Di- and Linear Tri-nuclear Carbonyl Ruthenium Clusters containing Asymmetrically Bridging 2,7-Disubstituted Naphthyridines†

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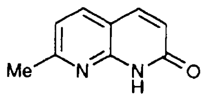
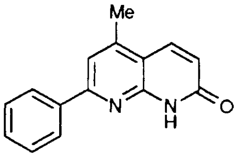
The diruthenium(I) complex *cis*-[$Ru_2(bmnapy)_2(CO)_4$] **1** was prepared by reaction of 2-benzylamino-7-methyl-1,8-naphthyridine (Hbmnapy) with [$Ru_3(CO)_{12}$] in benzene. The N^1,N^2 co-ordination mode of the bridging ligands is supplemented by N^8 as an axial donor atom. In contrast, the analogous reaction with 7-methyl-1,8-naphthyridin-2-one (Hmonapy) or the corresponding 5-methyl-7-phenyl derivative (Hmopnapy) afforded the respective trinuclear clusters *cis*-[$Ru_3(monapy)_2(CO)_6$] **2** and *cis*-[$Ru_3(mopnapy)_2(CO)_6$] **3**, which exhibit three-atom chains with 46 valence electrons. X-Ray structural analyses demonstrate that the Ru–Ru bond distance remains effectively unchanged on going from the Ru_2 unit in **1** [2.707(1) Å] to the Ru_3 sequence in **3** [average 2.701(2) Å], for which an Ru–Ru–Ru angle of 168.6(3)° is observed.

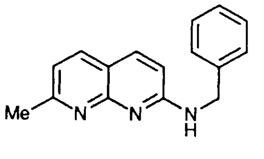
A number of complexes containing 2,7-disubstituted 1,8-naphthyridines as dinucleating ligands have been reported in the past decade. These include dirhodium(II) species of the type [$Rh_2(O_2CMe)_3L$]PF_6, which contain symmetrically substituted crescent-shaped ligands such as dpnapy [2,7-bis(2-pyridyl)-1,8-naphthyridine].[1] This neutral compound was also employed in the preparation of [$Ru_2Cl_2(bipy)_2(\mu$-dpnapy)][PF_6]$_2$ (bipy = 2,2′-bipyridine) and [$Ru_2(O_2CMe)_3(\mu$-dpnapy)]PF_6, both of which contain a Ru_2^{4+} core and axially co-ordinating dpnapy pyridine rings.[2] The latter complex and the structurally analogous Ru_2^{5+} species [$Ru_2(O_2CMe)_3$-(μ-dcnapy)] (dcnapy = 1,8-naphthyridine-2,7-dicarboxylate) were characterized by X-ray structural analyses.[2,3] We have also recently described[4] the quadruply bridged dinuclear complexes [$Mo_2(monapy)_4$] and [$Ru_2(monapy)_4$], in which the asymmetrically substituted ligands monapy (Hmonapy = 7-methyl-1,8-naphthyridin-2-one) display respectively N,O and N,N co-ordination modes. An extension of this approach led us to study the reaction of [$Ru_2Cl(O_2CMe)_4$] with Hmopnapy (5-methyl-7-phenyl-1,8-naphthyridin-2-one) in methanol at reflux, which leads to the successive formation of [$Ru_2Cl(mopnapy)_2(O_2CMe)_2$], [$Ru_2(mopnapy)_2(O_2CMe)_2$] and [$Ru_2(mopnapy)_4$].[5] The reduction of the Ru_2^{5+} core in the first complex is accompanied by a change in the co-ordination mode of the bridging naphthyridine derivatives from N,O to N,N in [$Ru_2(mopnapy)_2(O_2CMe)_2$]. Steric interactions between adjacent phenyl substituents must then be regarded as being responsible for the adoption of the electronically less favourable N,O binding pattern[5] by three of the bridging ligands in the fully substituted polar complex [$Ru_2(mopnapy)_4$].



Hmonapy



Hmopnapy



Hbmnapy

The establishment of ambidentate properties for such asymmetrically substituted naphthyridine derivatives in dinuclear complexes with Ru–Ru bonds prompted us to investigate the ability of these ligands to adopt a trinucleating role in a suitable linear three-atom metal cluster. Only one complex, [$Rh_3(\mu$-onapy$)_2(CO)_2(cod)_2$]ClO_4 (Honapy = 1,8-naphthyridin-2-one, cod = cycloocta-1,5-diene) is known,[6] albeit without direct metal–metal bonding [Rh···Rh distances 2.907(3) and 2.912(2) Å], in which a naphthyridine derivative co-ordinates three metal atoms. A tetranuclear complex [{$Mo_2(O_2CBu^t)_3$}$_2(\mu$-donapy)]·2thf (H_2donapy = 1,8-naphthyridine-2,7-dione, thf = tetrahydrofuran), containing two discrete Mo–Mo quadruple bonds of length 2.10 Å, in close proximity at a central Mo–Mo distance of 3.17 Å, has recently been studied by Chisholm and co-workers[7] as a molecular model for building blocks of stiff-chain polymers.

