Synthesis and Reactions with Electrophiles and Nucleophiles of the Ruthenium(I) Complex $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_6]$. Crystal Structure of $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4\{P(OPh)_3\}_2]$ ($C_{10}H_{10}N_2$ = 1,8-diaminonaphthalene)[†]

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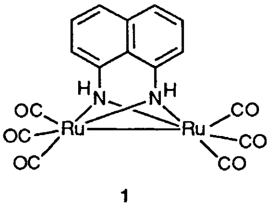
The ruthenium(I) complex $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_6]$ **1** ($C_{10}H_{10}N_2$ = 1,8-diaminonaphthalene) has been prepared by reaction of $[Ru_3(CO)_{12}]$ with an excess of 1,8-diaminonaphthalene under carbon monoxide, at 110 °C. Complex **1** reacts with halogens, tetrafluoroboric acid and dimethyl acetylenedicarboxylate to give the triply bridged complexes $[Ru_2(\mu\text{-}C_{10}H_8N_2)(\mu\text{-}X)(CO)_6]^+$ (X = I **2**, Br **3** or Cl **4**) $[Ru_2(\mu\text{-}C_{10}H_8N_2)(\mu\text{-}H)(CO)_6]BF_4$ **5** and $[Ru_2(\mu\text{-}C_{10}H_8N_2)\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ **6**, respectively. The complexes $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4L_2]$ [L = PPr^i_3 **7**, PPh_3 **8**, $P(OPh)_3$ **9** or dppm-κ*P* **12**], which contain the introduced ligands *trans* to the Ru–Ru bond, have been prepared by reaction of **1** with an excess of the appropriate P-donor ligand L. However the reaction of **1** with an excess of trimethyl phosphite renders the trisubstituted compound $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_3\{P(OMe)_3\}_3]$ **10**. The reaction of **1** with one equivalent of bis(diphenylphosphino)methane (dppm), at room temperature, has been found to give a mixture of oligomers containing bridging and monoco-ordinated dppm ligands. These oligomers aggregate in refluxing tetrahydrofuran to give the polymeric compound $[\{Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4(\mu\text{-}dppm)\}_n]$ **11**. The monosubstituted compound $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_5(py)]$ **13** has been prepared by reaction of complex **1** with pyridine (py). Infrared and ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra of all the compounds are presented and discussed in relation to their structures. The crystal structure of compound **9** has been determined by X-ray diffraction methods. Crystals of **9** are monoclinic, space group $P2_1/m$, with a = 9.520(4), b = 28.073(8), c = 10.070(5) Å, β = 117.15(2)° and Z = 2. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least squares to R = 0.0658 for 3626 observed reflections. The two Ru atoms are doubly bridged by the nitrogen atoms of the deprotonated 1,8-diaminonaphthalene ligand with a short Ru–Ru separation, 2.571(1) Å, consistent with a metal–metal bond.

In the last few years there has been an increased interest in ruthenium(I) compounds,[1–15] but despite this an oxidation state of one is still uncommon for this metal.[1–24] In fact, until recently, very few high-yield syntheses of ruthenium(I) complexes were known, the most important being those of $[Ru_2(\eta\text{-}C_5H_5)_2(CO)_4]$,[18] $[Ru_4H_4(CO)_{12}]$[19] and the carboxylate-bridged complexes $[Ru_2(\mu\text{-}RCO_2)_2(CO)_4L_2]$ (R = alkyl or aryl, L = *P*- or *N*-donor).[20–22] Very recently, we extended the known types of ruthenium(I) dimers by the high-yield syntheses of the pyrazolate-bridged complexes $[Ru_2(\mu\text{-}pz)_2(CO)_6]$[1] (pz = pyrazolate anion) and of the complexes $[Ru_2(\mu\text{-}L)_2(CO)_4(PPh_3)_2]$[2] (HL = 2-pyridone, *N*-methyl-2-mercaptoimidazole, pyrazole or 2-methylpropanethiol; H_2L_2 = 1,8-diaminonaphthalene).

Although the number of known ruthenium(I) dimers has grown considerably, a systematic study of their reactivity has only been carried out for the complexes $[Ru_2(\mu\text{-}RCO_2)_2(CO)_6]$[4–6,20–22] and $[Ru_2(\mu\text{-}pz)_2(CO)_6]$.[1,11] It is also of interest that some binuclear ruthenium(I) complexes have been postulated as intermediates in homogeneously catalysed reactions[25] and are catalytic precursors for the carbonylation of amines,[26] the hydroformylation of olefins,[12] the hydrogenation of carboxylic acids[21] and ketones,[27a] and the addition of acetic acid to alkynes.[27b]

We therefore decided to investigate the reactions of $[Ru_3(CO)_{12}]$ with some arenediamines[3] to attempt to prepare binuclear ruthenium(I) compounds with the doubly dehydrogenated form of the diamine bridging the two metal fragments, as occurs in some rhodium and iridium complex.[28] We also had in mind that $[Ru_3(CO)_{12}]$ reacts with arylamines to give compounds[29] which are catalyst precursors for the hydrogenation of olefins[30] or the carbonylation of nitrobenzene to give phenyl isocyanate.[31] We now report on the synthesis of $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_6]$ **1** ($C_{10}H_{10}N_2$ = 1,8-diaminonaphthalene) and its reactivity towards electrophilic and nucleophilic reagents. We also present the X-ray structure determination of $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4\{P(OPh)_3\}_2]$ **9**. Part of this work has been communicated in a preliminary form.[3]



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[†] μ-Naphthalene-1,8-diamido-$\kappa^2NN'{:}\kappa^2NN'$-bis[dicarbonyl(triphenyl phosphite)ruthenium(I)](*Ru–Ru*).

