The Reactions of $[Ru_3(CO)_{12}]$ with Nitrogen-containing Heterocycles. Crystal Structures of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ppy)(CO)_9]$ and $[Ru_3(\mu\text{-}napy)(\mu\text{-}CO)_3(CO)_7]$ †

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The reactions of $[Ru_3(CO)_{12}]$ with several nitrogen-containing heterocycles under thermal conditions have been studied. 1*H*-Pyrrolo[2,3-*b*]pyridine (Hppy) and benzimidazole (Hbzim) give the trinuclear clusters $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ppy)(CO)_9]$ (**1a**) and $[Ru_3(\mu\text{-}H)(\mu\text{-}bzim)(CO)_{10}]$ (**2a**), respectively. However, benzotriazole (Hbztz) affords the dinuclear complex $[Ru_2(\mu\text{-}bztz)_2(CO)_6]$ (**3a**). 1,8-Naphthyridine(napy) produces the carbonyl-bridged cluster $[Ru_3(\mu\text{-}napy)(\mu\text{-}CO)_3(CO)_7]$ (**4**). Complex (**4**) reacts with HBF_4 to give the cationic complex $[Ru_3(\mu\text{-}H)(\mu\text{-}napy)(CO)_{10}][BF_4]$ (**5**) which has all terminal carbonyls. Complex (**5**) regenerates complex (**4**) on reaction with NEt_3. 1,10-Phenanthroline(phen),2,2′-biquinoline(biquin) or 2,2′-bipyrimidine (bipym) react with $[Ru_3(CO)_{12}]$ to give $[Ru_3(L\text{–}L)(\mu\text{-}CO)_2(CO)_8]$ [L–L = phen (**6a**), biquin (**6b**), or bipym (**6c**)], in which the L–L ligand chelates one ruthenium, and two carbonyl groups bridge the same edge of the triangle. The structures of compounds (**1a**) and (**4**) have been established by *X*-ray diffraction studies. Complex (**1a**) crystallizes in the monoclinic space group $P2_1/a$ with a = 14.688(5), b = 16.251(7), c = 8.594(5) Å, β = 97.64(2)°, and Z = 4. Crystals of (**4**) are monoclinic, space group $P2_1/c$ with a = 15.374(7), b = 17.336(6), c = 16.167(7) Å, β = 98.02(3)°, and Z = 8. Both structures were solved from diffractometer data by direct and Fourier methods and refined by full-matrix [(**1a**)] and block-matrix [(**4**)] least-squares to R = 0.0349 for 3 211 observed reflections for (**1a**) and to R = 0.0405 for 4 205 observed reflections for (**4**). In (**1a**) the pyrrolopyridinate ligand is co-ordinated to three Ru atoms, through the pyridinic N atom to one metal and through the pyrrolic N atom symmetrically bridging the other two, which are involved also in a hydridic bridge. In (**4**) there are two independent, but very similar, complexes in which three carbonyls bridge the three edges of a triangular metal array; the 1,8-naphthyridine ligand bridges two metal atoms through the two N atoms.

Although the substitution of carbonyl groups in $[Ru_3(CO)_{12}]$ by uni-, bi-, or tri-dentate phosphorus- or arsenic-donor ligands has been extensively studied, relatively few derivatives of $[Ru_3(CO)_{12}]$ which contain nitrogen-donor ligands have been reported.[1] This may be due to the vigorous conditions required for reaction of the nitrogen compounds, which frequently lead to the break up of the cluster, for example as with Schiff bases,[2] diazepines,[3] or diazabutadienes.[4] However, some nitrogen-containing heterocycles, such as pyridines,[5,6] quinolines,[6,7] and pyridazine[8] are exceptional, giving substitution or cyclometallation reactions where the cluster framework remains unchanged. This contrasts with the extensive derivative chemistry of $[Os_3(CO)_{12}]$.[9]

The cluster $[Ru_3(NCMe)_2(CO)_{10}]$, reported recently,[10] reacts with a variety of nitrogen heterocycles under very mild conditions, but in some cases the products are different from those obtained from $[Ru_3(CO)_{12}]$ under thermal conditions. Thus, 2,2′-bipyridine (bipy) gives $[Ru_3(\mu\text{-}bipy)(CO)_{10}]$ from $[Ru_3(NCMe)_2(CO)_{10}]$,[11] whereas with $[Ru_3(CO)_{12}]$ it gives $[Ru_3(bipy)(\mu\text{-}CO)_2(CO)_8]$, a rare example of a triruthenium cluster with μ-CO ligands, with the bipy chelating one ruthenium atom.[5]

During the last few years we have focused our attention on the organometallic chemistry of pyrazoles,[12] imidazoles,[13] triazoles,[14] 1,8-naphthyridine,[15] and 1*H*-pyrrolo[2,3-*b*]pyridine(Hppy).[16] They have proved to be excellent binucleating ligands and afford structurally interesting complexes, as well as versatile catalysts.[17] We now report studies on the reactions of some of these heterocycles with $[Ru_3(CO)_{12}]$. In addition, direct formation of ethylene glycol and methanol from synthesis gas has been found to be catalysed markedly by $[Ru_3(CO)_{12}]$ combined with ligands such as benzimidazole or Hppy.[18]

Results and Discussion

1H-Pyrrolo[2,3-*b*]*pyridine*.—The reaction between $[Ru_3(CO)_{12}]$ and Hppy was carried out in refluxing n-hexane and gave a mixture of two complexes which were separated by column chromatography. The first product eluted ‡ was identified as the complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ppy)(CO)_9]$ (**1a**). Thus, the i.r. spectrum of (**1a**) shows the presence of terminal CO ligands and the absence of μ-CO and NH groups, while the ^1H n.m.r. spectrum contains a resonance at δ −10.66 p.p.m. for the μ-H ligand. The proton resonances of the pyridine moiety of the

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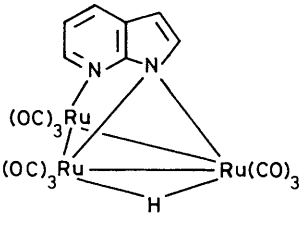
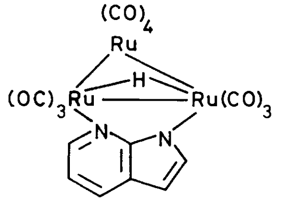
† 1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2-μ-hydrido-{μ_3-1*H*-pyrrolo[2,3-*b*]pyridinato(1−)-$N^1(Ru^{1,2})N^7(Ru^3)$}-*triangulo*-triruthenium and 1,2;1,3;2,3-tri-μ-carbonyl-1,1,1,2,2,3,3-heptacarbonyl-2,3-(μ-1,8-naphthyridine-N^1N^8)-*triangulo*-triruthenium respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

‡ The second product eluted still remains unidentified although we know it contains only terminal CO ligands and one hydride per ppy ligand (δ − 14.07 p.p.m. in $CDCl_3$).



(1a)



(1b)

heterocyclic ligand appear as three doublets of doublets, while those of the pyrrole moiety appear as a sharp singlet.