We now report the reaction of [$Ru_3(CO)_{12}$] with the naphthyridine derivatives Hbmnapy (2-benzylamino-7-methyl-1,8-naphthyridine), Hmonapy and Hmopnapy in benzene at reflux, which leads to the formation of *cis*-[$Ru_2(bmnapy)_2(CO)_4$] **1**, *cis*-[$Ru_3(monapy)_2(CO)_6$] **2** and *cis*-[$Ru_3(mopnapy)_2(CO)_6$] **3** respectively. The carbonyl ruthenium cluster [$Ru_3(CO)_{12}$] was chosen as the starting material as formation of a linear Ru–Ru–Ru chain might be expected to be possible with a minimum of reorganization of the original triangle of metal atoms.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Experimental

Solvents were dried and distilled under argon before use. The IR spectra were recorded as KBr discs on a Perkin-Elmer 1760 spectrometer, electronic spectra on a Perkin-Elmer Lambda 15 spectrometer, ^1H NMR spectra on a Bruker AM 400 spectrometer, and FAB mass spectra on a VG Autospec instrument with 3-nitrobenzyl alcohol as the matrix. Elemental analyses were performed on a Carlo Erba 1106 analyser. All reactions were carried out under argon by use of standard Schlenk techniques. The naphthyridine derivatives Hmonapy[8] and Hmopnapy[5] were synthesized according to literature procedures. The compound $[Ru_3(CO)_{12}]$ was obtained from Heraeus and used as received.

Syntheses.—Hbmnapy. A solution of 2-chloro-7-methyl-1,8-naphthyridine (11.16 g, 62.5 mmol) in benzylamine (30 cm^3) was refluxed for 8 h. After removal of the solvent in vacuum, the solid was recrystallized from toluene (20 cm^3) to afford Hbmnapy in 86% yield (13.35 g) (Found: C, 77.2; H, 6.7; N, 16.6. Calc. for $C_{16}H_{15}N_3$: C, 77.1; H, 6.1; N, 16.8%). FAB mass spectrum: *m/z* 250 (100%, $[M - H]^+$). ^1H NMR (CD_2Cl_2): δ 2.63 (s, 3 H, CH_3), 4.79 (d, 2 H, CH_2), 5.66 (s, 1 H, NH), 6.67 (d, 1 H, H^3), 7.03 (d, 1 H, H^6), 7.36 (m, 5 H, C_6H_5), 7.76 (d, 1 H, H^4) and 7.82 (d, 1 H, H^5). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 3202w, 3030w, 1624s, 1522s, 1344s, 1148w, 802w and 734m. UV/VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 344 (1347), 262 (1032) and 229 (1386).

cis-$[Ru_2(bmnapy)_2(CO)_4]$ **1**. The compound Hbmnapy (0.050 g, 0.2 mmol) and $[Ru_3(CO)_{12}]$ (0.043 g, 0.067 mmol) were refluxed in benzene solution (20 cm^3) for 1 h, during which time the colour changed from orange to red. After cooling, pentane (20 cm^3) was added and the resulting precipitate dried under vacuum to afford complex **1** in 82% yield (0.066 g). Suitable crystals were grown by gas diffusion of pentane into a toluene solution (Found: C, 53.9; H, 4.4; N, 9.8. Calc. for $C_{36}H_{28}N_6O_4Ru_2$: C, 53.3; H, 3.5; N, 10.3%). FAB mass spectrum: *m/z* 811 (100, M^+), 783 (19, $[M - CO]^+$), 755 (10, $[M - 2CO]^+$) and 654 {49%, $[M - Ru(CO)_2]^+$}. ^1H NMR (CD_2Cl_2): δ 2.25 (s, 3 H, CH_3), 4.76 (s, 2 H, CH_2), 6.26 (d, 1 H, H^3), 6.37 (d, 1 H, H^6), 6.94 (m, 5 H, C_6H_5), 7.16 (d, 1 H, H^4) and 7.35 (d, 1 H, H^5). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 2018s, 1941s (CO), 1623m, 1555m, 1440w and 1026w. UV/VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 402 (470), 348 (811) and 274 (1454).

cis-$[Ru_3(monapy)_2(CO)_6]$ **2**. A benzene solution (20 cm^3) of Hmonapy (0.032 g, 0.2 mmol) and $[Ru_3(CO)_{12}]$ (0.064 g, 0.1 mmol) was refluxed for 1 h changing from orange to red with the formation of a red precipitate, which was filtered off and dried under vacuum to afford complex **2** in 90% yield (0.071 g) (Found: C, 44.8; H, 3.0; N, 5.9. Calc. for $C_{24}H_{14}N_4O_8Ru_3$: C, 45.9; H, 2.4; N, 5.9%). FAB mass spectrum: *m/z* 791 (51, $[M + H]^+$), 763 (27, $[M + H - CO]^+$) and 633 {100%, $[M - Ru(CO)_2]^+$}. ^1H NMR (CD_2Cl_2): δ 2.62 (s, 3 H, CH_3), 6.98 (d, 1 H, H^3), 7.09 (d, 1 H, H^6), 7.66 (d, 1 H, H^4) and 7.84 (d, 1 H, H^5). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 2060s, 2017s, 1999s (CO), 1651m, 592m, 576m and 448w. UV/VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 422 (2757), 342 (8757) and 276 (9233).