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

Results and Discussion

Synthesis of $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_6]$ **1**.—The reaction of $[Ru_3(CO)_{12}]$ with a 4.5 fold excess of 1,8-diaminonaphthalene ($C_{10}H_{10}N_2$) in refluxing toluene, under an atmosphere of carbon monoxide, gives the binuclear ruthenium(I) compound $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_6]$ **1**, quantitatively, as indicated by the IR spectrum of the solution which shows, in the carbonyl stretching region, the expected five-band pattern of a hexacarbonyl with C_{2v} symmetry (Table 1). Its nuclearity was inferred from its fast atom bombardment mass spectrum, which shows the parent ion and the successive loss of six CO groups. The presence of two NH groups was confirmed by IR (Table 1) and ^1H NMR (Table 2) spectroscopies. Thus, the complex contains a doubly dehydrogenated 1,8-diaminonaphthalene ligand acting as a six-electron bridge between two $Ru(CO)_3$ fragments.

Table 1 Selected IR data[a]

Compound	ν(CO)/cm^{-1}	ν(NH)[b]/cm^{-1}
1	2084w, 2059m, 2009m, 1994s, 1940w[c]	3348m 3332w
2	2123s, 2072s, 2057m, 1978w[d]	3203s
3	2115s, 2083s, 2065s, 1958w[e]	3110m
4	2147s, 2130m, 2040s, 1993w[b]	3195m
5	2136w, 2121s, 2066s, 1991w[e]	3291s
6	2090s, 2038m, 2017s[d]	3302m 3292m
7	1993s, 1956m, 1921s[f]	3355w
8	1998s, 1968m, 1926s[f]	3342w 3333w
9	2027s, 1998m, 1957s[d]	3331w
10	1984s, 1923s[d]	3361m
11	2027m, 1989m, 1967s, 1925m[g]	3312w
12	1994s, 1960m, 1921s[d]	3340w
13	2054s, 2003s, 1976s, 1938m, 1783w[d]	3369m

[a] s = Strong, m = medium, w = weak. [b] Nujol mull. [c] Hexane solution. [d] Dichloromethane solution. [e] Acetone solution. [f] Toluene solution. [g] thf solution.

No intermediates were detected on monitoring the reaction by IR spectroscopy. However, when the reaction was carried out under nitrogen, in the absence of CO, several intermediates were observed before a dark brown, air-sensitive, solid was formed. The microanalysis of this solid suggests that it may be a polymer with a formula such as $[\{Ru(CO)_2(\mu\text{-}C_{10}H_8N_2)\text{-}Ru(CO)_2\}_n(\mu\text{-}C_{10}H_8N_2)_n]$, but its insolubility and instability prevented any other structural analysis. In the reaction under CO it is necessary to use a large excess of 1,8-diaminonaphthalene to reduce the reaction time, since even using a 4.5 fold excess of the ligand the reaction takes 6 h. Under identical conditions, the reaction of $[Ru_3(CO)_{12}]$ with 1,2-diaminobenzene ($C_6H_8N_2$) gives the trinuclear cluster $[Ru_3(\mu\text{-}C_6H_7N_2)(\mu\text{-}H)(CO)_9]$.[3]

Complex **1** can be handled in air in the solid state. It does not lose carbon monoxide (even *in vacuo*), in contrast to the analogous carboxylate $[Ru_2(\mu\text{-}RCO_2)_2(CO)_6]$ and pyridonate $[Ru_2(\mu\text{-}Opy)_2(CO)_6]$ (HOpy = 2-pyridone) complexes which undergo spontaneous decarbonylation to give polymeric $[\{Ru_2(\mu\text{-}RCO_2)_2(CO)_4\}_n]$[20] and $[\{Ru_2(\mu\text{-}Opy)_2(CO)_4\}_n]$,[32] respectively, probably because the bridge in complex **1** does not contain lone pairs available for further co-ordination.

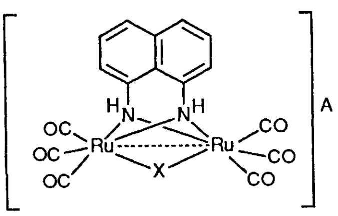
Reactions of Complex **1** *with Electrophiles*.—As expected from its diamagnetism, the 34-electron complex **1** should contain one Ru–Ru bond. This has been confirmed by X-ray crystallography for other ruthenium(I) dimers.[1,2,4,5] Since there are many examples in which metal–metal bonds donate electron density to electrophilic fragments,[33–35] we decided to investigate whether or not the Ru–Ru bond of complex **1** is basic enough to react with halogens, protons or alkynes.

Treatment of toluene solutions of complex **1** with an excess of iodine or bromine leads to the immediate precipitation of $[Ru_2(\mu\text{-}C_{10}H_8N_2)(\mu\text{-}X)(CO)_6]A$ (**2**: X = I, A = I_3; **3**: X = A = Br) as yellow solids very insoluble in toluene. The ionic nature of these complexes was confirmed by their conductivities in acetone, wherein they behave as 1:1 electrolytes. Their IR spectra (Table 1) are nearly identical, indicating that both compounds have the same structure, and show the ν(CO) absorptions at higher frequencies than those observed for **1**, as expected for a higher oxidation state of the metal centres. Their ^1H NMR spectra (Table 2) display the expected peaks for complexes of C_{2v} symmetry, with higher δ

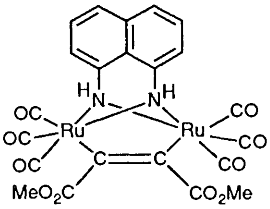
Table 2 Proton and $^{31}P\text{-}\{^1H\}$ NMR data[a]