The spectroscopic and microanalytical data were not sufficient to assign unequivocally the structure of this complex. A structure corresponding to the formulation $[Ru_3(\mu\text{-H})(\mu\text{-ppy})(CO)_{10}]$ (**1b**), with the ppy ligand spanning one edge of the triangle, was also possible since, as far as we know, all of the few pyrrolopyridinate complexes hitherto described contain this ligand bridging only two metals.[16,19] The *X*-ray structure determination of this compound, reported below, confirms that (**1a**) is the first example in which the ppy ligand behaves as a μ_3 ligand. This implies disruption of the ligand aromaticity, with the pyrrolic nitrogen sp^3 hybridized.

Other similar triruthenium carbonyl clusters containing μ_3 anionic ligands are known; examples are the clusters $[Ru_3(\mu\text{-OCPh})\{\mu_3\text{-PPh}(C_5H_4N)\}(CO)_9]$[20] and $[Ru_3(\mu\text{-H})(\mu_3\text{-mbt})(CO)_9]$[21] ($C_5H_4N$ = 2-pyridyl, Hmbt = 2-mercaptobenzothiazole), where the phosphorus or sulphur atoms bridge one edge of the triangle and the nitrogen atoms co-ordinate to the third ruthenium atom.

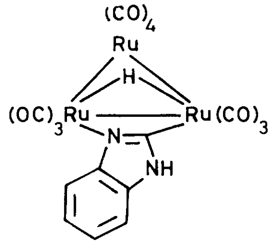
Benzimidazole.—The thermal reaction of $[Ru_3(CO)_{12}]$ with benzimidazole (Hbzim) in benzene gave $[Ru_3(\mu\text{-H})(\mu\text{-bzim})(CO)_{10}]$ (**2a**) as the only product isolated after column chromatography. Its ^{1}H n.m.r. spectrum shows the NH and μ-H resonances as singlets (at δ 12.04 and −14.39 p.p.m., respectively) and those of the six-membered ring as four multiplets, thus ruling out the structure (**2b**). Its i.r. spectrum also shows the NH group (3 469, 3 456 cm^{-1}, in Nujol) and the absence of bridging CO ligands.

These results contrast with those obtained from the reaction of $[Os_3(NCMe)_2(CO)_{10}]$ with benzimidazole, which gives a mixture of the osmium analogues of (**2a**) and (**2b**), the former being the minor product.[22]

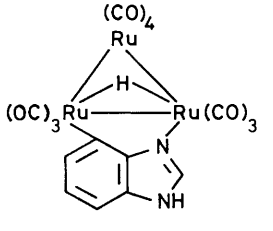
Benzotriazole.—Interestingly, benzotriazole (Hbztz) behaves quite differently from benzimidazole upon reaction with $[Ru_3(CO)_{12}]$, affording the dinuclear complex $[Ru_2(\mu\text{-bztz})_2(CO)_6]$ (**3a**), as well as some $[Ru_4H_4(CO)_{12}]$, regardless of the proportion of benzotriazole used. In no case did we obtain evidence of the formation of a trinuclear complex such as (**3b**) or an isomer thereof. Complex (**3a**) displays only terminal CO bands in its i.r. spectrum and no hydride resonances were observed in its ^{1}H n.m.r. spectrum. The nuclearity was determined by its mass spectrum which shows the molecular ion peak and the loss of six CO ligands.

This complex is similar to the complexes $[Ru_2(\mu\text{-pz})_2(CO)_6]$ (pz = pyrazolate, 3,5-dimethylpyrazolate, or indazolate), reported recently, which can be conveniently made from $RuCl_3\cdot nH_2O$, carbon monoxide, pyrazoles, and zinc.[23] However, the reaction of $[Ru_3(CO)_{12}]$ with pyrazoles in a 1:1 mol ratio gives the trinuclear clusters $[Ru_3(\mu\text{-H})(\mu\text{-pz})(CO)_{10}]$,[5] whereas using a 1:3 mol ratio the complexes $[Ru_2(\mu\text{-pz})_2(CO)_6]$ are obtained.[23]

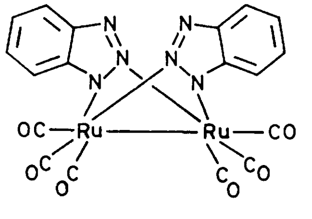
1,8-*Naphthyridine*.—Addition of 1,8-naphthyridine (napy) to a solution of $[Ru_3(CO)_{12}]$ in refluxing n-hexane precipitates



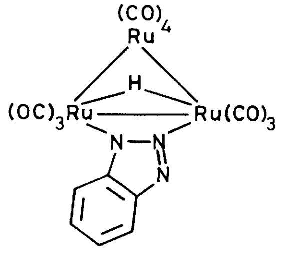
(2a)



(2b)



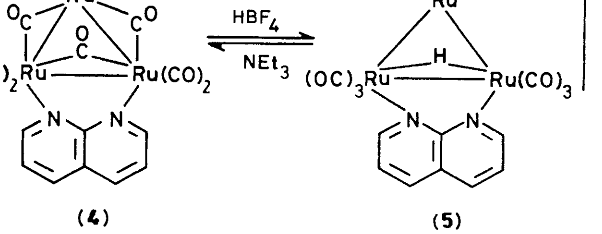
(3a)



(3b)

$[Ru_3(\mu\text{-napy})(\mu\text{-CO})_3(CO)_7]$ (**4**) as a dark brown (almost black) solid. Although insoluble in hydrocarbons, it dissolves in chlorinated solvents and in tetrahydrofuran (thf). Its i.r. spectrum clearly shows bridging (1 867, 1 821, and 1 807 cm^{-1}) as well as terminal carbonyls. That the napy ligand does not chelate one of the rutheniums is suggested by its ^{1}H n.m.r. spectrum, which displays only three doublets of doublets, indicating that the molecule contains a mirror plane that cuts the napy into two identical halves. In addition, although complexes with chelating napy are known,[15,24] its chelate 'bite' (2.2 Å)[25] and the parallel orientation of the nitrogen lone pairs favour binucleation.[15,26]

The structure of complex (**4**) has been confirmed by an *X*-ray diffraction study, discussed below. Only two other trinuclear ruthenium clusters with bridging carbonyls and nitrogen-donor ligands have been reported: $[Ru_3(\mu\text{-pydz})(\mu\text{-CO})_3(CO)_7]$ (pydz = pyridazine)[8] and $[Ru_3(\text{bipy})(\mu\text{-CO})_2(CO)_8]$.[5] Furthermore, simple substitution of the carbonyls of $[Ru_3(CO)_{12}]$ by phosphorus-donor ligands gives rise only to bridging carbonyls when tripodal phosphines are used.[27]



(4) **(5)**

Complex (**4**) reacts with an excess of tetrafluoroboric acid to give the orange cluster $[Ru_3(\mu\text{-H})(\mu\text{-napy})(CO)_{10}][BF_4]$ (**5**), as indicated by its i.r. spectrum, which does not show bridging carbonyl bands, and by its ^{1}H n.m.r. spectrum, which contains a hydride peak (δ −11.71 p.p.m.), with the resonances of the napy protons shifted towards higher frequencies than those of (**4**).