cis-$[Ru_3(mopnapy)_2(CO)_6]$ **3**. The compound Hmopnapy (0.047 g, 0.2 mmol) and $[Ru_3(CO)_{12}]$ (0.064 g, 0.1 mmol) were refluxed in benzene solution (20 cm^3) for 1 h, during which time the colour turned from orange to deep red. After cooling pentane (20 cm^3) was added and the resulting precipitate dried under vacuum to afford complex **3** in 94% yield (0.089 g). Suitable crystals were grown by gas diffusion of pentane into a solution of **3** in 1,2,4-trichlorobenzene (Found: C, 37.4; H, 2.2; N, 6.4. Calc. for $C_{36}H_{22}N_4O_8Ru_3$: C, 36.5; H, 1.8; N, 7.1%). FAB mass spectrum: *m/z* 942 (100, M^+), 914 (15, $[M - CO]^+$), 886 (9, $[M - 2CO]^+$), 785 {44, $[M - Ru(CO)_2]^+$} and 628 {23%, $[M - 2Ru(CO)_2]^+$}. ^1H NMR (CD_2Cl_2): δ 2.66 (s, 3 H, CH_3), 6.85 (d, 1 H, H^3), 7.27 (d, 1 H, H^6), 7.35, 7.82 (m, 5 H, C_6H_5) and 7.88 (d, 1 H, H^4). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 2042s, 1981s (CO), 1626m, 1575m, 1506m, 1442m, 1369m and 835w. UV/VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 441 (11 665), 351 (23 239) and 282 (21 242).

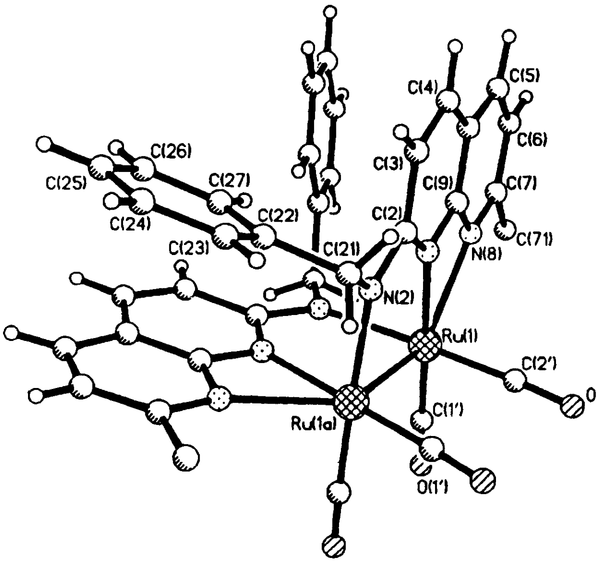


Fig. 1 Molecular structure of *cis*-$[Ru_2(bmnapy)_2(CO)_4]$ **1**

X-Ray Crystallography.—Crystal data and details of data collection and structure refinement for complexes **1** and **3** are presented in Table 1. Cell constants were determined by least-squares refinement on diffractometer angles for 25 reflections automatically centred on a Siemens P4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Data collection was performed in the ω mode with respective scan ranges of 1.0 and 1.1° and speed ranges of 2.0–14.6 and 3.0–14.6° min^{-1}. No significant alterations were observed in the control intensities registered every 100 reflections.

Structure analysis and refinement. Patterson synthesis (Ru atoms) followed by standard heavy-atom procedures. Full-matrix least squares on $|F|$ with hydrogen atoms for the naphthyridine ligands at calculated positions. The asymmetric unit of complex **1** contains 0.5 *cis*-$[Ru_2(bmnapy)_2(CO)_4]$ moieties and 0.5 toluene solvent molecules. That of **3** displays two independent *cis*-$[Ru_3(mopnapy)_2(CO)_6]$ molecules and three 1,2,4-trichlorobenzene solvent molecules. Anisotropic thermal parameters were introduced for the non-hydrogen atoms of *cis*-$[Ru_2(bmnapy)_2(CO)_4]$ **1** and the Ru and Cl atoms in the crystal lattice of **3**. Weighting scheme: $w = [\sigma^2(F_o) + pF_o^2]^{-1}$, $R' = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, with $p = 0.0$ (**1**) and 0.0003 (**3**). Structure solution and refinement with SHELXS 86 and SELX 76.[10]. Fractional atomic co-ordinates for **1** and **3** are listed in Table 2, selected bond lengths and angles in Table 3.

