The Different Reactivity of 2-Aminopyridines and 2-Pyridone with $[Ru_3(CO)_{12}]$. *X*-Ray Crystal Structure of $[Ru_3(\mu\text{-}H)(\mu_3\text{-anpy})(CO)_9]$ (Hanpy = 2-Anilinopyridine)†

Pedro L. Andreu, Javier A. Cabeza,* and Victor Riera
Departamento de Química Organometálica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain
Yves Jeannin and Daniel Miguel
Laboratoire de Chimie des Métaux de Transition, Université Pierre et Marie Curie, URA-CNRS 419, 4 Place Jussieu, 75252 Paris Cedex 05, France

---

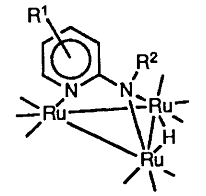
The complex $[Ru_3(CO)_{12}]$ reacts with 2-aminopyridines [2-aminopyridine, 2-amino-4-methylpyridine, -5-methylpyridine, and -6-methylpyridine, 2-(methylamino)pyridine, and 2-anilinopyridine] to give hydrido trinuclear clusters of the type $[Ru_3(\mu\text{-}H)(\mu_3\text{-}L)(CO)_9]$ (**1**)—(**6**) (L = a 2-aminopyridinate-type ligand). Although the presence of substituents on the pyridine ring or on the aminic nitrogen has no influence on the reactivity of the ligands towards $[Ru_3(CO)_{12}]$, it affects the fluxionality of the complexes they form. The solid-state structure of $[Ru_3(\mu\text{-}H)(\mu_3\text{-anpy})(CO)_9]$ (**6**) (Hanpy = 2-anilinopyridine) has been determined by *X*-ray diffraction methods: monoclinic, space group $P2_1/n$, $Z = 4$, $a = 12.705(1)$, $b = 10.621(2)$, $c = 18.427(2)$ Å, and $\beta = 107.349(7)°$. The structure was solved by direct and Fourier methods and refined by full-matrix least squares to $R = 0.019$, $R' = 0.021$, for 3 621 observed reflections. The reaction of $[Ru_3(CO)_{12}]$ with 2-(dimethylamino)pyridine (dmapy) gives $[Ru_3(\mu\text{-dmapy})(\mu\text{-}CO)_3(CO)_7]$. However, with 2-pyridone (HOpy) the polymer $[\{Ru_2(\mu\text{-}Opy)_2(CO)_4\}_n]$ (**8**) or the dimer $[Ru_2(\mu\text{-}Opy)_2(CO)_4(HOpy)_2]$ (**13**) are formed depending on the ratio of the reactants. The reactivity of the polymer (**8**) with neutral ligands to give the binuclear ruthenium(I) dimers $[Ru_2(\mu\text{-}Opy)_2(CO)_4L_2]$ [L = CO, (**9**); MeCN, (**10**); PPh_3, (**11**); $P(OPh)_3$, (**12**); or HOpy, (**13**)] is also reported.

Until recently, the substitution chemistry of $[Ru_3(CO)_{12}]$ had practically been limited to P- and As-donor ligands.[1] Substitution reactions with N-donor ligands have been little studied,[1–13] probably because they require high temperatures that may induce changes in the cluster framework[2–6] and ligand degradation to metallated fragments.[5–11] For example, the reactions of $[Ru_3(CO)_{12}]$ with diazabutadienes[2] or triazenes[5] produce binuclear complexes; however, pyridines,[7] quinolines,[8,9] or benzimidazole[11] give μ-hydrido trinuclear clusters containing orthometallated bridging ligands.

We now report the reactions of $[Ru_3(CO)_{12}]$ with two types of functionalized pyridines: several 2-aminopyridines and 2-pyridone. The deprotonated forms of these ligands have already proved to be excellent bridging fragments in bi- and poly-nuclear complexes of many different metals, their behaviour as bridging ligands being very similar in all cases,[14] even in their reactions with $[Os_3(CO)_{12}]$.[15] With this paper we extend the so far short derivative chemistry of $[Ru_3(CO)_{12}]$ with N-donor ligands, and we also show that 2-aminopyridines and 2-pyridone display a different behaviour towards $[Ru_3(CO)_{12}]$.

Results and Discussion

Reactions involving 2-Aminopyridines.—The reaction of $[Ru_3(CO)_{12}]$ with an excess of 2-aminopyridine (Hapy) in refluxing toluene gives $[Ru_3(\mu\text{-}H)(\mu_3\text{-apy})(CO)_9]$ (**1**), without detectable side reactions. Complex (**1**) was easily identified by its ^1H n.m.r. spectrum (Table 2), and particularly by its fast atom bombardment (f.a.b.) mass spectrum which showed the molecular ion and the loss of nine CO groups. This ruled out the formulation $[Ru_3(\mu\text{-}H)(\mu\text{-apy})(CO)_{10}]$ although a complex with such composition has to be an intermediate in the formation of (**1**). However, complex (**1**) remains unaltered when treated with carbon monoxide (1 atm ≈ 10^5 Pa) in toluene solution at 20 °C, producing a significant amount of $[Ru_3(CO)_{12}]$ at higher temperatures. I.r. monitoring of the reactions did not show any product different from $[Ru_3(CO)_{12}]$ and complex (**1**). These results contrast with those reported for the reaction of $[Os_3(CO)_{10}(C_8H_{14})_2]$ with 2-aminopyridine, which gives $[Os_3(\mu\text{-}H)(\mu\text{-apy})(CO)_{10}]$ at room temperature, and $[Os_3(\mu\text{-}H)(\mu_3\text{-apy})(CO)_9]$ in refluxing cyclohexane.[15] The reaction of $[Os_3(CO)_{12}]$ with an excess of 2-aminopyridine, at



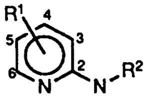
	R^1	R^2
(**1**)	H	H
(**2**)	4-Me	H
(**3**)	5-Me	H
(**4**)	6-Me	H
(**5**)	H	Me
(**6**)	H	Ph

---

† 1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2-μ-hydrido-μ_3-[phenyl(2′-pyridyl)-amido-$N(Ru^{1,2})N'(Ru^3)$]-*triangulo*-triruthenium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. ^{13}C-{^1H} N.m.r. data for complexes (**1**)—(**6**) (δ/p.p.m.)[a]



Compd.	C^2	C^3	C^4	C^5	C^6	R^1	R^2
(**1**)	178.4	111.3	137.9	118.4	153.7		
(**2**)	178.1	111.6	150.1	119.8	152.9	21.0	
(**3**)	178.0	112.4	140.6	130.1	154.6	18.9	
(**4**)	180.4	110.6	140.5	121.9	162.6	31.0	
(**5**)	179.3	109.2	137.8	118.0	154.8		64.4
(**6**)	180.8	117.2	136.6	127.3	154.5		160.4 (*i*),[b] 130.0 (*o*), 123.2 (*m*) 114.0 (*p*)

[a] For $CDCl_3$ solutions; all signals are singlets. [b] *i* = *ipso*, *o* = *ortho*, *m* = *meta*, and *p* = *para*.