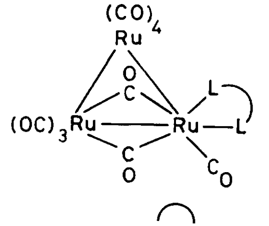
Complex (**5**) can be deprotonated with triethylamine to regenerate complex (**4**). As far as we know, this kind of

Table 1. Selected bond distances (Å) and angles (°) in [$Ru_3(\mu$-H)(μ_3-ppy)$(CO)_9$] (**1a**)

Ru(1)–Ru(2)	2.758(2)	N(1)–C(14)	1.331(7)	Ru(2)–C(5)	1.943(9)	C(1)–O(1)	1.111(10)
Ru(1)–Ru(3)	2.761(2)	N(2)–C(14)	1.389(7)	Ru(2)–C(6)	1.883(8)	C(2)–O(2)	1.121(8)
Ru(2)–Ru(3)	2.764(2)	N(2)–C(15)	1.426(9)	Ru(2)–N(2)	2.175(5)	C(3)–O(3)	1.150(9)
Ru(1)–C(1)	1.935(8)	C(10)–C(11)	1.397(9)	Ru(3)–H(1)	1.68(6)	C(4)–O(4)	1.136(10)
Ru(1)–C(2)	1.918(7)	C(11)–C(12)	1.407(10)	Ru(3)–C(7)	1.891(7)	C(5)–O(5)	1.131(11)
Ru(1)–C(3)	1.871(7)	C(12)–C(13)	1.394(10)	Ru(3)–C(8)	1.879(7)	C(6)–O(6)	1.134(9)
Ru(1)–N(1)	2.149(4)	C(13)–C(14)	1.398(8)	Ru(3)–C(9)	1.965(8)	C(7)–O(7)	1.132(9)
Ru(2)–H(1)	1.89(6)	C(13)–C(16)	1.451(10)	Ru(3)–N(2)	2.177(5)	C(8)–O(8)	1.129(9)
Ru(2)–C(4)	1.900(8)	C(15)–C(16)	1.351(9)	N(1)–C(10)	1.346(7)	C(9)–O(9)	1.124(9)
Ru(2)–Ru(1)–Ru(3)	60.1(1)	N(2)–Ru(3)–C(9)	98.7(2)	C(5)–Ru(2)–Ru(3)	112.0(3)	C(14)–C(13)–C(16)	105.6(6)
Ru(1)–Ru(2)–Ru(3)	59.9(1)	N(2)–Ru(3)–Ru(1)	76.7(1)	C(5)–Ru(2)–C(6)	94.0(3)	N(1)–C(14)–C(13)	126.3(6)
Ru(1)–Ru(3)–Ru(2)	59.9(1)	N(2)–Ru(3)–Ru(2)	50.6(1)	C(4)–Ru(2)–N(2)	96.9(3)	N(1)–C(14)–N(2)	121.9(5)
C(1)–Ru(1)–Ru(2)	101.7(2)	Ru(1)–N(1)–C(10)	128.1(4)	C(5)–Ru(2)–N(2)	96.0(3)	N(2)–C(14)–C(13)	111.7(5)
C(1)–Ru(1)–C(2)	100.8(3)	Ru(1)–N(1)–C(14)	115.9(4)	C(6)–Ru(2)–Ru(1)	92.5(3)	N(2)–C(15)–C(16)	112.2(6)
C(1)–Ru(1)–C(3)	92.4(3)	C(10)–N(1)–C(14)	116.0(5)	C(6)–Ru(2)–Ru(3)	117.0(3)	C(13)–C(16)–C(15)	106.7(6)
C(1)–Ru(1)–N(1)	92.2(2)	Ru(2)–N(2)–Ru(3)	78.9(2)	N(2)–Ru(2)–Ru(1)	76.8(1)	Ru(1)–C(1)–O(1)	175.4(7)
C(2)–Ru(1)–Ru(3)	97.2(2)	Ru(2)–N(2)–C(14)	114.1(4)	N(2)–Ru(2)–Ru(3)	50.6(1)	Ru(1)–C(2)–O(2)	176.5(6)
C(2)–Ru(1)–C(3)	92.0(3)	Ru(2)–N(2)–C(15)	122.5(4)	C(7)–Ru(3)–C(8)	91.7(3)	Ru(1)–C(3)–O(3)	178.7(6)
C(2)–Ru(1)–N(1)	92.9(2)	Ru(3)–N(2)–C(14)	114.1(4)	C(7)–Ru(3)–C(9)	98.9(3)	Ru(2)–C(4)–O(4)	179.1(7)
C(3)–Ru(1)–Ru(2)	89.7(2)	Ru(3)–N(2)–C(15)	122.7(4)	C(8)–Ru(3)–C(9)	93.8(3)	Ru(2)–C(5)–O(5)	174.1(7)
C(3)–Ru(1)–Ru(3)	90.3(2)	C(14)–N(2)–C(15)	103.8(5)	C(8)–Ru(3)–Ru(2)	117.0(2)	Ru(2)–C(6)–O(6)	179.2(7)
N(1)–Ru(1)–Ru(2)	83.6(1)	N(1)–C(10)–C(11)	123.0(6)	C(9)–Ru(3)–Ru(2)	110.8(2)	Ru(3)–C(7)–O(7)	178.3(6)
N(1)–Ru(1)–Ru(3)	83.5(1)	C(10)–C(11)–C(12)	119.7(6)	C(7)–Ru(3)–Ru(1)	89.7(2)	Ru(3)–C(8)–O(8)	177.5(6)
C(4)–Ru(2)–C(5)	99.1(3)	C(11)–C(12)–C(13)	117.9(6)	C(8)–Ru(3)–Ru(1)	89.7(2)	Ru(3)–C(9)–O(9)	172.2(6)
C(4)–Ru(2)–C(6)	90.4(3)	C(12)–C(13)–C(14)	117.1(6)	N(2)–Ru(3)–C(7)	94.4(2)		
C(4)–Ru(2)–Ru(1)	86.3(2)	C(12)–C(13)–C(16)	137.2(6)				

reactivity, with simultaneous reversible shift of the carbonyls from bridging to terminal in a trinuclear cluster, has not been reported previously.

1,10-*Phenanthroline*, 2,2′-*Biquinoline*, *and* 2,2′-*Bipyrimidine*.—Before the present work commenced, the cluster [Ru_3(bipy)(μ-$CO)_2(CO)_8$] was the only known ruthenium compound with a structure similar to that of [$Fe_3(CO)_{12}$].[5] We observed that the reaction of [$Ru_3(CO)_{12}$] with 1,10-phenanthroline (phen), 2,2′-biquinoline (biquin), and 2,2′-bipyrimidine (bipym) gives rise in all cases to the highly insoluble, very dark brown or black clusters [Ru_3(L–L)(μ-$CO)_2(CO)_8$] [L–L = phen (**6a**), biquin (**6b**), or bipym (**6c**)]. They were characterized by microanalysis and i.r. spectroscopy only, since their high insolubility prevented any other analysis. Nevertheless, their dark colour (which is indicative of bridging carbonyls) and the low wavenumbers of their μ-CO absorptions in their i.r. spectra (which are similar to those reported for [Ru_3(bipy)(μ-$CO)_2(CO)_8$], whose structure has been determined by *X*-ray diffraction methods[5]) suggested to us the tentative structural assignment shown below.