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

Results and Discussion

Reaction of Hbmnapy with $[Ru_3(CO)_{12}]$ in refluxing benzene leads to the formation of $[Ru_2(bmnapy)_2(CO)_4]$ **1**, independent of whether a 3:1 or 2:1 molar ratio is employed. As may be seen from Fig. 1, the bridging naphthyridine ligands in this diamagnetic diruthenium(I) complex display an N^1,N^2 co-ordination mode, in contrast to the N^1,N^8 binding pattern preferred by dinuclear ruthenium(II) complexes, in the absence of pronounced steric interactions.[5] Perusal of the bond lengths and angles in Table 3 indicates, however, that N(8) is involved in the co-ordination sphere of the ruthenium atom Ru(1), by

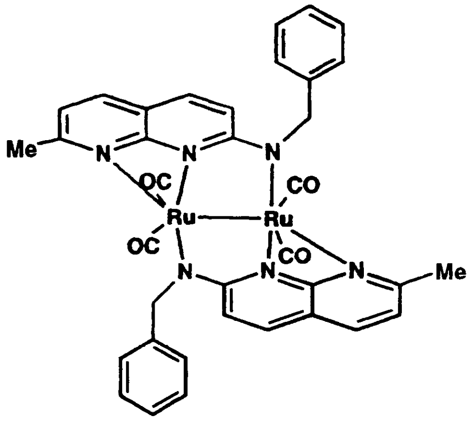
Table 1 X-Ray crystallographic data for complexes **1** and **3**

	1	**3**
Formula	$C_{36}H_{28}N_6O_4Ru_2\cdot C_6H_5CH_3$	$C_{36}H_{22}N_4O_8Ru_3\cdot 1.5C_6H_3Cl_3$
M	902.9	1213.9
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	Pn
T/K	293	173
a/Å	18.640(4)	16.828(3)
b/Å	14.503(3)	12.533(3)
c/Å	15.829(3)	21.497(4)
β/°	113.67(3)	106.66(3)
U/Å^3	3919(1)	4343(1)
Z	4	4
F(000)	1824	2388
D_c/g cm^{-3}	1.530	1.856
Crystal size/mm	0.69 × 0.26 × 0.14	0.52 × 0.43 × 0.38
μ/cm^{-1}	8.21	13.67
Absorption correction	ψ Scan	DIFABS[9]
2θ Scan range/°	$2\theta \leqslant 55$	$2\theta \leqslant 50$
Reflections measured	5217	8344
Reflections independent	4863	7959
Observed reflections [$I \geqslant 2\sigma(I)$]	2766	4248
$R_{\rm int}$	0.018	0.006
R	0.053	0.050
R'	0.053	0.050
Residual electron density/e Å^{-3}	0.97, −0.72	0.57, −0.36

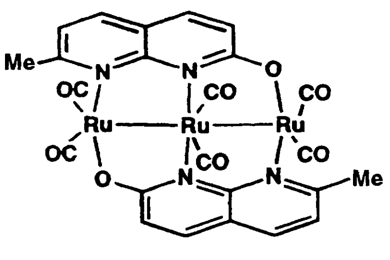
participation in a four-membered RuNCN chelate ring with Ru(1)–N(1) and Ru(1)–N(8) distances of respectively 2.066(6) and 2.377(7) Å. This N^1,N^8 co-ordination mode has previously been observed in $[Fe(napy)_4][ClO_4]_2$[11] and $[Ru(napy)_4]X_2$ (X = PF_6 or Cl).[12] Without involvement of N(8), the dinuclear complex **1** would exhibit a total electron count of only 30. This suggests that the symmetry-related N(8) atoms may be regarded as occupying the axial sites of the dinuclear complex, leading thereby to the expected 34 electron count. The associated stabilization of the Ru_2^{2+} core will presumably outweigh the energetic disadvantage of the N^1,N^2 bridging mode.

Complex **1** represents the first dinuclear ruthenium(I) species without additional axial ligands to be characterized. Despite the extremely distorted octahedral geometry at Ru(1), the Ru(1)–N(8) distance of 2.377(7) Å is only 0.073 Å longer than the average Ru–N$_{ax}$ distance to the axially co-ordinated pyridine-2-one (Hpyo) molecules in $[Ru_2(\mu\text{-pyo})_2(CO)_4(Hpyo)_2]$.[13] The Ru–Ru bond length of 2.707(1) Å in **1** is similar to distances observed in previously characterized diruthenium(I) complexes, for instance 2.670(1) Å in $[Ru_2(\mu\text{-pyo})_2(CO)_4(Hpyo)_2]$[13] or 2.711(1) Å in $[Ru_2(\mu\text{-pyo})_2(CO)_4(PPh_3)_2]$.[14] As a result of the marked difference of 0.45 Å between the N(1)···N(2) and Ru(1)–Ru(1a) distances in the RuNCNRu five-membered ring, the equatorial co-ordination planes of Ru(1) and Ru(1a) are inclined away from one another at an angle of 17.6°. A similar value of 16.2° was observed in $[Ru_2(\mu\text{-pyo})_2(CO)_4(PPh_3)_2]$.[14]