Table 2. Proton and ^{31}P-{^1H} n.m.r. data (δ/p.p.m.)[a]

Complex	^1H
(**1**)	8.09 (d, 1), 7.37 (t, 1), 6.71 (dd, 1), 6.51 (d, 1), 4.25 (s, 1), −11.40 (s, 1)
(**2**)	7.94 (d, 1), 6.53 (dd, 1), 6.37 (d, 1), 4.17 (s, 1), 2.21 (s, 3), −11.43 (s, 1)
(**3**)	7.89 (d, 1), 7.16 (dd, 1), 6.42 (d, 1), 4.23 (s, 1), 2.16 (s, 3), −11.45 (s, 1)
(**4**)	7.31 (t, 1), 6.73 (d, 1), 6.35 (d, 1), 4.42 (s, 1), 2.68 (s, 3), −11.42 (s, 1)
(**5**)	8.15 (dd, 1), 7.49 (ddd, 1), 6.72 (t, 1), 6.51 (d, 1), 3.09 (s, 3), −10.67 (s, 1)
(**6**)	8.18 (d, 1), 7.32 (t, 2), 7.18 (t, 1), 7.14 (t, 1), 7.10 (d, 2), 6.60 (dd, 1), 5.38 (d, 1), −11.19 (s, 1)
(**11**)[b]	7.6—7.2 (m, 16), 6.99 (ddd, 1), 5.98 (d, 1), 5.65 (dd, 1)
(**12**)[c]	8.18 (d, 1), 7.3—6.9 (m, 16), 6.28 (d, 1), 6.13 (t, 1)
(**13**)	13.41 (s, 1), 8.39 (d, 1), 7.67 (m, 1), 7.34 (m, 2), 6.88 (t, 1), 6.73 (d, 1), 6.56 (d, 1), 6.33 (t, 1)

[a] For $CDCl_3$ solutions. Multiplicity and integration in parentheses; s = singlet, d = doublet, t = triplet, and m = multiplet. [b] ^{31}P-{^1H}, δ 14.7 (s). [c] ^{31}P-{^1H}, δ 110.0 (s).

Table 3. Selected i.r. data (cm^{-1})[a]

Compound	ν(CO)	Other[b]
(**1**)	2 083m, 2 053s, 2 031s, 2 004s, 1 992s, 1 973w, 1 967w[c]	3 353m (NH)
(**2**)	2 082m, 2 052s, 2 030s, 2 002s, 1 991s, 1 972w, 1 965w[c]	3 366m (NH)
(**3**)	2 082m, 2 052s, 2 030s, 2 003s, 1 992s, 1 972w, 1 966w[c]	3 365m (NH)
(**4**)	2 082m, 2 053s, 2 027s, 2 002s, 1 992s, 1 970w, 1 961w[c]	3 367m (NH)
(**5**)	2 082m, 2 052s, 2 030s, 2 003s, 1 991s, 1 973w, 1 966w[c]	
(**6**)	2 082m, 2 053s, 2 033s, 2 002s, 1 994s, 1 971w, 1 966w[c]	
(**7**)	2 050m, 2 025s, 2 003s, 1 985s, 1 952m, 1 787w[d]	
(**8**)	2 030s, 1 995m, 1 986m, 1 944s, 1 923m, 1 917m[b]	
(**9**)	2 087m, 2 066s, 2 018m, 2 010s, 1 994m, 1 979w[c]	
(**10**)	2 027s, 1 978m, 1 943s, 1 911w[e]	
(**11**)	2 019s, 1 987m, 1 945s, 1 914w[d]	
(**12**)	2 044s, 2 005m, 1 977s, 1 952w[c]	
(**13**)	2 029s, 1 983m, 1 943s, 1 916w[d]	3 563m (OH)

[a] s = Strong; m = medium; w = weak. [b] Nujol mulls. [c] In hexane solution. [d] In thf solution. [e] In MeCN solution.

183 °C, gives two isomers of $[Os_2(\mu\text{-apy})_2(CO)_6]$.[15] It has also been reported that the complex $[Ru_3(\mu\text{-H})(\mu_3\text{-PhCNPh})(CO)_9]$ undergoes reversible carbonylation to give $[Ru_3(\mu\text{-H})(\mu\text{-PhCNPh})(CO)_{10}]$.[16]

The reactions of $[Ru_3(CO)_{12}]$ with some other 2-aminopyridines were also carried out to study whether or not the presence of substituents on the pyridine ring or on the aminic nitrogen affects the reactivity of this type of ligands. It was found that, as long as the aminic nitrogen bears at least one hydrogen, all the ligands [2-amino-4-methylpyridine, -5-methylpyridine, and -6-methylpyridine, 2-(methylamino)pyridine, and 2-anilinopyridine] behave in the same way, affording trinuclear compounds (**2**)—(**6**) similar to (**1**). All six complexes show the same pattern of ν(CO) absorptions in their i.r. spectra (Table 3), indicating a similar structure. This was confirmed by an *X*-ray structure determination on compound (**6**), which will be discussed below.