(**6a**) phen
(**6b**) biquin
(**6c**) bipym

Crystal Structures of [$Ru_3(\mu$-H)(μ-ppy)$(CO)_9$] (**1a**) *and* [$Ru_3(\mu$-napy)(μ-$CO)_3(CO)_7$] (**4**).—The structure of (**1a**) is represented in Figure 1 together with the atomic numbering scheme; important bond distances and angles are given in Table 1. The molecular unit consists of a nearly equilateral array of Ru atoms [Ru–Ru 2.758(2), 2.761(2), and 2.764(2) Å] bonded to nine terminal carbonyl groups, three attached to each metal atom, and to a pyrrolopyridinate(1 –) ligand interacting with all three metals. The Ru(2)–Ru(3) edge of the cluster is bridged

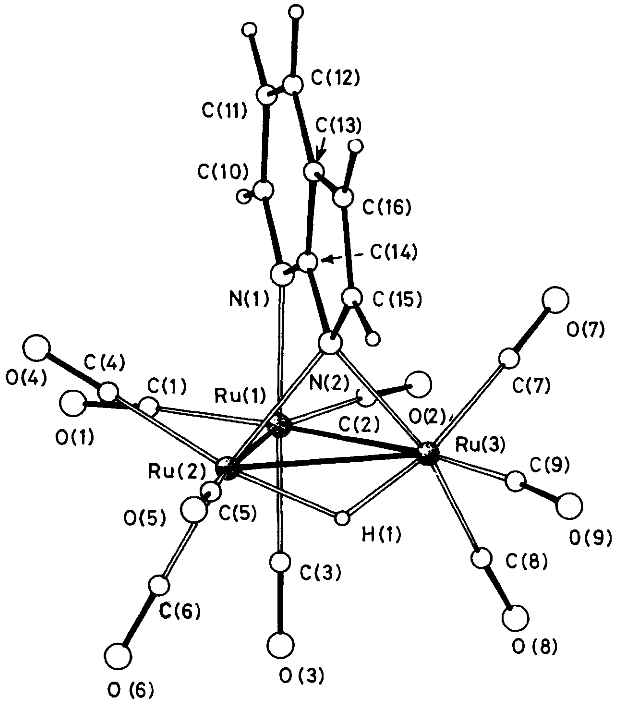


Figure 1. View of the complex [$Ru_3(\mu$-H)(μ_3-ppy)$(CO)_9$] (**1a**) with the atomic numbering scheme

Table 2. Selected bond distances (Å) and angles (°) in the two independent molecules of $[Ru_3(\mu\text{-napy})(\mu\text{-CO})_3(CO)_7]$ (**4**)

Ru(1)–Ru(2)	2.838(2)	2.872(2)	Ru(3)–N(2)	2.165(9)	2.187(8)	C(9)–O(9)	1.151(15)	1.134(15)
Ru(1)–Ru(3)	2.878(2)	2.848(2)	Ru(3)–C(7)	2.112(10)	2.113(11)	C(10)–O(10)	1.158(12)	1.175(13)
Ru(2)–Ru(3)	2.747(3)	2.731(3)	Ru(3)–C(8)	1.910(12)	1.879(10)	N(1)–C(11)	1.325(12)	1.339(12)
Ru(1)–C(1)	1.881(10)	1.882(10)	Ru(3)–C(9)	1.836(12)	1.864(11)	N(1)–C(18)	1.362(12)	1.377(11)
Ru(1)–C(2)	1.924(10)	1.933(11)	Ru(3)–C(10)	2.108(9)	2.095(10)	C(11)–C(12)	1.437(16)	1.384(15)
Ru(1)–C(3)	1.934(11)	1.939(12)	C(1)–O(1)	1.120(12)	1.130(13)	C(12)–C(13)	1.380(18)	1.382(15)
Ru(1)–C(4)	2.151(10)	2.290(12)	C(2)–O(2)	1.122(12)	1.129(14)	C(13)–C(14)	1.390(18)	1.401(15)
Ru(1)–C(10)	2.180(10)	2.108(10)	C(3)–O(3)	1.141(14)	1.134(15)	C(14)–C(15)	1.468(18)	1.434(15)
Ru(2)–N(1)	2.199(8)	2.190(8)	C(4)–O(4)	1.164(13)	1.148(14)	C(14)–C(18)	1.444(14)	1.399(13)
Ru(2)–C(4)	2.076(10)	2.053(10)	C(5)–O(5)	1.143(12)	1.125(14)	C(15)–C(16)	1.332(20)	1.377(14)
Ru(2)–C(5)	1.897(10)	1.884(11)	C(6)–O(6)	1.136(14)	1.130(14)	C(16)–C(17)	1.403(16)	1.405(14)
Ru(2)–C(6)	1.849(11)	1.872(12)	C(7)–O(7)	1.144(12)	1.141(12)	N(2)–C(17)	1.363(14)	1.346(11)
Ru(2)–C(7)	2.142(10)	2.159(10)	C(8)–O(8)	1.113(15)	1.123(13)	N(2)–C(18)	1.382(13)	1.387(11)