Evaluation of the molecular geometry of complex **1**, in which the asymmetrically 2,7-disubstituted naphthyridine derivative adopts the novel μ-1κN^1,N^8:2κN^2 co-ordination mode, suggests that such ligands could be capable of adopting a trinucleating function for linear Ru_3 chains with similar Ru–Ru distances. However, FAB mass spectra provide no evidence for the formation of a trinuclear species when the reaction between Hbmnapy and $[Ru_3(CO)_{12}]$ is carried out with a 3:1 molar ratio of the starting compounds. In contrast the diamagnetic triruthenium complexes *cis*-$[Ru_3(monapy)_2(CO)_6]$ **2** and *cis*-$[Ru_3(mopnapy)_2(CO)_6]$ **3** may be prepared under analogous conditions. The FAB mass spectra and elemental analyses are in both cases in accordance with the formulation as trinuclear species. Both complexes also display a characteristic loss of an $Ru(CO)_2$ fragment in their mass spectra, leading to the formation of the cation of the dinuclear species $[Ru_2L_2(CO)_4]^+$ (L = monapy or mopnapy). Crystals of **3**



1



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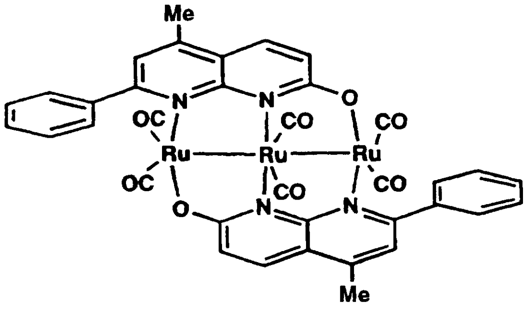