Although the presence of substituents in the ligands does not affect their reactivity, it affects the fluxionality of the complexes, as suggested by their ^{13}C n.m.r. spectra which display, apart from the resonances of the 2-aminopyridine ligands (Table 1), three types of patterns for the CO resonances at 20 °C (see Figure 1). Complexes (**1**) and (**3**) show one sharp and three broad resonances at δ *ca.* 202, 200, 197, and 185 p.p.m.,

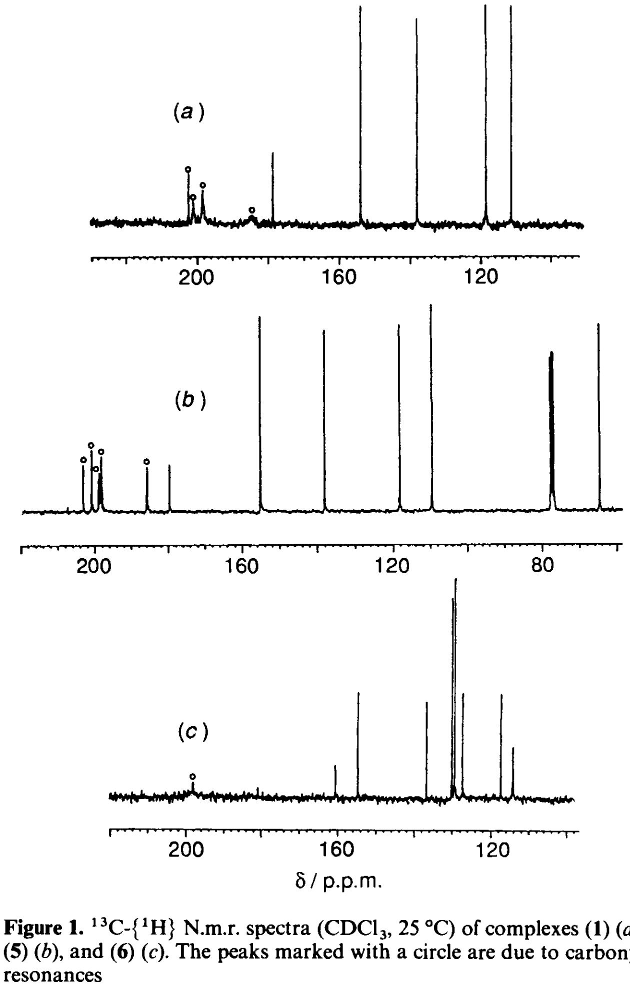


Figure 1. ^{13}C-{^1H} N.m.r. spectra ($CDCl_3$, 25 °C) of complexes (**1**) (*a*), (**5**) (*b*), and (**6**) (*c*). The peaks marked with a circle are due to carbonyl resonances

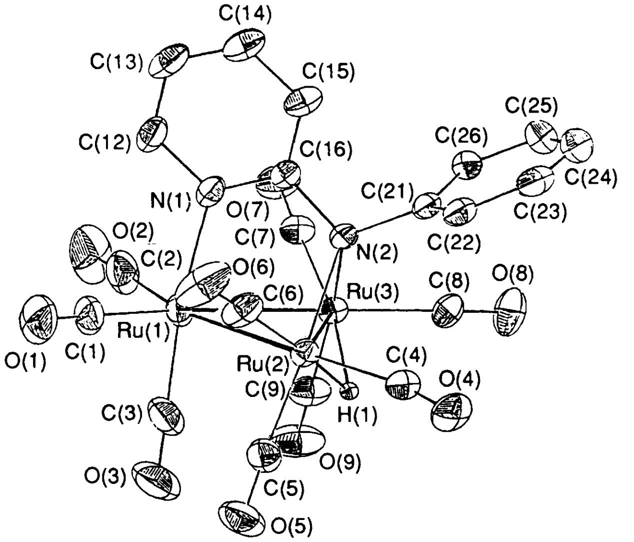


Figure 2. ORTEP diagram of $[Ru_3(\mu\text{-}H)(\mu_3\text{-anpy})(CO)_9]$ (**6**), showing the atomic numbering scheme

Table 4. Crystallographic data for compound (**6**)

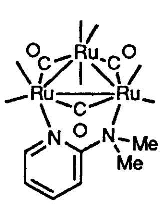
Formula	$C_{20}H_{10}N_2O_9Ru_3$
M	725.5
Crystal system, space group	Monoclinic, $P2_1/n$
a, *b*, *c*/Å	12.705(1), 10.621(2), 18.427(2)
α, β, γ/°	90, 107.349(7), 90
U/Å^3	2 373.4(7)
D_c/g cm^{-3}	2.0304
Z	4
F(000)	1 392
Crystal colour	Orange-red
Crystal size/mm	0.3 × 0.3 × 0.3
μ/cm^{-1}	19.01
Radiation, λ/Å	0.710 69
θ range/°	$1 \leqslant \theta \leqslant 25$
h, *k*, *l* (min., max.)	−15, 15; 0, 12; 0, 25
No of reflections	4 170
No used in refinement	3 621 [$I \geqslant 3\sigma(I)$]
No. of parameters	313
Absorption correction	max. 1.08, min. 1.00
Weighting scheme	Unit
Final *R*, *R′*	0.019, 0.021

respectively; (**6**) shows one broad and weak resonance at δ 198 p.p.m.; and (**2**), (**4**), and (**5**) show five sharp resonances at δ *ca.* 203, 200, 198, 197, and 185 p.p.m. These data indicate that complexes (**2**), (**4**), and (**5**) are not fluxional at room temperature, since five different CO resonances should be expected from their solid-state structure (C_s symmetry). We think that these differences in fluxional behaviour are due to electronic rather than to steric reasons. This is supported by the fact that although complexes (**4**) and (**5**) might be not fluxional because the methyl groups may impede movement of the CO ligands, (**2**) is also not fluxional though its methyl in the 4 position should not impede scrambling of the CO groups at all. The steric argument cannot explain why complex (**5**), which has a methyl on the aminic nitrogen, is rigid, whereas (**6**), which has a phenyl group in the same position, is highly fluxional.