Ru(2)–Ru(1)–Ru(3)	57.4(1)	57.0(1)	C(15)–C(14)–C(18)	116.4(10)	119.6(9)	C(9)–Ru(3)–C(10)	94.2(5)	90.5(4)
Ru(1)–Ru(2)–Ru(3)	62.0(1)	61.0(1)	N(1)–C(18)–N(2)	119.2(8)	116.9(8)	C(8)–Ru(3)–C(7)	101.7(5)	103.0(4)
Ru(1)–Ru(3)–Ru(2)	60.6(1)	61.9(1)	N(1)–C(18)–C(14)	119.4(9)	121.8(8)	C(8)–Ru(3)–C(10)	98.6(5)	96.6(4)
C(1)–Ru(1)–C(2)	86.1(4)	84.6(5)	N(2)–C(18)–C(14)	121.2(9)	121.3(8)	C(7)–Ru(3)–Ru(1)	110.8(3)	112.9(3)
C(1)–Ru(1)–C(3)	88.5(5)	88.3(5)	C(14)–C(15)–C(16)	120.1(10)	118.6(9)	Ru(1)–C(1)–O(1)	178.0(10)	173.1(10)
C(1)–Ru(1)–C(4)	102.7(5)	114.1(5)	C(15)–C(16)–C(17)	120.4(12)	118.4(8)	Ru(1)–C(2)–O(2)	173.7(9)	173.8(9)
C(1)–Ru(1)–C(10)	106.7(5)	96.6(4)	C(16)–C(17)–N(2)	123.0(11)	124.8(8)	Ru(1)–C(3)–O(3)	176.6(9)	176.2(10)
C(2)–Ru(1)–Ru(2)	95.3(3)	93.6(3)	C(17)–N(2)–C(18)	118.5(8)	117.3(8)	Ru(1)–C(4)–O(4)	135.2(9)	130.3(9)
C(2)–Ru(1)–Ru(3)	95.5(3)	96.2(3)	Ru(3)–N(2)–C(17)	116.3(7)	116.1(6)	Ru(2)–C(4)–O(4)	140.4(9)	147.1(10)
C(2)–Ru(1)–C(4)	89.8(4)	86.6(5)	Ru(3)–N(2)–C(18)	125.2(6)	126.6(6)	Ru(1)–C(4)–Ru(2)	84.3(4)	82.6(4)
C(2)–Ru(1)–C(10)	87.6(4)	91.9(4)	C(6)–Ru(2)–C(7)	92.3(4)	89.4(4)	Ru(2)–C(5)–O(5)	172.9(9)	177.3(10)
C(3)–Ru(1)–Ru(2)	89.9(3)	90.4(4)	C(6)–Ru(2)–Ru(1)	94.3(3)	95.2(4)	Ru(2)–C(6)–O(6)	177.6(8)	178.0(10)
C(3)–Ru(1)–Ru(3)	88.8(3)	93.8(4)	C(4)–Ru(2)–Ru(3)	111.0(3)	113.2(3)	Ru(2)–C(7)–O(7)	140.0(8)	137.8(8)
C(3)–Ru(1)–C(4)	92.5(4)	89.5(5)	C(5)–Ru(2)–C(4)	101.6(4)	102.9(5)	Ru(3)–C(7)–O(7)	140.0(8)	142.8(8)
C(3)–Ru(1)–C(10)	92.8(4)	96.3(5)	C(5)–Ru(2)–C(7)	98.1(4)	94.2(5)	Ru(2)–C(7)–Ru(3)	80.4(4)	79.5(4)
C(4)–Ru(1)–Ru(3)	104.1(3)	102.1(3)	C(7)–Ru(2)–Ru(1)	111.3(3)	110.5(3)	Ru(3)–C(8)–O(8)	177.8(10)	175.6(10)
C(10)–Ru(1)–Ru(2)	104.1(3)	104.1(3)	N(2)–Ru(3)–C(8)	90.5(4)	92.1(4)	Ru(3)–C(9)–O(9)	176.9(10)	179.5(10)
N(1)–Ru(2)–Ru(1)	86.0(2)	88.3(2)	N(2)–Ru(3)–C(7)	86.2(4)	88.2(4)	Ru(3)–C(10)–O(10)	140.4(8)	139.4(8)
N(1)–Ru(2)–Ru(3)	84.4(2)	85.3(2)	N(2)–Ru(3)–C(10)	90.4(4)	90.0(4)	Ru(1)–C(10)–O(10)	135.2(8)	135.3(10)
N(1)–Ru(2)–C(5)	91.5(4)	89.3(4)	N(2)–Ru(3)–Ru(1)	90.6(2)	88.0(2)	Ru(1)–C(10)–Ru(3)	84.3(4)	85.3(4)
N(1)–Ru(2)–C(4)	88.9(4)	89.8(4)	N(2)–Ru(3)–Ru(2)	85.4(2)	84.8(2)	C(11)–N(1)–C(18)	120.9(8)	116.9(7)
N(1)–Ru(2)–C(7)	89.1(4)	88.3(4)	C(10)–Ru(3)–Ru(2)	109.3(3)	109.4(3)	Ru(2)–N(1)–C(11)	114.4(6)	116.8(6)
C(6)–Ru(2)–Ru(3)	97.2(3)	95.3(4)	C(9)–Ru(3)–Ru(1)	94.6(4)	93.1(4)	Ru(2)–N(1)–C(18)	124.7(6)	126.2(6)
C(6)–Ru(2)–C(4)	90.1(5)	93.3(5)	C(9)–Ru(3)–Ru(2)	95.8(4)	96.1(3)	N(1)–C(11)–C(12)	122.2(9)	124.4(9)
C(6)–Ru(2)–C(5)	87.4(4)	88.1(5)	C(9)–Ru(3)–C(8)	86.0(5)	86.7(5)	C(11)–C(12)–C(13)	118.1(10)	119.0(9)
C(13)–C(14)–C(1)	124.2(10)	121.0(8)	C(9)–Ru(3)–C(7)	90.5(5)	91.7(4)	C(12)–C(13)–C(14)	119.9(10)	118.5(49)
C(13)–C(14)–C(18)	119.3(10)	119.3(9)						

by a hydride with the Ru(2)H(1)Ru(3) plane forming a dihedral angle of 121(3)° with the metal triangle. The pyrrolopyridinate(1 −) anion behaves as tridentate ligand: in fact it is bonded to the Ru(1) atom through the pyridinic nitrogen N(1) [Ru(1)–N(1) 2.149(4) Å] and through the pyrrolic nitrogen N(2) symmetrically bridging the other two Ru atoms [Ru(2)–N(2) 2.175(5), Ru(3)–N(2) 2.177(5) Å]. The Ru(2)–N(2)–Ru(3) bridge is nearly perpendicular to the metal plane [dihedral angle 97.6(1)°] and involves the edge already bridged by the hydride.

The ppy ligand is perfectly planar and nearly perpendicular to the Ru_3 plane [dihedral angle 90.1(1)°]; the plane through it and Ru(1) perpendicularly bisecting the Ru(2)–Ru(3) edge is roughly a mirror plane of the complex. Because of the bonding of the N(2) atom, the organic ligand loses the aromaticity in the pyrrolic moiety and the double bond is localized in the C(15)–C(16) bond [1.351(9) Å].

The structure of (**1a**) is comparable to that of $[Ru_3(\mu\text{-H})(\mu_3\text{-mbt})(CO)_9]$[21] in which the 2-mercaptobenzothiazolate ligand (mbt) interacts with all three metals through the thiazolic nitrogen atom to one Ru atom [Ru–N 2.177(9) Å] and through the exocyclic sulphur bridging the other two metals. In this case the edge bridged by the sulphur and by the hydride is slightly longer than the other two [2.836(5) *versus* 2.786(5) and 2.798(6) Å]. Also in $[Ru_3(\mu\text{-OCPh})\{\mu_3\text{-PPh}(C_5H_4N)\}(CO)_9]$[20] the fragment $PPh(C_5H_4N)$ interacts with a Ru atom through the N atom [Ru–N 2.165(8) Å] and through the P atom spans the other two Ru atoms, which are at a non-bonding distance of 3.639(1) Å; these two Ru atoms are bridged also by an acyl ligand.

In the crystals of (**4**) there are two independent, but almost identical molecules. The structure of one of them is represented in Figure 2; bond distances and angles are given in Table 2. In the complex the three Ru atoms are at the vertices of an isosceles triangle with Ru–Ru bonds of 2.747(3), 2.838(2), and 2.878(2) Å [2.731(3), 2.872(2), and 2.848(3) Å in the other independent molecule; hereafter values in brackets refer to this]. Ten carbonyl groups are bonded to the metal atoms, seven are terminal [three attached to the Ru(1) atom, two to each of the other two Ru atoms], and three more or less symmetrically bridge the three edges of the triangular cluster. The different asymmetries of these carbonyls in each of the two independent complexes are attributable rather to packing forces than to electronic factors. The carbon atoms of the bridging carbonyls are nearly coplanar with the metal triangle, the displacement of C(4), C(7), and C(10) from the triangle being 0.06(1), −0.06(1), and 0.16(1) Å respectively [0.09(1), −0.07(1), and 0.08(1) Å].

