3(PPh_3)(dppb)]$ **6**.—The compound $[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]\cdot C_6H_5Me$ (50 mg, 0.048 mmol) and $Ph_2P(CH_2)_4PPh_2$ (21 mg, 0.048 mmol) were refluxed for 45 min in toluene (3 cm^3). The brown-red solution was chromatographed and a yellow fraction eluted with toluene. The solvent was evaporated, the solid washed with cold hexane and the residue treated with hot hexane to extract a solution from which, after drying under vacuum, a yellow product was recovered. Yield 32 mg (60%) (Found: C, 62.05; H, 5.60; N, 2.30. $C_{61}H_{63}N_2O_3P_3Ru_2$ requires C, 62.80; H, 5.40; N, 2.40%). IR: ν(NH) 3342w (Nujol mull); ν(CO) 1971s and 1907vs cm^{-1} (toluene).

$[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(\mu-dppm)(CO)_2(PPh_3)_2]$ **7**.—The compound $[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]\cdot C_6H_5Me$ (50 mg, 0.048 mmol) and $(Ph_2P)_2CH_2$ (20 mg, 0.050 mmol) were boiled in toluene (2 cm^3) for 1 h. The brown solution was chromatographed to give an orange solution (eluted with toluene). Its volume was reduced to 2 cm^3 and hexane (4 cm^3) added. After 2 d at room temperature the orange crystals were collected, washed with hexane and dried *in vacuo*. Yield 33 mg (50%) (Found: C, 66.30; H, 4.60; N, 2.30. $C_{69}H_{58}N_2O_2P_4Ru_2$ requires C, 65.10; H, 4.55; N, 2.20%). IR: ν(NH) 3347w (Nujol mull); ν(CO) 1909vs and 1877w cm^{-1} (toluene).

Reaction of $[Ru\{1,2-(NH)_2C_6H_4\}(PPh_3)$(diphosphine)$]$ *with* $[Ru(CO)_3(PPh_3)_2]$.—All the above compounds **2**–**7** can be prepared from $[Ru\{1,2-(NH)_2C_6H_4\}(PPh_3)$(diphosphine)$]$ (0.1 mmol) and $[Ru(CO)_3(PPh_3)_2]$ (0.1 mmol) when refluxed in mesitylene (3 cm^3) for 1 h. The solutions were filtered or chromatographed (elution with toluene), followed by vacuum evaporation of toluene and addition of hexane (10–20 cm^3). After 1 or 2 d at room temperature the crystalline products were obtained. Yields were usually higher (70–80%) than those in the above procedures.

$[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(CO)_3(PPh_3)_3]$ **8**.—(*a*) The compound $[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]\cdot C_6H_5Me$ (65 mg, 0.063 mmol) and $[RuH_2(PPh_3)_4]$ (85 mg, 0.074 mmol) were refluxed in xylene (3 cm^3) for 1 h. The brown solution was chromatographed and the fraction eluted with toluene was dried under vacuum, the solid residue dissolved in toluene (3 cm^3), hexane (10 cm^3) added and filtered. After 3 d at room temperature orange crystals were obtained, washed with hexane and vacuum dried. Yield (based on binuclear complex) 45 mg (60%) (Found: C, 62.90; H, 4.40; N, 2.20. $C_{63}H_{51}N_2O_3P_3Ru_2$ requires C, 64.15; H, 4.35; N, 2.35%). IR: ν(NH) 3362w (Nujol mull); ν(CO) 1997s and 1913vs cm^{-1} (toluene).

(*b*) The compounds $[Ru_2\{\mu-1,2-(NH)_2C_6H_4\}(CO)_4(PPh_3)_2]\cdot C_6H_5Me$ (50 mg, 0.048 mmol) and $[Ru\{1,2-(NH)_2C_6H_4\}(PPh_3)_3]$ (70 mg, 0.070 mmol) were refluxed in xylene (2.5 cm^3) for 1 h. The solution was chromatographed and then method (*a*) was followed. Yield (based on binuclear complex) 25 mg (44%).