The reaction of $[Ru_3(CO)_{12}]$ with an excess of 2-(dimethylamino)pyridine (dmapy) in refluxing toluene precipitates $[Ru_3(\mu\text{-dmapy})(\mu\text{-}CO)_3(CO)_7]$ (**7**), as a black solid. Although insoluble in hydrocarbons, it dissolves (with decomposition to a black solid) in tetrahydrofuran. Its i.r. spectrum (Table 3) clearly shows bridging (1 787 cm^{-1}) as well as terminal carbonyls. The

Table 5. Fractional atomic co-ordinates for $[Ru_3(\mu\text{-}H)(\mu_3\text{-anpy})(CO)_9]$ (**6**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	1.077 15(2)	0.246 42(3)	0.223 74(2)
Ru(2)	0.925 87(2)	0.071 36(3)	0.144 41(2)
Ru(3)	0.894 22(2)	0.195 57(2)	0.267 38(1)
O(1)	1.240 7(3)	0.247 8(4)	0.130 9(3)
O(2)	1.182 6(3)	0.446 8(4)	0.341 6(3)
O(3)	1.206 5(3)	0.045 7(4)	0.328 2(2)
O(4)	0.759 7(3)	−0.136 2(3)	0.072 5(2)
O(5)	1.092 1(3)	−0.138 9(3)	0.184 4(2)
O(6)	0.995 5(4)	0.151 7(3)	0.008 1(2)
O(7)	0.914 3(3)	0.462 0(3)	0.328 6(2)
O(8)	0.682 1(3)	0.127 2(3)	0.305 8(2)
O(9)	1.030 1(3)	0.092 4(3)	0.418 5(2)
C(1)	1.179 8(4)	0.248 8(4)	0.165 0(3)
C(2)	1.142 2(4)	0.375 6(5)	0.296 3(3)
C(3)	1.156 2(3)	0.121 0(5)	0.288 1(3)
C(4)	0.813 2(3)	−0.053 3(4)	0.098 8(2)
C(5)	1.031 2(4)	−0.057 8(4)	0.169 3(3)
C(6)	0.968 8(4)	0.121 4(4)	0.059 0(3)
C(7)	0.907 3(3)	0.362 3(4)	0.304 9(2)
C(8)	0.757 6(3)	0.150 5(4)	0.287 6(2)
C(9)	0.979 2(4)	0.133 0(4)	0.361 9(2)
N(1)	0.968 7(2)	0.376 4(3)	0.147 3(2)
N(2)	0.823 8(2)	0.238 3(2)	0.145 8(1)
C(12)	1.008 1(3)	0.482 0(4)	0.123 5(3)
C(13)	0.943 7(4)	0.560 4(4)	0.069 4(3)
C(14)	0.837 3(4)	0.530 2(4)	0.037 1(2)
C(15)	0.793 4(4)	0.424 3(4)	0.060 5(2)
C(16)	0.860 9(3)	0.348 9(3)	0.117 6(2)
C(21)	0.702 8(3)	0.229 7(3)	0.116 4(2)
C(22)	0.650 6(3)	0.165 2(3)	0.050 4(2)
C(23)	0.535 0(4)	0.161 6(4)	0.025 1(2)
C(24)	0.473 7(3)	0.221 0(5)	0.063 9(3)
C(25)	0.525 4(3)	0.288 1(4)	0.127 0(3)
C(26)	0.638 9(3)	0.294 8(3)	0.153 2(2)
H(1)	0.906(3)	0.039(4)	0.230(2)



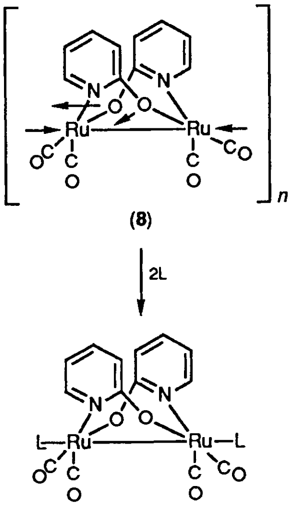
(**7**)

tentative structural assignment is based on microanalysis and the i.r. spectrum only, since its instability and low solubility prevented any other analysis. Nevertheless, the dark colour, the low wavenumber of the μ-CO absorption, and the low solubility suggest that it is similar to $[Ru_3(\mu\text{-pydz})(\mu\text{-}CO)_3(CO)_7]$ (pydz = pyridazine)[17] and to $[Ru_3(\mu\text{-napy})(\mu\text{-}CO)_3(CO)_7]$ (napy = 1,8-naphthyridine),[11] the structures of which have been determined by *X*-ray diffraction methods.

Description of the X-*Ray Structure of Complex* (**6**).—The structure is shown in Figure 2,as well as the atomic numbering scheme; important bond distances and angles are given in Table 6. The cluster consists of a nearly equilateral triangle of ruthenium atoms [Ru–Ru 2.759 1(4), 2 730 2(4), and 2.753 1(4) Å], bonded to nine carbonyl groups (three to each metal atom) and to the two nitrogen atoms of a 2-anilinopyridinate ligand. The Ru(2)–Ru(3) edge is bridged by a hydride [Ru(2)–H(1) 1.71(4), Ru(3)–H(1) 1.83(4) Å], with the Ru(2)–H(1)–Ru(3) plane forming a dihedral angle of 123(1)° with the metal

Table 6. Selected bond distances (Å) and angles (°) for $[Ru_3(\mu\text{-}H)(\mu_3\text{-}anpy)(CO)_9]$ (**6**)

Ru(1)–Ru(2)	2.759 1(4)	Ru(1)–Ru(3)	2.730 2(4)
Ru(1)–C(1)	1.927(5)	Ru(1)–C(2)	1.923(5)
Ru(1)–C(3)	1.865(5)	Ru(1)–N(1)	2.152(3)
Ru(2)–Ru(3)	2.753 1(4)	Ru(2)–C(4)	1.947(4)
Ru(2)–C(5)	1.876(4)	Ru(2)–C(6)	1.890(4)
Ru(2)–N(2)	2.201(3)	Ru(2)–H(1)	1.71(4)
Ru(3)–C(7)	1.891(4)	Ru(3)–C(8)	1.941(4)
Ru(3)–C(9)	1.876(4)	Ru(3)–N(2)	2.198(3)
Ru(3)–H(1)	1.83(4)	O(1)–C(1)	1.134(5)
O(2)–C(2)	1.129(5)	O(3)–C(3)	1.146(6)
O(4)–C(4)	1.130(4)	O(5)–C(5)	1.135(5)
O(6)–C(6)	1.135(5)	O(7)–C(7)	1.138(4)
O(8)–C(8)	1.134(4)	O(9)–C(9)	1.136(4)
N(2)–C(16)	1.420(4)	N(2)–C(21)	1.474(4)
Ru(3)–Ru(1)–Ru(2)	60.20(1)	Ru(3)–Ru(2)–Ru(1)	59.38(1)
Ru(2)–Ru(3)–Ru(1)	60.42(1)	N(2)–Ru(2)–Ru(3)	51.22(7)
N(2)–Ru(3)–Ru(2)	51.30(7)	Ru(3)–N(2)–Ru(2)	77.49(8)
C(21)–N(2)–C(16)	109.9(3)	N(2)–C(16)–N(1)	116.0(3)
Ru(3)–H(1)–Ru(2)	102.2(19)		