	^1H (δ)		
Compound	Naphthalene	NH	Other
1[b]	7.50 (d, 7.7), 7.19 (t, 7.7), 7.08 (d, 7.7)	5.14 (s, br)	
2[b]	7.77 (d, 7.8), 7.73 (d, 7.8), 7.45 (t, 7.8)	7.53 (s, br)	
3[c]	8.03 (d, 7.8), 7.73 (d, 7.8), 7.42 (t, 7.8)	8.41 (s, br)	
5[d]	7.82 (d, 7.7), 7.60 (d, 7.7), 7.43 (t, 7.7)	7.56 (s, br)	−10.95 (s)
6[b]	7.47 (d, 7.6), 7.25 (t, 7.6), 7.05 (d, 7.6)	3.88 (m)[e]	3.80 (s)
7[b,f]	7.20 (d, 7.7), 6.97 (t, 7.7), 6.75 (d, 7.7)	4.04 (s, br)	1.51 (m), 0.88 (m)
8[b,g]	6.83 (d, 7.8), 6.39 (t, 7.8), 5.98 (d, 7.8)	4.23 (s, br)	7.9–6.9 (m)
9[c,h]		5.72 (s, br)	7.5–6.7 (m)
10[b,i]	7.28 (d, 7.5), 7.24 (d, 7.5), 6.98 (t, 7.5), 6.95 (t, 7.5), 6.81 (d, 7.5), 6.74 (d, 7.5)	4.52 (m)	3.78 (d, 11.4), 3.20 (d, 11.8), 3.18 (d, 11.8)
12[b,j]	6.78 (d, 7.7), 6.03 (t, 7.7), 5.58 (d, 7.7)	4.29 (s, br)	6.8–7.1 (m), 1.78 (m)
13[c,k]	7.33 (dd, 7.4, 1.2), 7.06 (m), 6.81 (dd, 7.4, 1.2)	5.89 (s, br)	8.07 (d, br, 7.7), 7.39 (tt, 7.7, 1.2), 7.04 (m)

[a] s = Singlet, d = doublet, t = triplet, m = multiplet, br = broad; multiplicity and coupling constants, *J*/Hz, are given in parentheses. [b] In $CDCl_3$. [c] In $[^2H_6]$acetone. [d] In $[^2H_6]$acetone containing 10% $HBF_4\cdot OEt_2$. [e] Tentative assignment. [f] $\delta(^{31}P)$ 49.0 ppm (s). [g] $\delta(^{31}P)$ 27.7 ppm (s). [h] The naphthalene proton resonances overlap with those of the $P(OPh)_3$ ligands; $\delta(^{31}P)$ 124.1 ppm (s). [i] $\delta(^{31}P)$ 165.8 (dd, 27.9, 20.0), 153.1 (dd, 200.7, 27.9) and 142.1 ppm (d, br, 200.7). [j] $\delta(^{31}P)$ AA′XX′ spin system: 18.9 (m) and − 24.2 ppm (m). [k] The naphthalene resonance at δ 7.06 overlaps with the pyridine resonance at δ 7.04.



	X	A
2	I	I_3
3	Br	Br
4	Cl	Cl
5	H	BF_4



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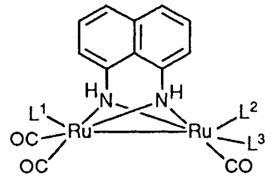


	L^1	L^2	L^3
7	PPr^i_3	PPr^i_3	CO
8	PPh_3	PPh_3	CO
9	$P(OPh)_3$	$P(OPh)_3$	CO
10	$P(OMe)_3$	$P(OMe)_3$	$P(OMe)_3$
12	dppm	dppm	CO
13	CO	py	CO

values than those of complex **1**. The reaction of a toluene solution of **1** with an excess of chlorine gave a very air-sensitive white solid, compound **4**, insoluble in all common solvents. Its microanalysis and IR spectrum in Nujol mull, which is similar to those of **2** or **3**, suggest a formulation such as $[Ru_2(\mu\text{-}C_{10}H_8N_2)(\mu\text{-}Cl)(CO)_6]Cl$. However, an alternative formulation such as $[Ru_2(\mu\text{-}C_{10}H_8N_2)Cl_2(CO)_6]$ cannot be ruled out, since it has been reported that $[Ru_2(\mu\text{-}Cl)_2(CO)_4(PBu^t_3)_2]$ reacts with chlorine to give the neutral ruthenium(II) dimer $[Ru_2Cl_2(\mu\text{-}Cl)_2(CO)_4(PBu^t_3)_2]$.[23b,23f]

The reactivity of compound **1** with halogens is comparable to that described for the pyrazolate-bridged dimer $[Ru_2(\mu\text{-}pz)_2(CO)_6]$.[1] These results suggest a heterolytic cleavage of the halogen molecule X_2 to give the electrophile X^+, which then attacks the Ru–Ru bond. Other studies on the cleavage of metal–metal bonds by halogens for $[M_2(\eta\text{-}C_5H_5)_2(CO)_6]$ (M = Mo or W[33a]), $[M_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (M = Fe[33b] or Ru[33c]) and $[Mn_2\{\mu\text{-}(EtO)_2POP(OEt)_2\}_2(CO)_6]$[33d] have revealed that the reaction frequently proceeds through halogen-bridged cationic intermediates, their stabilities depending on the nature of the halogen, the metal–ligand fragments and the reaction conditions.