The 1,8-naphthyridine ligand acts as a bridge between the two Ru atoms of the shortest edge, through the two pyridinic N atoms, with Ru–N bonds of 2.199(8) and 2.165(9) Å [2.190(8) and 2.187(8) Å]. The organic ligand presents no peculiar structural factors, it is only roughly planar with the two

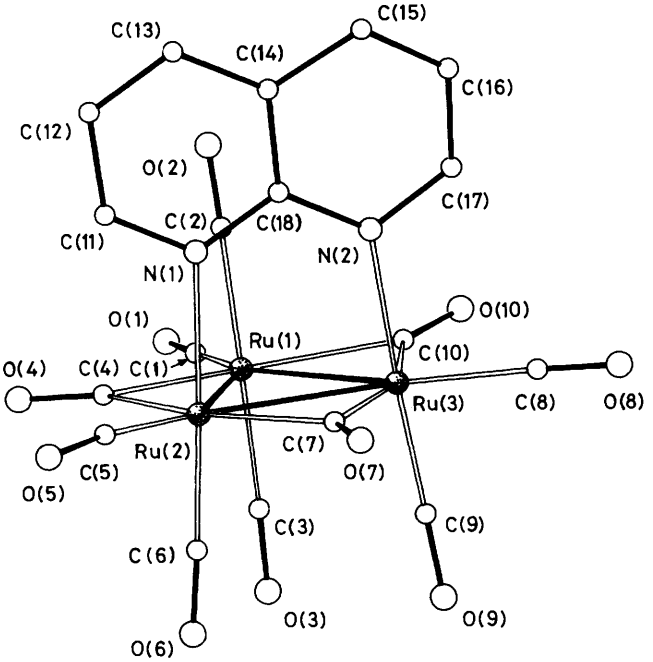


Figure 2. View of one of the two independent molecules of [Ru_3(μ-napy)(μ-CO)$_3$(CO)$_7$] (**4**) with the atomic numbering scheme

Table 3. Experimental data for the *X*-ray diffraction study of (**1a**) and (**4**)*

	(**1a**)	(**4**)
Molecular formula	$C_{16}H_6N_2O_9Ru_3$	$C_{18}H_6N_2O_{10}Ru_3$
M	673.44	713.46
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/c$
a/Å	14.688(5)	15.374(7)
b/Å	16.251(7)	17.336(6)
c/Å	8.594(5)	16.167(7)
β/°	97.64(2)	98.02(3)
U/Å^3	2 033(2)	4 267(3)
Z	4	8
D_c/g cm^{-3}	2.200	2.221
F(000)	1 280	2 720
Crystal dimensions (mm)	0.15 × 0.24 × 0.28	0.20 × 0.22 × 0.30
Linear absorption (μ/cm^{-1})	22.09	21.15
2θ range (°)	6—54	6—50
Unique total data	4 448	7 697
Unique observed data [$I > 2\sigma(I)$]	3 211	4 205
R	0.0349	0.0405
R'	0.0440	0.0491

* Details common to both: Nb-filtered Mo-K_α radiation (λ = 0.710 69 Å); Siemens AED diffractometer; θ/2θ scan, speed 3—12° min^{-1}, width [(θ − 0.55) − (θ + 0.55 + 0.346 tan θ)]°; reflections measured ±*h*, ±*k*, ±*l*; standard reflections, one every 50.

pyridinic moieties making an angle of 6.7(3)° [4.0(3)°] and the mean plane through it is quasi-perpendicular to the metal triangle, the dihedral angle being 85.6(1)° [91.2(2)°].

The complex as a whole has approximate C_s symmetry with the mirror plane bisecting the naphthyridine molecule and the Ru(2)–Ru(3) edge.

The structure of (**4**) is comparable with that of [Ru_3(μ-pydz)(μ-CO)$_3$(CO)$_7$][8] in which the two nitrogen atoms of the organic ligand interact with the two Ru atoms of the shortest edge of the metal triangle [2.743(4) *versus* 2.857(4) and 2.859(4) Å] and the three carbonyl bridges are all slightly asymmetric. In [Ru_3(bipy)(μ-CO)$_2$(CO)$_8$][5] the bipyridyl ligand chelates one Ru atom and a double carbonyl bridge involves the shortest edge of the triangle [Ru–Ru bonds 2.757(1), 2.836(1), and 2.855(1) Å].

Experimental

General Procedures and Measurements.—All reactions were carried out under nitrogen. Elemental analyses were carried out on a Perkin-Elmer 240-C microanalyzer. I.r. spectra were recorded on a Perkin-Elmer 783 spectrophotometer and were calibrated against a sharp peak (1 601.4 cm^{-1}) of polystyrene film. ^{1}H N.m.r. spectra were recorded on a Varian XL200 spectrometer at 20 °C with $SiMe_4$ as internal reference (δ = 0 p.p.m.). Mass spectra were obtained by using the fast atom bombardment (f.a.b) technique on a Kratos MS-80 spectrometer, using xenon as bombarding gas.

Materials.—Tetrahydrofuran (thf) and diethyl ether were distilled from sodium–benzophenone under N_2. Dichloromethane and n-hexane were distilled from P_4O_{10} and CaH_2 respectively. 1,8-Naphthyridine was prepared as described elsewhere.[28] [$Ru_3(CO)_{12}$] (Strem) and all other reagents (Aldrich) were used as purchased commercially.

Preparation of [Ru_3(μ-H)(μ-ppy)(CO)$_9$] (**1a**).—[$Ru_3(CO)_{12}$] (200 mg, 0.313 mmol) and Hppy (37.8 mg, 0.32 mmol) were stirred in refluxing n-hexane (20 cm^3) for 3 h. The red-orange solution was evaporated to dryness and the residue dissolved in dichloromethane (*ca.* 2 cm^3) and chromatographed on a silica-gel column. n-Hexane afforded two fractions. The first one contained a small amount of [$Ru_3(CO)_{12}$] (i.r. identification). From the second fraction, orange crystals of (**1a**) were obtained on evaporation (60 mg, 28%). Subsequent elution of the column with dichloromethane–n-hexane (1:2) afforded a yellow fraction of an as yet unidentified compound [Found for (**1a**): C, 29.0; H, 0.8; N, 4.2. Calc. for $C_{16}H_6N_2O_9Ru_3$: C, 28.5; H, 0.9; N, 4.2%]. I.r. (n-hexane): ν(CO) 2 092m (sh), 2 089s, 2 058vs, 2 037vs, 2 018s (sh), 2 008vs, 1 999vs (sh), 1 978m (sh), 1 975m cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 7.92 (dd, *J* = 5.5 and 1.3, 1 H), 7.78 (dd, *J* = 7.9 and 1.3, 1 H), 7.05 (dd, *J* = 7.9 and 5.5 Hz, 1 H), 6.46 (s, 2 H), −10.66 p.p.m. (s, 1 H). M.s. (*m*/*e*): 674 (M^+).