L
(**9**) CO
(**10**) MeCN
(**11**) PPh_3
(**12**) $P(OPh)_3$
(**13**) HOpy

Scheme.

triangle. The 2-anilinopyridinate ligand is bonded to the Ru(1) atom through the pyridinic nitrogen N(1) [Ru(1)–N(1) 2.152(3) Å], while the exocyclic nitrogen N(2) bridges the other two ruthenium atoms [Ru(2)–N(2), 2.201(3), Ru(3)–N(2) 2.198(3) Å], the plane Ru(2)–N(2)–Ru(3) being nearly perpendicular to the metal plane. The pyridine ring is roughly planar and almost perpendicular to the Ru_3 plane [dihedral angle 96.5(1)°] and to the phenyl-ring plane [dihedral angle 88.4(1)°].

The structure of complex (**6**) parallels that of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ppy)(CO)_9]$ (Hppy = 1*H*-pyrrolo[2,3-*b*]pyridine),[11] in which the pyrrolic nitrogen spans one Ru–Ru edge and the pyridinic nitrogen is attached to the third ruthenium atom. It is also comparable to those of $[Os_3(\mu\text{-}H)(\mu_3\text{-}apy)(CO)_9]$[15] and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}mbt)(CO)_9]$ (Hmbt = 2-mercaptobenzothiazole], but in the latter one edge of the metal triangle is bridged by a sulphur, instead of a nitrogen atom.[18,*]

Reactions involving 2-Pyridone.—The reaction of $[Ru_3(CO)_{12}]$ with 3 equivalents of 2-pyridone, in refluxing toluene, gives $[\{Ru_2(\mu\text{-}Opy)_2(CO)_4\}_n]$ (**8**) as a yellow solid, insoluble in all common solvents. I.r. monitoring of the reaction showed that $[Ru_4H_4(CO)_{12}]$, the dimeric complex $[Ru_2(\mu\text{-}Opy)_2(CO)_4(HOpy)_2]$ (**13**), and the insoluble solid (**8**) are formed while $[Ru_3(CO)_{12}]$ is being consumed; but $[Ru_4H_4(CO)_{12}]$ and complex (**13**) slowly disappear as the reaction progresses to give the polymer (**8**) quantitatively. The presence of $[Ru_4H_4(CO)_{12}]$ during the reaction is not surprising since hydrogen has to be released during the synthesis of (**8**) and (**13**), and $[Ru_3(CO)_{12}]$ reacts with hydrogen to give $[Ru_4H_4(CO)_{12}]$.[19] In separate experiments we demonstrated that $[Ru_4H_4(CO)_{12}]$ reacts with complex (**13**) or with 2-pyridone to give (**8**), and that (**8**) reacts further with 2-pyridone to give (**13**). The final product from the reaction of $[Ru_3(CO)_{12}]$ with 6 equivalents of 2-pyridone is the dimer (**13**). These results contrast with those reported for the reaction of $[Os_3(CO)_{12}]$ with an excess of 2-pyridone, which gives $[Os_3(\mu\text{-}H)(\mu\text{-}Opy)(CO)_{10}]$ (145 °C, toluene, sealed tube), $[Os_3(\mu\text{-}H)(\mu_3\text{-}Opy)(CO)_9]$ (refluxing toluene), or two isomers of $[Os_2(\mu\text{-}Opy)_2(CO)_6]$ (210 °C, nonane, sealed tube).[15]

The polymeric structure we propose for complex (**8**) is based on its insolubility and on its reactivity. Similar polymeric structures have been proposed for the products of the reactions of $[Ru_3(CO)_{12}]$ with carboxylic acids, $[\{Ru_2(\mu\text{-}O_2CR)_2(CO)_4\}_n]$ (R = alkyl[20,21] or aryl[21]).

Polymer (**8**) reacts with neutral ligands to give binuclear ruthenium(I) complexes (Scheme). The reaction with carbon monoxide (1 atm) in refluxing hexane gives a very pale yellow solution whose i.r. spectrum shows six ν(CO) absorptions (Table 3), as expected for the hexacarbonyl complex of C_2 symmetry $[Ru_2(\mu\text{-}Opy)_2(CO)_6]$ (**9**). This complex could not be isolated as a solid, since it readily regenerates the polymer (**8**) as soon as the carbon monoxide atmosphere is removed. The same situation has been reported for the carboxylates $[Ru_2(\mu\text{-}O_2CR)_2(CO)_6]$;[20] however, the dimers $[Ru_2(\mu\text{-}pz)_2(CO)_6]$ (pz = a pyrazolate ligand) are stable,[4] probably because the nitrogen atoms of their bridges have no lone pairs available for further co-ordination. The two isomers of the osmium dimer $[Os_2(\mu\text{-}Opy)_2(CO)_6]$ are also stable.[15]

The reaction of polymer (**8**) with boiling acetonitrile gives a pale yellow solution whose i.r. spectrum indicated that it contained a single compound, tentatively identified as $[Ru_2(\mu\text{-}Opy)_2(CO)_4(MeCN)_2]$ (**10**); but, on removing the solvent *in vacuo*, the complex decomposes to a somewhat insoluble solid whose acetonitrile content varies from one preparation to another. Triphenylphosphine, triphenyl phosphite, and 2-pyridone react with polymer (**8**) to give the stable dimeric compounds (**11**), (**12**), and (**13**). This kind of reactivity parallels that of the carboxylato complexes $[\{Ru_2(\mu\text{-}O_2CR)_2(CO)_4\}_n]$.[20–22] The i.r. spectra in the ν(CO) region of complexes (**10**)—(**13**) are very similar (Table 3), as expected for compounds of the same structure. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of complexes (**11**) and (**12**) are singlets (Table 2), suggesting that the bridging ligands are in a head-to-tail arrangement, since a head-to-head disposition would have given doublets. Both head-to-head and head-to-tail arrangements have been described for complexes of other metals bridged by two 2-pyridonate ligands.[15,23]

Complex (**11**) can also be made by thermal reaction of $[Ru_3(CO)_9(PPh_3)_3]$ with 2-pyridone.[24] While this work was in progress, Singleton and co-workers[25] published an alternative synthesis of complex (**11**) {by metathesis of $[Ru_2(\mu\text{-}$

---

* In this complex the edge bridged by the sulphur and the hydride is slightly longer than the other two [2.836(5) *versus* 2.786(5) and 2.798(6) Å].