Complex **1** can be protonated easily with tetrafluoroboric acid in dichloromethane to give $[Ru_2(\mu\text{-}C_{10}H_8N_2)(\mu\text{-}H)(CO)_6]BF_4$ **5** as a yellow solid, insoluble in hydrocarbons and chlorinated solvents. Although it is soluble in acetone, in this solvent it undergoes deprotonation, regenerating the neutral complex **1** unless an excess of tetrafluoroboric acid is present in the solution. As expected, the ν(CO) absorptions of its IR spectrum are shifted towards higher frequencies than those of complex **1**. Its ^1H NMR spectrum, in a mixture of $[^2H_6]$acetone and $HBF_4{\cdot}OEt_2$, displays a singlet at δ − 10.95, assignable to the bridging hydride. As far as we are aware, the only other ruthenium(I) dimer which has been reported to undergo protonation is $[Ru_2(\eta\text{-}C_5H_5)_2(CO)_4]$.[34e,36] Interestingly, the pyrazolate-bridged dimer $[Ru_2(\mu\text{-}pz)_2(CO)_6]$ is stable in 98% sulphuric acid,[1b] but the acetate-bridged osmium(I) dimer $[Os_2(\mu\text{-}MeCO_2)_2(CO)_4(PPh_3)_2]$ can be protonated with trifluoroacetic acid to give $[Os_2(\mu\text{-}MeCO_2)_2(\mu\text{-}H)(CO)_4(PPh_3)_2]^+$.[34c]

Complex **1** remains unaltered upon treatment with phenylacetylene or diphenylacetylene. However, it does react with an excess of dimethyl acetylenedicarboxylate to give the yellow complex $[Ru_2(\mu\text{-}C_{10}H_8N_2)\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ **6**. Although stable in the solid state, it slowly dissociates the alkyne in solution regenerating the starting material. Its IR and ^1H NMR spectra are in agreement with a ligand orientation parallel to the Ru–Ru vector. Thus, the alkyne behaves as a two-electron ligand as for instance in $[Rh_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}C_2(CF_3)_2\}(\mu\text{-}CO)(CO)_2]$.[35a] An alkyne bonded in a perpendicular fashion to the metal–metal vector always acts as a four-electron donor and, generally, substitution of ligands of the original complex occurs. Thus, $[Rh_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}C_2(CF_3)_2\}(\mu\text{-}CO)(CO)_2]$ reacts with trimethylamine oxide to give $[Rh_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}C_2(CF_3)_2\}(CO)_2]$,[35b] in which the co-ordinated alkyne is perpendicular to the Rh–Rh vector. The only ruthenium(I) dimer which has been reported to add alkynes is $[Ru_2(\eta\text{-}C_5H_5)_2(CO)_4]$, but in this case the alkyne (C_2R_2) undergoes insertion into a metal–carbonyl bond to give $[Ru_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C_2R_2CO)(CO)_2]$.[37]

Reactions of Complex **1** *with Nucleophiles*.—Complex **1** reacts with triisopropylphosphine, triphenylphosphine and triphenyl phosphite to give the disubstituted compounds $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4(PR_3)_2]$ (R = Pr^i **7**, Ph **8** or OPh **9**). Their spectroscopic data (Tables 1 and 2) indicate that substitution has taken place *trans* to the Ru–Ru bond, as has been found in many other ruthenium(I) dimers.[4–8,20–23] However, similar reactions with the complex $[Ru_2(\mu\text{-}dmpz)_2(CO)_6]$ (dmpz = 3,5-dimethylpyrazolate) produce only monosubstituted pentacarbonyl derivatives.[1b] Recently, we have reported an alternative preparation of complex **8** by reaction of $[Ru_3(CO)_9(PPh_3)_3]$ with 1,8-diaminonaphthalene in refluxing toluene.[2]

Interestingly, the trisubstituted compound $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_3\{P(OMe)_3\}_3]$ **10** was formed immediately upon reaction of complex **1** with an excess of trimethyl phosphite. Its $^{31}P\text{-}\{^1H\}$ NMR spectrum (Table 2) shows two doublets of doublets and one broad doublet, as expected for a complex having two $P(OMe)_3$ ligands *trans* to the Ru–Ru bond and one $P(OMe)_3$ ligand *trans* to one Ru–N bond. The ^3J(P–Ru–Ru–P) coupling constant, 200.7 Hz, is much higher than the reported values of 59.3 Hz for $[Os_2(\mu\text{-}MeCO_2)_2(CO)_4(PMe_2Ph)(PPh_3)]$,[38] 60 Hz for $[Os_2(\mu\text{-}MeCO_2)_2(CO)_4(dppm\text{-}\kappa P)_2]$[39] and 115 Hz for $[Ru_2(\mu\text{-}MeCO_2)_2(CO)_4(dppm\text{-}\kappa P)_2]$[5] (dppm = bis(diphenylphosphino)methane]. The ease with which the trisubstituted compound **10** is formed has to be related to the small size and high co-ordination ability of trimethyl phosphite and with the low steric demand for the bridging ligand, which is planar and perpendicular to the Ru–Ru bond.[2]

The products of the reaction of complex **1** with bis(diphenylphosphino)methane, dppm, depend upon the complex to ligand ratio used and upon the reaction conditions. Thus, the reaction of **1** with one equivalent of dppm at room temperature gives a mixture of oligomers containing bridging and monoco-ordinated dppm ligands. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of this mixture (Fig. 1) indicates that the chain length of the oligomers is rather short, since most of the signals are doublets. However, aggregation of these oligomers takes place in refluxing tetrahydrofuran, giving a rather insoluble com-