Cleavage of the Ru–Ru *Bond by Diphosphine.*—The prepar-

Table 4 Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of compound **7**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ru(1)	1793(1)	2085(1)	2885(1)	C(31)	4324(6)	2788(5)	2014(6)
Ru(2)	1295(1)	2507(1)	3954(1)	C(32)	3977(5)	2501(4)	2517(5)
P(1)	1851(1)	1302(1)	1956(1)	C(33)	3824(4)	2008(4)	4040(4)
P(2)	3013(1)	2487(1)	3407(1)	C(34)	4538(5)	2296(4)	4383(5)
P(3)	2430(1)	2956(1)	4713(1)	C(35)	5153(6)	1943(5)	4892(6)
P(4)	497(1)	2409(1)	4732(1)	C(36)	5041(6)	1324(5)	5041(6)
O(1)	1389(3)	3169(3)	1740(4)	C(37)	4344(6)	1026(5)	4692(6)
O(2)	632(3)	3762(3)	3291(4)	C(38)	3725(5)	1389(4)	4186(5)
N(1)	1840(4)	1580(3)	3965(4)	C(39)	3003(4)	3150(3)	4087(4)
N(2)	666(3)	1943(3)	2953(4)	C(40)	3070(4)	2447(3)	5497(4)
C(1)	1550(4)	2740(4)	2167(4)	C(41)	3858(4)	2530(4)	5801(5)
C(2)	903(4)	3292(4)	3564(4)	C(42)	4319(5)	2117(5)	6384(5)
C(3)	1273(5)	1100(4)	3784(5)	C(43)	3998(6)	1648(5)	6681(6)
C(4)	1295(7)	511(4)	4086(6)	C(44)	3210(5)	1571(5)	6392(5)
C(5)	641(10)	121(5)	3832(9)	C(45)	2757(5)	1971(4)	5808(5)
C(6)	2(9)	334(7)	3284(10)	C(46)	2489(4)	3721(4)	5219(4)
C(7)	−50(6)	932(5)	2937(6)	C(47)	2668(5)	3761(5)	6019(6)
C(8)	584(5)	1309(4)	3200(5)	C(48)	2688(6)	4344(5)	6407(7)
C(9)	1937(4)	1583(4)	1007(4)	C(49)	2508(6)	4880(6)	5969(7)
C(10)	1598(6)	1263(5)	312(6)	C(50)	2314(6)	4854(5)	5155(6)
C(11)	1673(7)	1477(6)	−389(8)	C(51)	2307(5)	4276(4)	4787(5)
C(12)	2082(6)	2016(5)	−396(7)	C(52)	810(5)	1932(4)	5642(5)
C(13)	2416(6)	2346(5)	300(6)	C(53)	901(5)	1271(5)	5588(6)
C(14)	2332(5)	2122(4)	991(5)	C(54)	1217(7)	910(6)	6266(7)
C(15)	2601(4)	699(4)	2277(4)	C(55)	1428(7)	1209(6)	6985(7)
C(16)	3166(5)	641(4)	1961(5)	C(56)	1363(7)	1813(6)	7070(7)
C(17)	3738(7)	171(5)	2247(7)	C(57)	1048(5)	2211(5)	6387(5)
C(18)	3711(6)	−239(5)	2824(6)	C(58)	161(5)	3138(4)	5076(5)
C(19)	3155(5)	−192(4)	3139(6)	C(59)	584(5)	3679(4)	5183(5)
C(20)	2608(5)	288(4)	2876(5)	C(60)	335(7)	4241(6)	5455(7)
C(21)	979(4)	807(4)	1554(4)	C(61)	−356(7)	4235(6)	5597(7)
C(22)	292(5)	1120(4)	1239(5)	C(62)	−764(7)	3697(6)	5493(7)
C(23)	−391(6)	793(5)	905(6)	C(63)	−519(6)	3146(5)	5239(6)
C(24)	−384(7)	152(5)	904(6)	C(64)	−461(5)	2093(4)	4166(5)
C(25)	282(7)	−173(6)	1195(7)	C(65)	−792(6)	1586(5)	4410(6)
C(26)	973(6)	162(5)	1524(6)	C(66)	−1548(8)	1400(6)	3919(8)
C(27)	3475(4)	2868(4)	2776(4)	C(67)	−1909(8)	1722(7)	3247(8)
C(28)	3310(5)	3474(4)	2510(5)	C(68)	−1590(6)	2215(5)	2996(7)
C(29)	3669(6)	3749(5)	2009(6)	C(69)	−854(5)	2389(4)	3450(5)
C(30)	4182(6)	3393(5)	1790(6)				

ation of complexes **2**–**5** from [$Ru_2\{\mu$-1,2-$(NH)_2C_6H_4\}(CO)_4(PPh_3)_2$], and a large excess of diphosphines (for **6** in a 1:1 ratio) in boiling toluene led to lower yields than those obtained following the above procedures, always recovered from the first yellow fractions by chromatographic separation on Al_2O_3. Once the first fractions had been collected, the second purple fractions eluted with thf contained the main reaction products. By solvent evaporation and further addition of thf and hexane, pale solids were recovered and identified as [$Ru(CO)_2(PPh_3)$(diphosphine)]: dppe, ν(CO) 1912s and 1865vs; dppen, 1919m and 1872vs; dppbz, 1919m and 1871vs; dppp, 1902m and 1850vs; dppb, 1900m and 1844vs cm^{-1} (toluene solutions). By concentration of the residual solutions, the purple complexes [$Ru\{1,2$-$(NH)_2C_6H_4\}(CO)$(diphosphine)] were identified: dppe, ν(CO) 1925; dppen, 1935; dppbz, 1918; dppp, 1911; and dppb, 1909 cm^{-1} (toluene solutions).