$O_2CR)_2(CO)_4(PPh_3)_2]$ with sodium pyridonate}, as well as its *X*-ray crystal structure, which confirms our structural assignment. Also a significant development appeared and increased the interest in ruthenium(I) dimers: the carboxylato complexes $[Ru_2(\mu\text{-}O_2CR)_2(CO)_4L_2]$ (R = alkyl or aryl; L = a P-donor ligand) catalyse the hydroformylation of olefins under very mild conditions, the catalytic species being binuclear complexes.[26]

Conclusion

From the work described in this paper three conclusions can be drawn. (*a*) Although 2-aminopyridinate and 2-pyridonate ligands may look very similar, and in fact form many similar complexes with a wide range of metallic fragments,[14,15] their behaviour towards $[Ru_3(CO)_{12}]$ is quite different: the 2-aminopyridinate derivatives are trinuclear, whereas those derived from 2-pyridonate are polymeric or binuclear. The reason for this behaviour is still obscure, since the reaction of $[Ru_3(CO)_{12}]$ with 8-hydroxyquinoline gives a trinuclear complex[27] and the reactions of $[Os_3(CO)_{12}]$ with 2-aminopyridine and 2-pyridone give similar compounds.[15] (*b*) The presence of substituents on the pyridine ring or on the aminic nitrogen of 2-aminopyridine moieties does not affect their reactivity towards $[Ru_3(CO)_{12}]$, but affects the fluxionality of the complexes obtained. (*c*) The synthesis of the polymer (**8**) opens an important path to the preparation of new binuclear ruthenium(I) dimers whose catalytic properties are now being investigated.

Experimental

General Procedures and Instrumentation.—Unless otherwise noted, all reactions were carried out under nitrogen. All solvents were distilled under nitrogen over sodium (hexane, toluene), sodium diphenylketyl [tetrahydrofuran (thf), Et_2O], or CaH_2 (CH_2Cl_2). The complex $[Ru_3(CO)_{12}]$ was prepared from $RuCl_3 \cdot nH_2O$ and carbon monoxide as described elsewhere.[28] All ligands were commercially available analytical grade chemicals used without further purification. Product isolations were generally carried out in air. Column chromatography was performed using a 10 × 3 cm column packed with neutral alumina (activity I) as solid support. Elemental analyses were obtained with a Perkin-Elmer 240-B microanalyser. Mass spectra were recorded on a Kratos MS-80 spectrometer using the f.a.b. ionization mode. The $^{13}C\text{-}\{^1H\}$ (Table 1), ^1H and $^{31}P\text{-}\{^1H\}$ (Table 2) n.m.r. spectra were obtained on a Bruker AC-300 instrument, in $CDCl_3$ solutions at 298 K, using internal $SiMe_4$ (^{13}C, ^1H) and external 85% H_3PO_4 (^{31}P) as standards. I.r. spectra (Table 3) were recorded on Perkin-Elmer 298 (Nujol mulls) and FT 1720-X (solution samples) spectrophotometers.

Preparation of $[Ru_3(\mu\text{-}H)(\mu_3\text{-apy})(CO)_9]$ (**1**) (Hapy = 2-*Aminopyridine*) *and Related Complexes.*—The complex $[Ru_3(CO)_{12}]$ (0.2 g, 0.313 mmol) and 2-aminopyridine (0.057 g, 0.62 mmol) were stirred in refluxing toluene (30 cm^3) for 45 min. I.r. monitoring of the reaction indicated that it was complete after 30 min. The solution was concentrated to *ca.* 10 cm^3 and transferred to a chromatography column. Hexane eluted the toluene and a trace amount of unreacted $[Ru_3(CO)_{12}]$. Toluene–thf (5:1) eluted an orange band which on evaporation to dryness gave complex (**1**) as an orange-red solid (0.13 g, 64%) (Found: C, 26.10; H, 0.90; N, 4.60. $C_{14}H_6N_2O_9Ru_3$ requires C, 25.90; H, 0.95; N, 4.30%); *m/z* 649 (M^+, ^{101}Ru).

Complexes (**2**)—(**6**) were prepared by the same method, starting from the appropriate ligand (0.6 mmol) and $[Ru_3(CO)_{12}]$ (0.2 g, 0.313 mmol): (**2**), yield 0.16 g (77%) (Found: C, 27.55; H, 1.35; N, 3.90. $C_{15}H_8N_2O_9Ru_3$ requires C, 27.15; H, 1.20; N, 4.20%); (**3**), 0.13 g (63%) (Found: C, 26.90; H, 1.30; N, 4.20. $C_{15}H_8N_2O_9Ru_3$ requires C, 27.15; H, 1.20; N, 4.20%); (**4**), 0.13 g, (63%) (Found: C, 27.60; H, 1.10; N, 4.70. $C_{15}H_8N_2O_9Ru_3$ requires C, 27.15; H, 1.20; N, 4.20%), *m/z* 663 (M^+, ^{101}Ru); (**5**), 0.11 g (53%) (Found: C, 27.60; H, 1.20; N, 4.25. $C_{15}H_8N_2O_9Ru_3$ requires C, 27.15; H, 1.20; N, 4.20%); (**6**) 0.15 g (66%) (Found: C, 33.60; H, 1.35; N, 4.50. $C_{20}H_{10}N_2O_9Ru_3$ requires C, 33.10; H, 1.40; N, 3.85%), *m/z* 725 (M^+, ^{101}Ru).