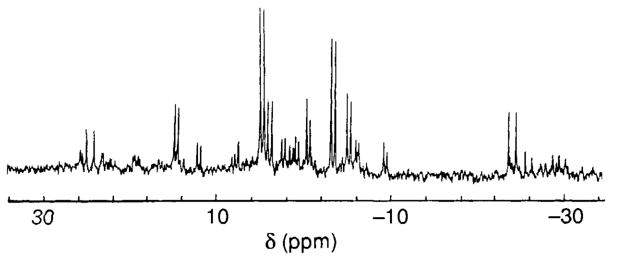
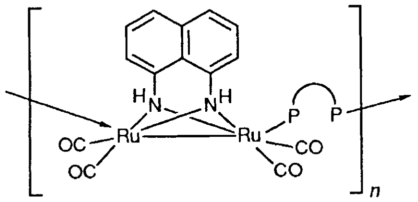


Fig. 1 $^{31}P-\{^1H\}$ NMR spectrum ($CDCl_3$, 20 °C, 121.5 MHz) of the mixture of oligomers obtained from the reaction of complex **1** with dppm at room temperature



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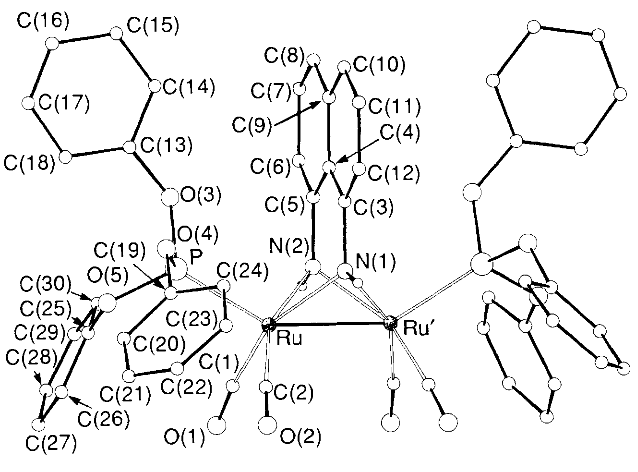

Fig. 2 View of the molecular structure of the dimeric complex $[Ru_2(\mu-C_{10}H_8N_2)(CO)_4\{P(OPh)_3\}_2]$ **9** with the atomic numbering scheme

pound, the $^{31}P-\{^1H\}$ NMR spectrum of which only shows one singlet at δ 40 ppm and two very small multiplets at δ 1 and 18 ppm. These data are in agreement with a polymeric formulation such as $[\{Ru_2(\mu-C_{10}H_8N_2)(CO)_4(\mu\text{-dppm})\}_n]$ **11**. The analogous dppm bridged carboxylate polymeric complexes $[\{M_2(\mu-MeCO_2)_2(CO)_4(\mu\text{-dppm})\}_n]$ (M = Ru[5] or Os[39]) have been reported.

The reaction of compound **1** with two equivalents of dppm gives the binuclear complex $[Ru_2(\mu-C_{10}H_8N_2)(CO)_4(\text{dppm-}\kappa P)_2]$ **12**, which contains two monodentate dppm ligands as inferred from its $^{31}P-\{^1H\}$ NMR spectrum which consists in an AA'XX' spin system at 18.9 and −24.2 ppm. Again, the substitution of the two CO ligands has taken place at the positions *trans* to the Ru–Ru bond [three ν(CO) bands in its IR spectrum, Table 1]. The analogous acetate complexes $[M_2(\mu-MeCO_2)_2(CO)_4(\text{dppm-}\kappa P)_2]$ (M = Ru[5] or Os[39]) have been reported.

Complex **1** also reacts with an excess of pyridine at room temperature giving the monosubstituted compound $[Ru_2(\mu-C_{10}H_8N_2)(CO)_5(py)]$ **13**. Its spectroscopic data (Tables 1 and 2) are also in accordance with a carbonyl substitution *trans* to the Ru–Ru bond.

Description of the X-Ray Structure of $[Ru_2(\mu-C_{10}H_8N_2)(CO)_4\{P(OPh)_3\}_2]$ **9**.—The structure of complex **9** is depicted in Fig. 2; selected bond distances and angles are given in Table 3. The complex has a crystallographically imposed C_s symmetry with the mirror containing the doubly deprotonated 1,8-diaminonaphthalene ligand perpendicular to the Ru–Ru bond. Both nitrogen atoms of the ligand bridge the two Ru atoms symmetrically [Ru–N(1) 2.112(7) and Ru–N(2) 2.138(8) Å]. The Ru_2N_2 framework is in a butterfly arrangement with the two 'wing' bridges forming a dihedral angle of 96.7(4)°. The Ru–Ru separation, 2.571(1) Å, is consistent with a metal–metal bond. Each Ru atom is in a severely distorted octahedral arrangement determined by two carbon atoms from terminal carbonyls, two nitrogen atoms from the bridging ligand, a phosphorus atom from the triphenyl phosphite ligand and the other Ru atom. The distortion in the octahedral arrangement is evidenced especially by the P–Ru–Ru' and P'–Ru'–Ru angles, 148.9(1)°, the N(1)–Ru–Ru' and N(2)–Ru–Ru' angles, 52.5(1) and 53.0(1)° respectively, and the N(1)–Ru–N(2) and N(1')–Ru–N(2') angles, 73.0(1)°, which differ significantly from the theoretical 180 and 90°, respectively. As expected, the carbonyl groups are *trans* to the nitrogen atoms and the $P(OPh)_3$ ligands *trans* to the Ru–Ru bond. The Ru–Ru separation is shorter than in other binuclear $Ru^I–Ru^I$ complexes with bridging ligands, which lie in the range of 2.639(1)–2.759(4) Å.[1,4] Both the distortions in the octahedral arrangement and the rather short Ru–Ru separation must be caused by the strain imposed by the ligand in order to put both nitrogen atoms in a favourable position to act as bridges between the metal atoms. Within the bridging ligand this strain also determines very narrow Ru–N(1)–Ru' and Ru–N(2)–Ru' angles, 75.0(1) and 73.9(1)° respectively against the theoretical 109.5°, but do not influence the N(1) ··· N(2) separation, 2.53(1) Å, which is similar to C(3) ··· C(5), 2.48(2) Å, and the angles N(1)–C(3)–C(4) and N(1)–C(3)–C(12), 118.5(11) and 121.2(11)°, and N(2)–C(5)–C(4) and N(2)–C(5)–C(6), 119.2(9) and 120.3(13)°, remain practically equal and very close to the theoretical values.