3

Table 2 Fractional atomic coordinates (× 10^4) for complexes **1** and **3** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Compound **1**							
Ru(1)	−783(1)	1199(1)	2266(1)	C(27)	1501(4)	−1626(5)	3430(5)
C(1′)	−1161(4)	2067(6)	1333(7)	C(3)	209(4)	−961(5)	4388(5)
O(1′)	−1404(4)	2615(5)	766(5)	C(4)	−471(4)	−1280(6)	4367(5)
C(2′)	−634(4)	2097(6)	3138(6)	C(5)	−1979(6)	−1100(7)	3580(6)
O(2′)	−520(3)	2681(4)	3682(5)	C(6)	−2568(6)	−633(7)	2945(7)
N(1)	−440(3)	163(4)	3244(4)	C(7)	−2443(4)	58(7)	2459(7)
C(2)	250(4)	−207(5)	3818(5)	C(71)	−3109(5)	594(7)	1683(7)
N(2)	882(3)	141(4)	3747(4)	N(8)	−1719(3)	316(4)	2584(4)
C(21)	1657(4)	−181(5)	4421(5)	C(9)	−1121(4)	−150(5)	3214(5)
C(22)	1957(4)	−1031(5)	4128(5)	C(10)	−1204(4)	−872(5)	3730(5)
C(23)	2746(4)	−1244(6)	4614(5)	C(31)	0	6396(10)	2500
C(24)	3069(5)	−2024(6)	4384(6)	C(32)	−167(10)	4995(8)	1656(5)
C(25)	2596(5)	−2598(6)	3675(6)	C(33)	−111(10)	5956(8)	1678(5)
C(26)	1828(5)	−2395(5)	3222(6)	C(34)	0	4566(10)	2500
Compound **3**							
Ru(11)	−1638(1)	1533(4)	−609(3)	O(232)	−1677(14)	5309(12)	3349(9)
Ru(13)	1626(1)	1587(4)	637(3)	N(31)	471(15)	2544(25)	4119(12)
Ru(12)	0	1348(4)	0	C(32)	1264(14)	2182(33)	4200(11)
C(111)	−1692(25)	573(22)	−1264(13)	O(32)	1795(13)	2274(13)	4777(8)
O(111)	−1618(17)	−132(16)	−1591(12)	C(33)	1442(20)	1509(28)	3712(13)
C(112)	−1974(18)	549(17)	−95(13)	C(34)	868(14)	1203(32)	3163(16)
O(112)	−2088(15)	−171(11)	203(9)	C(35)	−635(15)	1245(27)	2527(12)
C(121)	174(22)	371(19)	−582(13)	C(351)	−517(23)	615(24)	1996(14)
O(121)	366(15)	−217(17)	−927(10)	C(36)	−1425(18)	1671(27)	2542(13)
C(122)	−96(20)	138(21)	459(17)	C(37)	−1554(14)	2210(26)	3062(12)
O(122)	−24(13)	−568(11)	822(9)	C(371)	−2413(16)	2428(30)	3090(14)
C(131)	2041(22)	823(24)	62(14)	C(372)	−2665(17)	2092(27)	3623(14)
O(131)	2253(20)	309(20)	−306(12)	C(373)	−3484(16)	2363(23)	3583(12)
C(132)	1677(21)	450(19)	1185(14)	C(374)	−3935(17)	2941(21)	3042(10)
O(132)	1721(13)	−234(11)	1556(8)	C(375)	−3665(15)	3312(22)	2526(11)
N(11)	−199(14)	2561(25)	690(13)	C(376)	−2859(16)	3009(28)	2549(15)
C(12)	−988(13)	2957(33)	584(13)	N(38)	−867(13)	2510(30)	3553(12)
O(12)	−1620(13)	2666(15)	98(9)	C(39)	−99(11)	2178(20)	3590(10)
C(13)	−1231(20)	3562(28)	1070(13)	C(310)	28(13)	1519(21)	3072(11)
C(14)	−637(16)	3782(33)	1627(16)	N(41)	174(18)	2180(21)	5401(16)
C(15)	794(15)	3684(28)	2319(13)	C(42)	−590(14)	1693(22)	5277(13)
C(151)	671(26)	4245(27)	2872(16)	O(42)	−1219(14)	2101(11)	4834(9)
C(16)	1644(17)	3425(27)	2366(13)	C(43)	−752(21)	843(22)	5675(14)
C(17)	1790(14)	2863(25)	1861(12)	C(44)	−139(19)	465(34)	6179(18)
C(171)	2628(16)	2521(30)	1836(14)	C(45)	1281(20)	559(31)	6831(18)
C(172)	3247(12)	1931(21)	2272(13)	C(451)	1228(23)	−343(20)	7241(13)
C(173)	4035(13)	1771(19)	2197(11)	C(46)	2081(20)	1038(22)	6900(15)
C(174)	4291(16)	2193(20)	1685(11)	C(47)	2183(15)	1912(28)	6544(17)
C(175)	3694(19)	2780(32)	1231(18)	C(471)	3012(16)	2419(23)	6646(11)
C(176)	2910(23)	2891(35)	1325(17)	C(472)	3428(17)	2914(25)	7230(13)
N(18)	1203(13)	2586(30)	1294(12)	C(473)	4217(20)	3269(28)	7237(15)
C(19)	406(11)	2813(20)	1227(11)	C(474)	4466(19)	3391(25)	6676(11)
C(110)	191(17)	3401(30)	1739(13)	C(475)	4049(18)	2900(25)	6090(14)
N(21)	83(16)	2745(21)	−608(15)	C(476)	3320(18)	2387(26)	6108(12)
C(22)	853(14)	3221(22)	−438(12)	N(48)	1547(17)	2228(23)	6019(14)
O(22)	1431(14)	2983(10)	96(9)	C(49)	771(14)	1894(34)	5936(19)
C(23)	1011(19)	4199(22)	−733(13)	C(410)	656(21)	952(27)	6294(17)
C(24)	417(14)	4530(21)	−1265(13)	Cl(11)	−6312(10)	536(14)	−1230(9)
C(25)	−1047(19)	4402(31)	−2007(18)	Cl(12)	−6280(12)	2704(13)	−503(8)
C(251)	−965(24)	5224(21)	−2460(14)	Cl(14)	−3205(12)	1946(17)	928(8)
C(26)	−1843(19)	3887(22)	−2130(14)	C(11′)	−5444(15)	963(22)	−624(15)
C(27)	−1917(16)	3158(28)	−1672(16)	C(12′)	−5401(14)	1898(22)	−259(18)
C(271)	−2736(19)	2664(30)	−1712(12)	C(13′)	−4667(15)	2195(22)	208(14)
C(272)	−3188(19)	2245(25)	−2310(14)	C(14′)	−4047(13)	1420(19)	334(14)
C(273)	−3901(18)	1620(26)	−2417(15)	C(15′)	−3984(16)	410(19)	78(14)
C(274)	−4305(19)	1646(26)	−1935(11)	C(16′)	−4772(16)	288(25)	−361(15)
C(275)	−3850(17)	2089(26)	−1345(13)	Cl(21)	6594(11)	4495(14)	6102(7)
C(276)	−3065(17)	2559(26)	−1188(12)	Cl(22)	6552(10)	2214(13)	5424(9)
N(28)	−1275(16)	2739(23)	−1188(14)	Cl(24)	3474(10)	3088(12)	3899(5)
C(29)	−540(14)	3230(28)	−1054(16)	C(21′)	5747(15)	4164(21)	5449(15)
C(210)	−383(16)	4047(22)	−1485(13)	C(22′)	5737(15)	3123(18)	5210(14)
Ru(21)	1914(1)	3471(4)	5466(3)	C(23′)	5107(14)	2757(22)	4675(15)
Ru(22)	274(1)	3654(4)	4863(1)	C(24′)	4402(12)	3401(18)	4481(12)
Ru(23)	−1350(1)	3405(4)	4221(3)	C(25′)	4420(16)	4381(18)	4796(12)

Table 2 (*contd.*)