Reaction of [$Ru_2\{\mu$-1,2-$(NH)_2C_6H_4\}(CO)_4(PPh_3)_2$] *with* $Ph_2P(CH_2)_4PPh_2$.—The compounds [$Ru_2\{\mu$-1,2-$(NH)_2C_6H_4\}(CO)_4(PPh_3)_2$]·$C_6H_5Me$ (75 mg, 0.072 mmol) and $Ph_2P(CH_2)_4PPh_2$ (92 mg, 0.216 mmol) were refluxed in toluene (4 cm^3) for 1 h. The purple solution was chromatographed (Al_2O_3, activity IV) and toluene used as a first eluting solvent to collect a yellow fraction, the solvent evaporated under vacuum and the solid washed with cold hexane. The residue was treated with hot hexane, filtered and the solvent evaporated to afford *ca.* 30 mg of the yellow solid [$Ru_2\{\mu$-1,2-$(NH)_2C_6H_4\}(CO)_3$(dppb-*P*)(dppb-*PP′*)] **9**. IR: ν(NH) 3341w (Nujol mull); ν(CO) 1967s and 1903vs cm^{-1} (toluene). After washing the above residue twice with hot hexane, *ca.* 8 mg remained undissolved. The ^1H and ^{31}P NMR spectra of this solid revealed a mixture of a small amount of compound **9** and [$Ru_2\{\mu$-1,2-$(NH)_2C_6H_4\}$(μ-dppb)$(CO)_2(PPh_3)_2$] **10** and [$Ru_2\{\mu$-1,2-$(NH)_2C_6H_4\}(CO)_2$(dppb-*PP′*)$_2$] **11**. A second purple fraction was eluted with thf, the solvent evaporated to afford a brown-purple residue (*ca.* 10 mg), in which the complexes [$Ru\{1,2$-$(NH)_2C_6H_4\}(CO)$(dppb)] (trace) and [$Ru(CO)_2$(dppb-*P*)(dppb-*PP′*)] **12** were identified. Complexes **9**, **10** and **12** were also obtained, as a mixture, from the reaction between compound **6** and an excess of $Ph_2P(CH_2)_4PPh_2$ in boiling toluene. A mixture of the complexes [$Ru(CO)_2(PPh_3)$(dppb)] and **12** was obtained by refluxing [$Ru(CO)_3(PPh_3)_2$] with an excess of dppb in toluene during 1 h. By adding hexane a solid residue of both compounds was collected.

Crystal Structure Determination of [$Ru_2\{\mu$-1,2-$(NH)_2C_6H_4\}$(μ-dppm)$(CO)_2(PPh_3)_2$] **7**.—A crystal of approximate dimensions 0.20 × 0.22 × 0.35 mm was used for the X-ray analysis. Unit-cell parameters were obtained by least-squares refinement of the θ values of 30 accurately measured reflections (θ 11–18°).

Crystal data. $C_{69}H_{58}N_2O_2P_4Ru_2$·$C_7H_8$, $M = 1365.41$, monoclinic, space group $P2_1/n$, $a = 18.563(8)$, $b = 21.066(9)$, $c = 17.936(7)$ Å, $\beta = 110.47(2)°$, $U = 6571(5)$ Å^3, $Z = 4$, $D_c = 1.380$ g cm^{-3}, $F(000) = 2800$, μ(Mo-Kα) $= 5.92$ cm^{-1}.

Data were collected at room temperature on a Siemens AED single-crystal diffractometer using niobium-filtered Mo-Kα radiation ($\bar{\lambda} = 0.710\,73$ Å) and the θ–2θ scan mode. All reflections with θ in the range 3–24° were measured; of 10 353 independent reflections, 6679, having $I \geqslant 2\sigma(I)$, were considered observed and used in the analysis. The individual profiles were analysed according to Lehmann and Larsen.[21] The intensity of one standard reflection was measured after 50 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. No correction for absorption effects was applied because of the low absorbance of the sample.

The structure was solved by Patterson and Fourier methods, and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms except those of the phenyl groups of the phosphine ligands and of the toluene molecule of solvation. The toluene molecule was found disordered and distributed in two positions of equal occupancy. Only the two imino-hydrogen atoms, clearly localized in the final ΔF map, were refined isotropically. The other hydrogen atoms, except those of the solvent molecule, were placed at their geometrically calculated positions (C–H 1.00 Å) and refined 'riding' on the corresponding carbon atoms. A weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement with $K = 0.796$ and $g = 0.0029$. Final R and R' values were 0.0524 and 0.0701 respectively.

The SHELX 76 and 86 systems of computer programs were used.[22] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 23. Final atomic coordinates for the non-hydrogen atoms are given in Table 4. All calculations were carried out on the CRAY X-MP/48 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the GOULD POWERNODE 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

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

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