The structure of **9** is very similar to that of $[Ru_2(\mu-C_{10}H_8N_2)(CO)_4(PPh_3)_2]$ **8**,[2] in which triphenylphosphine replace the triphenyl phosphite. In **8** the Ru–Ru separation is practically identical, 2.579(1) Å, the Ru–N bonds are comparable, ranging from 2.132(3) to 2.163(3) Å, whereas the

Table 3 Selected bond distances (in Å) and angles (in °) with estimated standard deviations (e.s.d.s) in parentheses for compound **9***

Ru–Ru'	2.571(1)	P–O(3)	1.569(5)
Ru–N(1)	2.112(7)	P–O(4)	1.631(7)
Ru–N(2)	2.138(8)	P–O(5)	1.600(6)
Ru–C(1)	1.877(9)	O(3)–C(13)	1.398(8)
Ru–C(2)	1.884(9)	O(4)–C(19)	1.409(10)
Ru–P	2.293(2)	O(5)–C(25)	1.445(13)
C(1)–O(1)	1.149(11)	N(1)–C(3)	1.426(10)
C(2)–O(2)	1.132(11)	N(2)–C(5)	1.431(12)

Ru'–Ru–C(1)	102.8(2)	Ru–P–O(5)	119.2(3)
Ru'–Ru–C(2)	103.5(3)	O(3)–P–O(4)	95.2(3)
C(1)–Ru–C(2)	91.0(4)	O(3)–P–O(5)	106.8(3)
Ru'–Ru–N(1)	52.5(1)	O(4)–P–O(5)	96.8(3)
Ru'–Ru–N(2)	53.0(1)	P–O(3)–C(13)	128.8(4)
N(1)–Ru–C(1)	155.3(2)	P–O(4)–C(19)	123.9(6)
N(1)–Ru–C(2)	93.2(3)	P–O(5)–C(25)	122.4(5)
N(2)–Ru–C(1)	94.2(3)	Ru–N(1)–Ru'	75.0(1)
N(2)–Ru–C(2)	156.5(3)	Ru–N(1)–C(3)	122.1(1)
N(1)–Ru–N(2)	73.0(1)	Ru–N(2)–Ru'	73.9(1)
Ru'–Ru–P	148.9(1)	Ru–N(2)–C(5)	120.5(1)
P–Ru–C(1)	99.8(2)	Ru–C(1)–O(1)	173.4(7)
P–Ru–C(2)	97.2(3)	Ru–C(2)–O(2)	176.2(8)
P–Ru–N(1)	103.9(1)	N(1)–C(3)–C(4)	118.5(11)
P–Ru–N(2)	104.5(1)	N(1)–C(3)–C(12)	121.2(11)
Ru–P–O(3)	116.5(2)	N(2)–C(5)–C(4)	119.2(9)
Ru–P–O(4)	118.2(2)	N(2)–C(5)–C(6)	120.3(13)

* The primed atoms are related to the unprimed ones by the transformation: $x, \frac{1}{2} - y, z$.

Ru–P bonds to triphenylphosphine, 2.379(1) and 2.391(1) Å, are longer than those to the triphenyl phosphite, 2.293(2) Å, in agreement with the better π acceptor character of the phosphite compared with the phosphine ligand.

Experimental

Unless otherwise noted, all reactions were carried out at room temperature, using standard Schlenk techniques. All solvents were dried and distilled under nitrogen over sodium (hexane, toluene), sodium diphenylketyl [tetrahydrofuran (thf), diethyl ether] or CaH_2 (dichloromethane). All reagents were commercially available analytical grade chemicals and were used without further purification, except for 1,8-diaminonaphthalene which was sublimed prior to use. Elemental analyses were obtained with a Perkin-Elmer 240-B microanalyser. Proton and $^{31}P-\{^1H\}$ NMR spectra were obtained with a Bruker AC-300 instrument at 22 °C with $SiMe_4$ (internal, ^1H) or 85% H_3PO_4 (external, ^{31}P) as references (δ 0 ppm). Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer. Molar conductivities were measured with a Jenway PCM 3 conductivity meter.

Preparations.—$[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_6]$ **1**. The compounds $[Ru_3(CO)_{12}]$ (300 mg, 0.469 mmol) and 1,8-diaminonaphthalene (500 mg, 3.16 mmol) were refluxed in toluene (20 cm^3) under an atmosphere of carbon monoxide for 6 h. During this time the solution changed from orange-red to pale yellow. Vacuum concentration of this solution to *ca*. 6 cm^3 produced an orange solid, which redissolved on exposing the suspension to carbon monoxide. This solution was transferred under CO to a chromatography column (15 × 3 cm) packed with neutral alumina (activity IV) in hexane. Toluene–hexane (1:3) eluted a pale yellow band which on evaporation to dryness gave complex **1** (240 mg, 65%) (Found: C, 36.9; H, 1.6; N, 5.65. $C_{16}H_8N_2O_6Ru_2$ requires C, 36.5; H, 1.55; N, 5.3%).