Preparation of [Ru_3(μ-H)(μ-bzim)(CO)$_{10}$] (**2a**).—[$Ru_3(CO)_{12}$] (200 mg, 0.313 mmol) and benzimidazole (60 mg, 0.51 mmol) were stirred in refluxing benzene (30 cm^3) for 4 h. The dark red solution was evaporated to dryness and the residue was chromatographed on a silica-gel column. Elution with n-hexane afforded some [$Ru_3(CO)_{12}$] (i.r. identification). Subsequent elution with dichloromethane afforded an orange fraction from which orange-red crystals, crystallized from dichloromethane–n-hexane, of (**2a**) were obtained (81 mg, 38%) (Found: C, 29.3; H, 1.0; N, 4.0. Calc. for $C_{17}H_6N_2O_{10}Ru_3$: C, 29.1; H, 0.9; N, 4.0%). I.r. (n-hexane): ν(CO) 2 102m, 2 061vs, 2 053vs, 2 022s (sh), 2 019vs, 2 002s, 1 987w, 1 974w cm^{-1}. ^{1}H N.m.r. [$(CD_3)_2CO$]: δ 12.04 (s, br, NH), 7.43 (ddd, *J* = 7.6, 1.3, and 0.9, 1 H), 7.32 (ddd, *J* = 7.8, 1.6, and 0.9, 1 H), 7.17 (td, *J* = 7.8 and 1.3, 1 H), 7.13 (ddd, *J* = 7.8, 7.6, and 1.6 Hz, 1 H), −14.39 p.p.m. (s, 1 H). M.s. (*m*/*e*): 675 (M^+ − CO).

Preparation of [Ru_2(μ-bztz)$_2$(CO)$_6$] (**3a**).—[$Ru_3(CO)_{12}$] (200 mg, 0.313 mmol) and benzotriazole (119 mg, 0.92 mmol) were stirred in refluxing benzene (30 cm^3) for 4 h. The solvent was removed from the red solution and the residue was chromatographed on a silica-gel column. Elution with n-hexane afforded some [$Ru_3(CO)_{12}$] and [$Ru_4H_4(CO)_{12}$] (i.r. identification). Subsequent elution with dichloromethane afforded an

Table 4. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for the non-hydrogen atoms of (**1a**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	2 833(1)	365(1)	6 066(1)	C(2)	3 153(4)	−727(4)	6 787(7)
Ru(2)	1 937(1)	1 860(1)	5 944(1)	C(3)	1 954(5)	−30(4)	4 465(8)
Ru(3)	1 478(1)	641(1)	7 944(1)	C(4)	3 048(5)	2 321(4)	5 430(9)
O(1)	4 196(4)	623(4)	3 734(7)	C(5)	1 256(6)	2 869(5)	6 161(9)
O(2)	3 298(4)	−1 378(3)	7 173(6)	C(6)	1 498(5)	1 738(5)	3 796(9)
O(3)	1 426(4)	−284(4)	3 473(6)	C(7)	2 121(4)	−29(4)	9 521(8)
O(4)	3 709(4)	2 593(4)	5 103(9)	C(8)	822(5)	−267(4)	7 021(8)
O(5)	862(6)	3 467(4)	6 153(9)	C(9)	471(5)	1 003(4)	9 075(8)
O(6)	1 226(4)	1 670(4)	2 505(6)	C(10)	4 601(4)	779(4)	8 458(8)
O(7)	2 526(4)	−422(4)	10 457(7)	C(11)	5 102(4)	1 191(4)	9 718(8)
O(8)	448(4)	−831(4)	6 503(7)	C(12)	4 665(5)	1 783(4)	10 556(8)
O(9)	−162(3)	1 142(4)	9 632(7)	C(13)	3 736(5)	1 936(4)	10 080(8)
N(1)	3 706(3)	0 927(3)	7 978(5)	C(14)	3 310(4)	1 487(3)	8 798(6)
N(2)	2 388(3)	1 693(3)	8 439(6)	C(15)	2 250(4)	2 303(4)	9 578(8)
C(1)	3 724(4)	544(4)	4 632(8)	C(16)	3 026(5)	2 462(4)	10 562(8)

Table 5. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for the non-hydrogen atoms of (**4**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(11)	1 342(1)	1 094(1)	−751(1)	Ru(12)	6 324(1)	1 043(1)	4 413(1)
Ru(21)	2 605(1)	1 947(1)	328(1)	Ru(22)	7 703(1)	2 132(1)	4 920(1)
Ru(31)	2 948(1)	419(1)	61(1)	Ru(32)	7 742(1)	733(1)	5 701(1)
O(11)	−413(5)	1 038(5)	−1 826(5)	O(12)	4 701(5)	305(5)	3 491(5)
O(21)	1 993(5)	1 510(5)	−2 386(4)	O(22)	7 143(5)	404(6)	2 936(5)
O(31)	406(5)	617(5)	730(5)	O(32)	5 148(6)	1 801(5)	5 569(6)
O(41)	973(5)	2 820(5)	−483(5)	O(42)	6 340(5)	2 615(5)	3 430(5)
O(51)	3 236(6)	3 454(4)	1 158(5)	O(52)	8 762(6)	3 573(5)	4 776(6)
O(61)	1 702(6)	1 753(5)	1 833(5)	O(62)	6 770(6)	2 959(4)	6 170(5)
O(71)	4 318(5)	1 267(4)	1 302(5)	O(72)	9 231(5)	1 874(4)	6 360(5)
O(81)	4 120(6)	−985(5)	314(6)	O(82)	8 508(6)	−497(5)	6 890(5)
O(91)	2 183(6)	−163(5)	1 542(5)	O(92)	6 712(6)	1 225(5)	7 054(5)
O(101)	1 788(5)	−581(4)	−1 237(5)	O(102)	6 398(5)	−563(4)	5 200(5)
N(11)	3 257(5)	2 144(4)	−781(4)	N(12)	8 479(5)	1 566(4)	4 057(4)
N(21)	3 645(5)	835(5)	−925(5)	N(22)	8 509(5)	360(4)	4 731(4)
C(11)	238(7)	1 048(7)	−1 417(6)	C(12)	5 293(7)	625(6)	3 815(7)
C(21)	1 799(6)	1 368(6)	−1 760(6)	C(22)	6 887(6)	642(7)	3 506(6)
C(31)	778(7)	792(6)	196(6)	C(32)	5 603(7)	1 516(7)	5 166(7)
C(41)	1 426(7)	2 282(6)	−364(6)	C(42)	6 675(7)	2 244(7)	3 971(7)
C(51)	3 029(7)	2 898(6)	805(6)	C(52)	8 349(7)	3 045(6)	4 832(7)
C(61)	2 044(7)	1 810(5)	1 257(6)	C(62)	7 107(7)	2 642(6)	5 693(7)
C(71)	3 687(7)	1 234(6)	836(6)	C(72)	8 613(7)	1 675(6)	5 940(6)
C(81)	3 692(7)	−467(7)	205(7)	C(82)	8 253(7)	−23(6)	6 448(6)
C(91)	2 459(7)	52(6)	957(7)	C(92)	7 105(7)	1 039(6)	6 545(6)
C(101)	1 950(6)	−34(6)	−834(6)	C(102)	6 681(6)	63(6)	5 155(6)
C(111)	3 210(7)	2 864(6)	−1 058(6)	C(112)	8 692(7)	1 993(6)	3 425(6)
C(121)	3 639(8)	3 109(7)	−1 748(6)	C(122)	9 194(7)	1 733(6)	2 835(6)
C(131)	4 164(7)	2 584(8)	−2 087(7)	C(132)	9 508(7)	985(6)	2 890(6)
C(141)	4 195(6)	1 822(7)	−1 817(6)	C(142)	9 287(6)	513(6)	3 533(5)
C(151)	4 685(7)	1 208(9)	−2 174(6)	C(152)	9 543(6)	−283(6)	3 588(6)
C(161)	4 607(7)	479(8)	−1 935(7)	C(162)	9 263(6)	−733(5)	4 201(6)
C(171)	4 072(7)	293(7)	−1 328(6)	C(172)	8 750(6)	−387(5)	4 753(6)
C(181)	3 716(6)	1 600(6)	−1 147(5)	C(182)	8 774(6)	815(5)	4 106(5)

orange solution. The solvent was removed and methanol (5 cm^3) was added to the oily residue which then solidified, giving (**3a**) as a yellow-orange powder (141 mg, 49%) (Found: C, 35.0; H, 1.5; N, 13.7. Calc. for $C_{18}H_8N_6O_6Ru_2$: C, 35.6; H, 1.3; N, 13.9%). I.r. (CH_2Cl_2): ν(CO) 2 087m, 2 078m (sh), 2 035vs, 1 995s, 1 967vs, 1 943m (sh) cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 7.3 p.p.m. (m). M.s. (*m*/*e*): 607 (M^+) and the successive loss of six CO ligands.