Preparation of $[Ru_3(\mu\text{-dmapy})(\mu\text{-}CO)_3(CO)_7]$ (**7**) [dmapy = 2-(*Dimethylamino*)*pyridine*].—The complex $[Ru_3(CO)_{12}]$ (0.2 g, 0.313 mmol) and an excess of 2-(dimethylamino)pyridine (0.1 cm^3) were stirred in refluxing toluene (10 cm^3) for 2 h, to give a dark brown solution and a black oil adhering to the flask walls. The mixture was allowed to cool to room temperature and the solution was decanted off. Addition of diethyl ether (3 × 10 cm^3) to the oily residue, with stirring, led to precipitation of complex (**7**) as a black solid (0.19 g, 86%) (Found: C, 29.15; H, 1.50; N, 4.20. $C_{17}H_{10}N_2O_{10}Ru_3$ requires C, 28.95; H, 1.45; N, 3.95%).

Preparation of $[\{Ru_2(\mu\text{-Opy})_2(CO)_4\}_n]$ (**8**) (HOpy = 2-pyridone).—The complex $[Ru_3(CO)_{12}]$ (0.2 g, 0.313 mmol) and 2-pyridone (0.088 g, 0.94 mmol) were refluxed in toluene (20 cm^3) for 2 h, to give a yellow solid and a pale yellow solution. The solution contained a small amount of $[Ru_4H_4(CO)_{12}]$ (i.r. identification). The solid was washed with diethyl ether (2 × 10 cm^3) and dried under vacuum (0.16 g, 68%). It should be stored under nitrogen (Found: C, 34.00; H, 1.75; N, 5.35. $C_{14}H_8N_2O_6Ru_2$ requires C, 33.45; H, 1.60; N, 5.60%).

Reactions of Polymer (**8**).—*With carbon monoxide.* Carbon monoxide was bubbled through a suspension of polymer (**8**) (0.05 g, 0.1 mmol) in hexane (30 cm^3), at reflux temperature. After 30 min all the solid had dissolved, giving a very pale yellow solution. The i.r. spectrum of this solution indicated (Table 3) that it contained only $[Ru_2(\mu\text{-Opy})_2(CO)_6]$ (**9**). This complex could not be isolated since its solutions only are stable under carbon monoxide, depositing the polymer (**8**) on standing under nitrogen or when they are concentrated under vacuum.

With acetonitrile. A suspension of polymer (**8**) (0.05 g, 0.1 mmol) in acetonitrile (10 cm^3) was stirred at reflux temperature until all the solid had dissolved (*ca.* 20 min), to give a pale yellow solution whose i.r. spectrum showed that it contained only $[Ru_2(\mu\text{-Opy})_2(CO)_4(MeCN)_2]$ (**10**) (Table 3). Vacuum evaporation to dryness and washing the residue with hexane (10 cm^3) afforded an unknown solid of variable composition, indicating that complex (**10**) is stable only in acetonitrile solution.

Preparation of $[Ru_2(\mu\text{-Opy})_2(CO)_4(PPh_3)_2]$ (**11**).—Triphenylphosphine (0.053 g, 0.2 mmol) and polymer (**8**) (0.05 g, 0.1 mmol) were stirred in thf (20 cm^3) at reflux temperature until all the solid had dissolved (*ca.* 1 h). The pale yellow solution was evaporated to dryness and the residue washed with hexane (10 cm^3) to give complex (**11**) as a yellow solid (0.087 g, 85%) (Found: C, 58.15; H, 3.70; N, 2.70. $C_{50}H_{38}N_2O_6P_2Ru_2$ requires C, 58.50; H, 3.70; N, 2.75%).

Preparation of $[Ru_2(\mu\text{-Opy})_2(CO)_4\{P(OPh)_3\}_2]$ (**12**).—Triphenyl phosphite (53 µl, 0.062 g, 0.2 mmol) and polymer (**8**) (0.05 g, 0.1 mmol) were stirred in thf (20 cm^3) at reflux temperature until all the solid had dissolved (*ca.* 1 h). The solution was evaporated to dryness to give complex (**12**) as a pale yellow solid, soluble in all organic solvents, in quantitative yield (Found: C, 54.60; H, 2.95; N, 2.65. $C_{50}H_{38}N_2O_{12}P_2Ru_2$ requires C, 53.50; H, 3.40; N, 2.50%).

Preparation of $[Ru_2(\mu\text{-Opy})_2(CO)_4(HOpy)_2]$ (**13**).—The complex $[Ru_3(CO)_{12}]$ (0.15 g, 0.235 mmol) and 2-pyridone

(0.145 g, 1.525 mmol) were stirred in toluene (20 cm^3), at reflux temperature, for 1.5 h. The yellow solution was evaporated to dryness and the residue washed with hexane (10 cm^3) to give complex (**13**) as a yellow solid (0.2 g, 83%) (Found: C, 41.85; H, 2.55; N, 7.90. $C_{24}H_{18}N_4O_8Ru_2$ requires C, 41.60; H, 2.60; N, 8.10%).

X-Ray Data Collection, Structure Determination, and Refinement for Compound (**6**).—The relevant details of the crystal structure determination are collected in Table 4. A single crystal of compound (**6**) (grown from CH_2Cl_2–hexane) was selected and mounted on an Enraf–Nonius CAD-4 diffractometer. Unit-cell parameters were obtained by least-squares refinement on setting angles of 25 centred reflections in the range $14 \leqslant \theta \leqslant 15°$. Data were collected at room temperature in ω—2θ mode with ω scan width $1.2 + 0.34\tan\theta$ (extended by 25% on either side for background determination). Two standard reflections were measured every 2 h. An empirical absorption correction (based on a ψ scan) was applied.[29] All three Ru atoms were found by direct methods with SHELX,[30] and the remaining non-hydrogen atoms with subsequent Fourier maps. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations. The hydride atom H(1) was found in a Fourier difference map and was refined isotropically. The remaining hydrogen atoms (those on the phenyl and pyridine rings) were placed in calculated positions (C–H 0.96 Å, overall thermal parameter 0.8 $Å^2$) and their co-ordinates, not refined, were recalculated after each cycle. All calculations were performed with CRYSTALS.[31] Scattering factors with correction for anomalous dispersion were also from CRYSTALS.

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

Acknowledgements

Financial support from the Dirrecíon Generale de Investigación Científica Y Téchica (Spain) (Project no. 85-0402) and the Centre National de la Recherche Scientifique (France) is gratefully acknowledged. We also thank Dr. D. W. Bruce and Mr. P. Ashton (University of Sheffield) for the f.a.b. mass spectra.