$[Ru_2(\mu\text{-}C_{10}H_8N_2)(\mu\text{-}I)(CO)_6]I_3$ **2**. Iodine (153 mg, 0.6 mmol) was added to a solution of compound **1** (153 mg, 0.29 mmol) in toluene (5 cm^3). A yellow solid was formed immediately. After stirring (30 min), hexane (20 cm^3) was added and the solid filtered off, washed with hexane (3 × 15 cm^3 portions) and dried to afford compound **2** (255 mg, 85%) (Found: C, 19.0; H, 0.9; N, 2.8. $C_{16}H_8I_4N_2O_6Ru_2$ requires C, 18.6; H, 0.75; N, 2.7%); Λ_M (10^{-3} mol dm^{-3} acetone solution) 114 ohm^{-1} cm^2 mol^{-1}.

$[Ru_2(\mu\text{-}C_{10}H_8N_2)(\mu\text{-}Br)(CO)_6]Br$ **3**. A solution of bromine in carbon tetrachloride (0.74 cm^3, 0.8 mol dm^{-3}, 0.59 mmol) was added to a solution of complex **1** (100 mg, 0.19 mmol) in toluene (5 cm^3). A yellow solid was formed immediately. The liquid was decanted off, the solid was washed with dichloromethane (2 × 5 cm^3 portions) and hexane (2 × 10 cm^3 portions) and dried to give compound **3** (105 mg, 81%) (Found: C, 27.3; H, 1.05; N, 3.6. $C_{16}H_8Br_2N_2O_6Ru_2$ requires C, 28.0; H, 1.2; N, 4.1%; Λ_M (10^{-3} mol dm^{-3} acetone solution) 123 ohm^{-1} cm^2 mol^{-1}.

$[Ru_2(\mu\text{-}C_{10}H_8N_2)(\mu\text{-}Cl)(CO)_6]Cl$ **4**. A solution of chlorine in carbon tetrachloride (0.55 cm^3, 1.5 mol dm^{-3}, 0.83 mmol) was added to a solution of complex **1** (100 mg, 0.19 mmol) in toluene (5 cm^3). A white solid was formed immediately. The liquid was decanted off, the solid was washed with dichloromethane (5 cm^3) and hexane (2 × 10 cm^3 portions) and dried (90 mg, 79%). This white solid changes to violet on exposure to air and is insoluble in all common solvents (Found: C, 32.45; H, 1.45; N, 4.75. $C_{16}H_8Cl_2N_2O_6Ru_2$ requires C, 32.15; H, 1.35; N, 4.7%).

$[Ru_2(\mu\text{-}C_{10}H_8N_2)(\mu\text{-}H)(CO)_6]BF_4$ **5**. An excess of $HBF_4\cdot OEt_2$ (*ca*. 0.1 cm^3) was added to a solution of complex **1** (100 mg, 0.19 mmol) in dichloromethane (5 cm^3) to give a yellow microcrystalline solid. The suspension was vacuum evaporated to dryness and the residue washed with diethyl ether (3 × 3 cm^3 portions) and dichloromethane (2 × 2 cm^3 portions) and dried to give complex **5** (62 mg, 53%) (Found: C, 31.4; H, 1.55; N, 4.65. $C_{16}H_9BF_4N_2O_6Ru_2$ requires C, 31.3; H, 1.5; N, 4.55%).

$[Ru_2(\mu\text{-}C_{10}H_8N_2)\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ **6**. Dimethyl acetylenedicarboxylate (20 μl, 0.163 mmol) was injected into a solution of complex **1** (40 mg, 0.076 mmol) in dichloromethane (5 cm^3). The pale yellow solution was vacuum evaporated to dryness to give a yellow solid, which was washed with hexane (2 × 5 cm^3 portions) and dried (22 mg, 20%) (Found: C, 39.75; H, 2.25; N, 3.95. $C_{22}H_{14}N_2O_{10}Ru_2$ requires C, 39.55; H, 2.1; N, 4.2%).

$[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4(PR_3)_2]$ [PR_3 = PPr^i_3 **7**, PPh_3 **8** or $P(OPh)_3$ **9**]. Triisopropylphosphine (1.1 cm^3, 5.8 mmol) was injected into a solution of complex **1** (1.48 g, 2.8 mmol) in toluene (15 cm^3). The release of CO bubbles was observed. The solution was stirred for 10 min and then evaporated to dryness to give a yellow solid. Washing the solid with hexane (2 × 3 cm^3 portions) gave the complex **7** (1.67 g, 75%) (Found: C. 48.55; H, 6.4; N, 3.65. $C_{32}H_{50}N_2O_4P_2Ru_2$ requires C, 48.6; H, 6.35; N, 3.55%).

Complexes **8** and **9** were prepared by the same method. **8**: Yield 83% (Found: C, 60.5; H, 3.85; N, 2.85. $C_{50}H_{38}N_2O_4P_2Ru_2$ requires C, 60.35; H, 3.85; N, 2.8%). **9**: Yield 73% (Found: C, 55.4; H, 3.5; N, 2.45. $C_{50}H_{38}N_2O_{10}P_2Ru_2$ requires C, 55.05; H, 3.5; N, 2.55%).

$[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_3\{P(OMe)_3\}_3]$ **10**. Trimethyl phosphite (72 μl, 0.66 mmol) was injected into a solution of complex **1** (100 mg, 0.19 mmol) in toluene (5 cm^3). The solution was evaporated to dryness and the residue was washed with hexane (3 × 5 cm^3 portions) and dried (76 mg, 49%) (Found: C, 32.55; H, 4.4; N, 3.65. $C_{22}H_{35}N_2O_{12}P_3Ru_2$ requires C, 32.45; H, 4.35; N, 3.45%).