Preparation of $[Ru_3(\mu\text{-napy})(\mu\text{-CO})_3(CO)_7]$.—$[Ru_3(CO)_{12}]$ (200 mg, 0.313 mmol) and 1,8-naphthyridine (42.5 mg, 0.326 mmol) were stirred in refluxing n-hexane (30 cm^3) for 1 h to give a dark brown solid. The solid was filtered hot, washed with hot n-hexane and recrystallized from dichloromethane–n-hexane to give black crystals of (**4**) (198 mg, 88%) (Found: C, 30.3; H, 1.0; N, 4.1. Calc. for $C_{18}H_6N_2O_{10}Ru_3$: C, 30.3; H, 0.8; N, 3.9%). I.r. (CH_2Cl_2): ν(CO) 2 084m, 2 027vs, 2 003vs, 1 976m (sh), 1 962s, br, 1 940m (sh), 1 867w (sh), 1 821s (sh), 1 807s, br cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 9.66 (dd, *J* = 5.2 and 1.7, 1 H), 8.26 (dd, *J* = 8.1 and 1.7, 1 H), 7.52 p.p.m. (dd, *J* = 8.1 and 5.2 Hz, 1 H). M.s. (*m*/*e*): 714 (M^+).

Preparation of $[Ru_3(\mu\text{-H})(\mu\text{-napy})(CO)_{10}][BF_4]$ (**5**).—An excess of HBF_4 (0.5 cm^3, 53% w/w solution in diethyl ether) was injected dropwise into a solution of complex (**4**) (60 mg, 0.084 mmol) in thf (5 cm^3). The initial dark brown solution changed to orange during 10 min, an orange solid appearing in suspension. After stirring for 30 min, the solvent was removed and diethyl ether (10 cm^3) was added to the oily residue which then solidified. The product was filtered off, washed with portions (5 × 5 cm^3) of diethyl ether (to remove the excess HBF_4) and dried to afford (**5**) as orange crystals (60 mg, 89%) (Found: C, 26.9; H, 1.2; N, 3.3. Calc. for $C_{18}H_7BF_4N_2O_{10}Ru_3$: C, 27.0; H, 0.9; N, 3.5%). I.r. (CH_2Cl_2): ν(CO) 2 060s, vbr (with several shoulders), 2 024vs, vbr (with several shoulders), 2 005s vbr cm^{-1} (with several shoulders). ^{1}H N.m.r. [$(CD_3)_2CO$]: δ 10.15 (dd, J = 5.1 and 1.4, 2 H), 9.02 (dd, J = 8.2 and 1.4, 2 H), 8.05 (dd, J = 8.2 and 5.1 Hz, 2 H), −11.71 p.p.m. (s, 1 H). M.s. (*m/e*): 715 ($M^+ - BF_4$).

Reaction of Complex (**5**) *with* NEt_3.—An excess of NEt_3 (0.1 cm^3) was injected into a solution of complex (**5**) (20 mg, 0.025 mmol) in dichloromethane (5 cm^3). The solution immediately changed from orange to dark brown. I.r. analysis of this solution confirmed the quantitative transformation of (**5**) into (**4**).

General Procedure for the Synthesis of $[Ru_3(L\text{–}L)(\mu\text{-}CO)_2(CO)_8]$ [L–L = phen (**6a**), biquin (**6b**), bipym (**6c**)].—$[Ru_3(CO)_{12}]$ (200 mg, 0.313 mmol) and the appropriate L–L ligand (0.32 mmol) were refluxed in thf (30 cm^3) for 3 h. The resulting black or very dark brown solid was filtered hot, washed with diethyl ether and dried. (**6a**): yield 84% (Found: C, 34.7; H, 1.3; N, 3.8. Calc. for $C_{22}H_8N_2O_{10}Ru_3$: C, 34.6; H, 1.1; N, 3.4%). I.r. (Nujol mull): ν(CO) 2 060—1 920vs, vbr, 1 800w (sh), 1 745m, vbr cm^{-1}. (**6b**): yield 69% (Found: C, 39.5; H, 2.0; N, 3.6. Calc. for $C_{28}H_{12}N_2O_{10}Ru_3$: C, 40.0; H, 1.4; N, 3.3%). I.r. (Nujol mull): ν(CO) 2 050—1 920vs, vbr, 1 755m, vbr, cm^{-1}). (**6c**): yield 73% (Found: C, 28.9; H, 1.2; N, 7.7. Calc. for $C_{18}H_6N_4O_{10}Ru_3$: C, 29.2; H, 0.80; N, 7.6%). I.r. (Nujol mull): ν(CO) 2 075—1 940vs, vbr. 1 745m, vbr cm^{-1}.

Crystal Structure Determinations of Complexes (**1a**) *and* (**4**).—Crystals of the complexes (**1a**) and (**4**) were selected for the *X*-ray analyses. The crystallographic data for both complexes are collected in Table 3. Unit-cell parameters were obtained by least-squares refinement of the θ values (in the range 10—16°) of 30 carefully centred reflections chosen from different regions of the reciprocal space. Data were collected at room temperature, the individual profiles having been analyzed following Lehmann and Larsen.[29] The structure amplitudes were obtained after usual Lorentz and polarization reduction. No corrections were applied for the absorption effects because of the low absorbance of the samples.

Both structures were solved by direct and Fourier methods and refined by full-matrix [(**1a**)] and block-matrix [(**4**)] least-squares using the SHELX system of computer programs[30] first with isotropic and then anisotropic thermal parameters for all the non-hydrogen atoms. All the hydrogen atoms of (**1a**) were located from the final difference Fourier map and refined isotropically. The hydrogen atoms of (**4**) were placed at their geometrically calculated positions and introduced in the final structure factor calculation with fixed isotropic thermal parameters.

The weighting scheme used in the last cycles of refinement was $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, with $K = 0.874$ [(**1a**)] and 0.796 [(**4**)], and $g = 0.0051$ [(**1a**)] and 0.0056 [(**4**)]. Atomic scattering factors, corrected for the anomalous dispersion of Ru, were taken from ref. 31. Final atomic co-ordinates for the non-hydrogen atoms are given in Tables 4 and 5. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom co-ordinates, and remaining bond distances and angles.

The calculations were carried out on the CRAY X-MP/12 computer of the Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (CINECA, Casalecchio, Bologna) and on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma.

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