References

1 For recent reviews see, M. I. Bruce, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 4, p. 843; M. I. Bruce, *Coord. Chem. Rev.*, 1987, **76**, 1.
2 L. H. Staal, L. H. Polm, R. W. Balk, G. van Koten, K. Vrieze, and A. M. F. Brouwers, *Inorg. Chem.*, 1972, **11**, 1453.
3 F. Calderazzo, C. Floriani, R. Henzi, and F. L'Eplattenier, *J. Chem. Soc. A*, 1969, 1378.
4 J. A. Cabeza, C. Landázuri, L. A. Oro, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Organomet. Chem.*, 1987, **322**, C16; J. A. Cabeza, C. Landázuri, L. A. Oro, D. Belletti, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.*, 1989, 1093; F. Neumann and G. Süss-Fink, *J. Organomet. Chem.*, 1989, **367**, 175.
5 S. F. Colson, S. D. Robinson, M. Motevalli, and M. D. Hursthouse, *Polyhedron*, 1988, **7**, 1919.
6 D. P. Maddern, A. J. Carty, and T. Birchall, *Inorg. Chem.*, 1972, **11**, 1453; J. A. Cabeza, V. Riera, M. A. Pellinghelli, and A. Tiripicchio, *J. Organomet. Chem.*, 1989, **376**, C23.
7 M. I. Bruce, M. G. Humphrey, M. R. Snow, E. R. T. Tiekink, and R. C. Wallis, *J. Organomet. Chem.*, 1986, **314**, 311.
8 A. Eisenstadt, C. M. Giandomenico, M. F. Frederick, and R. M. Laine, *Organometallics*, 1985, **4**, 311.
9 R. H. Fish, T-J. Kim, J. L. Stewart, J. H. Bushweller, R. K. Rosen, and J. W. Dupon, *Organometallics*, 1986, **5**, 2193.
10 G. A. Foulds, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, 1985, **294**, 123.
11 J. A. Cabeza, L. A. Oro, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.*, 1988, 1437; M. A. Pellinghelli, A. Tiripicchio, J. A. Cabeza, and L. A. Oro, *J. Chem. Soc., Dalton Trans.*, 1990, 1509.
12 F. A. Cotton and D. J. Jamerson, *J. Am. Chem. Soc.*, 1976, **98**, 5396.
13 T. Vanäläinen, J. Pursiainen, and T. A. Pakkanen, *J. Chem. Soc., Chem. Commun.*, 1985, 1348.
14 See, for example, F. A. Cotton, R. H. Niswander, and J. C. Sekutowski, *Inorg. Chem.*, 1978, **17**, 3541; A. R. Chakravarty, F. A. Cotton, and E. S. Shamshoum, *ibid.*, 1984, **23**, 4216; L. A. Oro, M. A. Ciriano, F. Viguri, C. Foces-Foces, and F. H. Cano, *Inorg. Chim. Acta*, 1987, **128**, 119; A. R. Chakravarty, F. A. Cotton, and D. A. Tocher, *Inorg. Chem.*, 1985, **24**, 172; T. V. O'Halloran, M. M. Roberts, and S. J. Lippard, *ibid.*, 1986, **25**, 957.
15 A. J. Deeming, R. Peters, M. B. Hursthouse, and J. D. J. Backer-Dirks, *J. Chem. Soc., Dalton Trans.*, 1982, 1205.
16 A. Basu, S. Bhaduri, K. Sharma, and P. G. Jones, *J. Chem. Soc., Chem. Commun.*, 1987, 1126.
17 F. A. Cotton and D. J. Jamerson, *J. Am. Chem. Soc.*, 1976, **98**, 5396.
18 S. Jeannin, Y. Jeannin, and G. Lavigne, *Inorg. Chem.*, 1978, **17**, 2103.
19 S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 3942.
20 G. R. Crooks, B. F. G. Johnson, J. Lewis, J. G. Williams, and G. Gamlen, *J. Chem. Soc. A*, 1969, 2761.
21 M. Rotem, I. Goldberg, U. Shmueli, and Y. Shvo, *J. Organomet. Chem.*, 1986, **314**, 185.
22 H. Schumann, J. Opitz, and J. Pickardt, *J. Organomet. Chem.*, 1977, **128**, 253; H. Schumann and J. Opitz, *Chem. Ber.*, 1980, **113**, 989; S. Sherlock, M. Cowie, E. Singleton, and M. M. de V. Steyn, *Organometallics*, 1988, **7**, 1663.
23 See, for example, G. S. Rodmen and K. R. Mann, *Inorg. Chem.*, 1985, **24**, 258; D. P. Bancroft, F. A. Cotton, L. R. Falvello, and W. Schwotzer, *ibid.*, 1986, **25**, 763; L. S. Hollis and S. J. Lippard, *ibid.*, 1983, **22**, 3637; M. A. Ciriano, B. E. Villarroya, L. A. Oro, M. C. Apreda, C. Foces-Foces, and F. H. Cano, *J. Organomet. Chem.*, 1989, **366**, 377.
24 P. L. Andreu, J. A. Cabeza, V. Riera, F. Robert, and Y. Jeannin, *J. Organomet. Chem.*, 1989, **372**, C15.
25 S. J. Sherlock, M. Cowie, E. Singleton, and M. M. de V. Steyn, *J. Organomet. Chem.*, 1989, **361**, 353.
26 J. Jenk, P. Kalck, E. Pinelli, M. Siani, and A. Thorez, *J. Chem. Soc., Chem. Commun.*, 1988, 1428.
27 J. A. van Doorn and P. W. M. N. van Loeuwen, *J. Organomet. Chem.*, 1981, **222**, 299.
28 M. I. Bruce, J. G. Matisons, R. C. Wallis, J. M. Patrick, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 2365.
29 M. R. Churchill, F. J. Hollander, and J. S. Hutchinson, *Inorg. Chem.*, 1977, **16**, 2655.
30 G. M. Sheldrick, SHELX Program for Crystal Structure Determination, University of Cambridge, 1976.
31 J. R. Carruthers and D. W. Watkin, CRYSTALS, an Advanced Crystallographic Computer Program, Chemical Crystallography Laboratory, University of Oxford, 1985.

Received 18*th October* 1989; *Paper* 9/04495G