C(211)	1963(17)	4582(15)	6030(11)	C(26′)	5036(14)	4794(21)	5323(12)
O(211)	2090(14)	5234(13)	6429(8)	Cl(31)	1612(11)	1818(11)	8517(7)
C(212)	2109(19)	4517(17)	4919(13)	Cl(32)	1660(6)	3728(5)	7652(5)
O(212)	2320(14)	5001(14)	4535(8)	Cl(34)	−1542(16)	2965(24)	6370(10)
C(221)	119(22)	4567(19)	5486(12)	C(31′)	694(10)	2096(15)	7916(9)
O(221)	83(15)	5221(14)	5856(10)	C(32′)	759(9)	2971(16)	7527(10)
C(222)	321(20)	4813(19)	4347(17)	C(33′)	38(12)	3193(19)	7026(10)
O(222)	458(14)	5627(12)	4139(10)	C(34′)	−668(13)	2576(21)	6984(12)
C(231)	−1689(22)	4322(22)	4771(15)	C(35′)	−765(13)	1690(21)	7350(12)
O(231)	−1971(15)	4863(17)	5089(10)	C(36′)	−23(11)	1483(18)	7830(10)
C(232)	−1556(20)	4566(18)	3681(14)				

Table 3 Selected bond lengths (Å) and angles (°)

Compound **1**			
Ru(1)–Ru(1a)	2.707(1)	Ru(1)–N(8)	2.377(7)
Ru(1)–N(1)	2.066(6)	Ru(1)–N(2a)	2.173(6)
Ru(1)–C(1′)	1.851(9)	Ru(1)–C(2′)	1.838(9)
Ru(1a)–Ru(1)–N(1)	79.6(2)	Ru(1a)–Ru(1)–N(8)	138.1(1)
Ru(1a)–Ru(1)–N(2a)	88.0(2)	Ru(1a)–Ru(1)–C(1′)	104.0(3)
Ru(1a)–Ru(1)–C(2′)	88.5(2)	N(1)–Ru(1)–N(8)	58.8(2)
N(1)–Ru(1)–N(2a)	87.1(2)	N(1)–Ru(1)–C(1′)	175.2(3)
N(1)–Ru(1)–C(2′)	92.5(3)	N(2a)–Ru(1)–N(8)	85.6(2)
N(2a)–Ru(1)–C(1′)	90.0(3)	N(2a)–Ru(1)–C(2′)	175.6(3)
C(1′)–Ru(1)–C(2′)	90.7(4)	C(1′)–Ru(1)–N(8)	117.3(3)
C(2′)–Ru(1)–N(8)	97.1(3)	Ru(1)–N(1)–C(2)	135.8(6)
Ru(1)–N(1)–C(9)	102.6(4)	Ru(1)–N(8)–C(9)	88.1(5)
Ru(1)–N(8)–C(7)	154.7(5)	Ru(1)–N(2a)–C(2a)	121.0(4)
N(1)–C(2)–N(2)	115.4(7)	N(1)–C(9)–N(8)	110.5(7)
Compound **3**			
Ru(11)–Ru(12)	2.701(2)	Ru(12)–Ru(13)	2.702(3)
Ru(11)–N(28)	2.15(3)	Ru(11)–O(12)	2.08(2)
Ru(11)–C(111)	1.83(3)	Ru(11)–C(112)	1.83(3)
Ru(12)–N(11)	2.22(3)	Ru(12)–N(21)	2.21(3)
Ru(12)–C(121)	1.83(3)	Ru(12)–C(122)	1.84(3)
Ru(13)–N(18)	2.16(3)	Ru(13)–O(22)	2.07(2)
Ru(13)–C(131)	1.85(3)	Ru(13)–C(132)	1.84(3)
Ru(11)–Ru(12)–Ru(13)	168.6(3)	Ru(12)–Ru(11)–N(28)	85.5(6)
Ru(12)–Ru(11)–O(12)	84.5(6)	Ru(12)–Ru(11)–C(111)	97.8(12)
Ru(12)–Ru(11)–C(112)	95.6(8)	N(28)–Ru(11)–O(12)	89.7(10)
N(28)–Ru(11)–C(111)	88.7(13)	N(28)–Ru(11)–C(112)	177.2(12)
O(12)–Ru(11)–C(111)	177.1(12)	O(12)–Ru(11)–C(112)	87.8(10)
C(111)–Ru(11)–C(112)	93.7(13)	Ru(11)–Ru(12)–N(11)	86.4(6)
Ru(11)–Ru(12)–N(21)	82.8(7)	Ru(11)–Ru(12)–C(121)	93.8(10)
Ru(11)–Ru(12)–C(122)	95.5(10)	Ru(13)–Ru(12)–N(11)	84.9(6)
Ru(13)–Ru(12)–N(21)	89.2(7)	Ru(13)–Ru(12)–C(121)	94.7(11)
Ru(13)–Ru(12)–C(122)	92.9(10)	N(11)–Ru(12)–N(21)	84.3(11)
N(11)–Ru(12)–C(121)	94.3(12)	N(11)–Ru(12)–C(122)	98.8(13)
N(21)–Ru(12)–C(121)	94.3(12)	N(21)–Ru(12)–C(122)	176.4(13)
C(121)–Ru(12)–C(122)	82.6(14)	Ru(12)–Ru(13)–N(18)	85.4(6)
Ru(12)–Ru(13)–O(22)	80.5(6)	Ru(12)–Ru(13)–C(131)	97.2(10)
Ru(12)–Ru(13)–C(132)	95.2(11)	N(18)–Ru(13)–O(22)	81.3(11)
N(18)–Ru(13)–C(131)	175.3(13)	N(18)–Ru(13)–C(132)	89.6(14)
O(22)–Ru(13)–C(131)	95.2(11)	O(22)–Ru(13)–C(132)	170.3(13)
C(131)–Ru(13)–C(132)	94.0(14)		