$[\{Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4(\mu\text{-dppm})\}_n]$ **11**. Complex **1** (45 mg, 0.085 mmol) and dppm (32 mg, 0.083 mmol) were refluxed in thf (10 cm^3) for 1.5 h to give a dark brown solid in a dark brown solution. The suspension was evaporated to dryness and the residue washed with hexane (2 × 5 cm^3 portions) and dried (60 mg, 82%) (Found: C, 53.9; H, 3.65; N, 2.8. $C_{39}H_{30}N_2O_4P_2Ru_2$ requires C, 54.8; H, 3.55; N, 2.3%).

$[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4(dppm)_2]$ **12**. A solution of complex **1** (40 mg, 0.076 mmol) in dichloromethane (3 cm^3) was added to a solution of dppm (59 mg, 0.154 mmol) in the same solvent (3 cm^3). The reaction was instantaneous (IR spectroscopy). The solution was evaporated to dryness and the yellow solid was washed with diethyl ether (2 × 2 cm^3 portions) and dried (71 mg, 75%) (Found: C, 61.3; H, 4.45; N, 2.15. $C_{64}H_{52}N_2O_4P_4Ru_2$ requires C, 62.05; H, 4.25; N, 2.25%).

$[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_5(py)]$ **13**. Pyridine (50 μl) was injected into a solution of complex **1** (80 mg, 0.152 mmol) in hexane (20 cm^3). The solution was evaporated to dryness to give yellow-orange crystals, which were washed with hexane (2 × 3 cm^3 portions) and dried (75 mg, 85%). Both in the solid state and in solution, this complex should be stored under nitrogen (Found: C, 42.1; H, 2.5; N, 7.05. $C_{20}H_{13}N_3O_5Ru_2$ requires C, 41.6; H, 2.25; N, 7.3%).

Crystal Structure Determination of $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4\{P(OPh)_3\}_2]$ **9**.—A crystal of approximate dimensions 0.20 × 0.24 × 0.26 mm was used for the X-ray analysis.

Crystal data. $C_{50}H_{38}N_2O_{10}P_2Ru_2$, M = 1090.95, monoclinic, space group $P2_1/m$, a = 9.520(4), b = 28.073(8), c = 10.070(5) Å, β = 117.15(2)°, U = 2395(2) $Å^3$ (by least-squares refinement from the θ values of 30 accurately measured reflections, $\bar{\lambda}$ = 1.541 838 Å), Z = 2, D_c = 1.513 g cm^{-3}, $F(000)$ = 1100, μ(Cu-Kα) = 63.59 cm^{-1}.

Data collection and processing. Siemens AED single-crystal diffractometer (θ–2θ scan mode, nickel-filtered Cu-Kα radiation). All reflections with θ in the range 3–70° were measured; of 4665 independent reflections, 3626, having $I \geqslant 2\sigma(I)$, were considered observed and used in the analysis. The individual profiles have been analysed according to Lehmann and Larsen.[40] A correction for the absorption effects was applied,[41] using the program ABSORB[42] (maximum and minimum transmission factors values were 1.3206 and 0.6594).

Structure solution and refinements. Direct and Fourier

Table 4 Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of compound **9**

Atom	X/a	Y/b	Z/c
Ru	2523(1)	2042(1)	969(1)
P	3781(2)	1342(1)	2024(2)
O(1)	−822(7)	1845(3)	410(9)
O(2)	1640(8)	1817(3)	−2244(6)
O(3)	4966(6)	1358(2)	3733(5)
O(4)	5052(6)	1130(2)	1511(6)
O(5)	2761(6)	866(2)	1748(7)
N(1)	4374(8)	2500	1179(8)
N(2)	3011(11)	2500	2825(9)
C(1)	474(8)	1894(3)	660(10)
C(2)	1988(9)	1886(3)	−1025(9)
C(3)	5870(11)	2500	2473(12)
C(4)	5903(14)	2500	3866(12)
C(5)	4536(14)	2500	4093(10)
C(6)	4668(21)	2500	5480(14)
C(7)	6264(26)	2500	6762(14)
C(8)	7531(23)	2500	6584(17)
C(9)	7418(16)	2500	5156(14)
C(10)	8766(14)	2500	4953(19)
C(11)	8673(17)	2500	3583(22)
C(12)	7236(12)	2500	2359(19)
C(13)	6153(8)	1033(2)	4578(7)
C(14)	7535(9)	1219(3)	5633(10)
C(15)	8746(11)	921(3)	6544(11)
C(16)	8543(12)	433(3)	6380(11)
C(17)	7189(12)	256(3)	5366(10)
C(18)	5950(11)	543(3)	4425(9)
C(19)	4729(9)	1062(3)	12(8)
C(20)	3783(14)	697(4)	−822(12)
C(21)	3629(17)	626(5)	−2227(14)
C(22)	4384(18)	895(5)	−2757(13)
C(23)	5295(15)	1265(4)	−1976(14)
C(24)	5483(11)	1358(3)	−536(11)
C(25)	1384(9)	842(3)	1999(11)
C(26)	161(11)	631(3)	865(14)
C(27)	−1259(15)	571(5)	1032(23)
C(28)	−1191(21)	746(7)	2376(27)
C(29)	78(22)	950(6)	3341(20)
C(30)	1382(16)	1016(5)	3202(15)

methods, full-matrix least-squares refinements with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms. The two hydrogen atoms bonded to the nitrogen atoms, H(1)N(1) and H(1)N(2), were clearly localized and refined isotropically, all remaining H atoms were placed at their 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 $K = 1.0712$ and $g = 0.0044$. Final R and R' values were 0.0658 and 0.0900 respectively. The SHELX 76 and SHELX 86 systems of computer programs were used.[43] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 44. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 4. All calculations were carried out on the CRAY X-MP/12 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 co-ordinates, thermal parameters and remaining bond lengths and angles.

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