suitable for an X-ray structural analysis were grown by gas diffusion of pentane into a solution of the complex in 1,2,4-trichlorobenzene. The asymmetric unit in the polar space group *Pn* contains three solvent molecules and two three-atom clusters, the structure of the first of which is depicted in Fig. 2. The positions of the Ru atoms of the two $[Ru_3(mop\text{-}napy)_2(CO)_6]$ molecules are related by a pseudo inversion centre. As the metrical data for the independent clusters are similar, only the first molecule will be discussed in detail.

Clusters **2** and **3** represent the first examples of three-atom chains bridged by naphthyridine derivatives. The ligands adopt a head-to-tail orientation and display a μ_3-1κO^2:2κN^1:3κN^8 co-ordination mode. Inspection of the Ru–Ru bond lengths in **3** [2.701(2), 2.702(3) Å] indicates that these are effectively unchanged in comparison to the diruthenium(I) complex **1** [2.707(1) Å]. The Ru–Ru–Ru angle displays a value of 168.6(3)°. As a result of the blocking of the axial sites by the respective 7-methyl and 7-phenyl substituents in **2** and **3**, these clusters exhibit an unusual electron count of 46. Such linear three-atom chains can invariably be described by a localized bonding description and many examples are known of metal carbonyl clusters with 50 valence electrons,[15] including the triruthenium compound $[Ru_3(\eta\text{-}C_5H_5)_2(CO)_8]$.[16] To our knowledge, with the exception of the unusual compound $[Mn_3(3\text{-}MeC_5H_6)_4]$

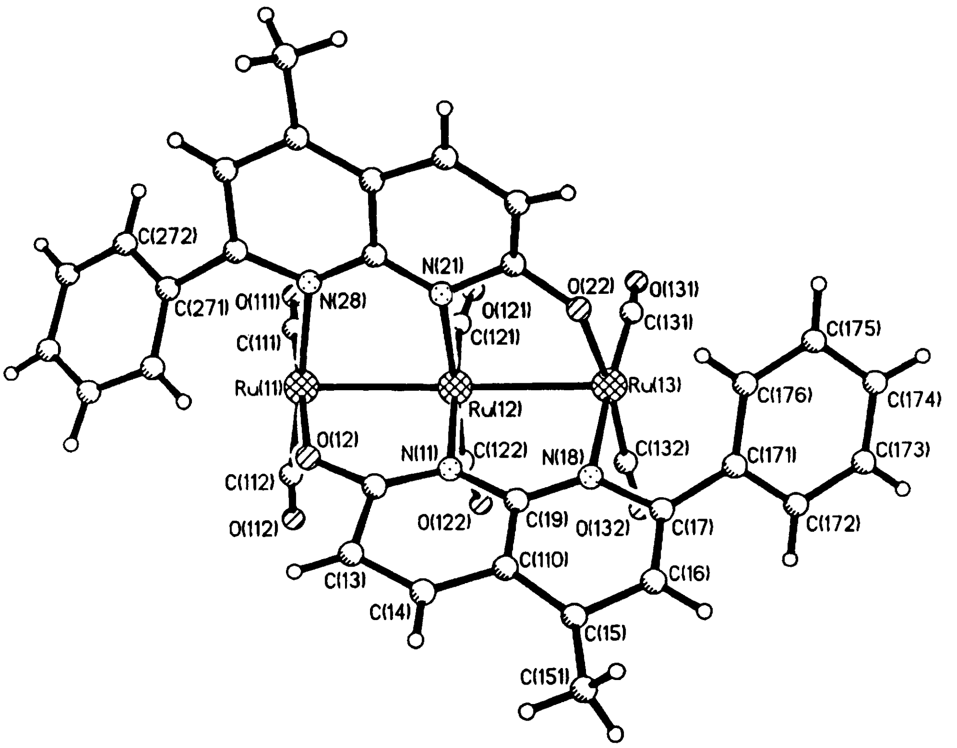

Fig. 2 Structure of the first independent molecule of *cis*-[$Ru_3(mopnapy)_2(CO)_6$] **3**

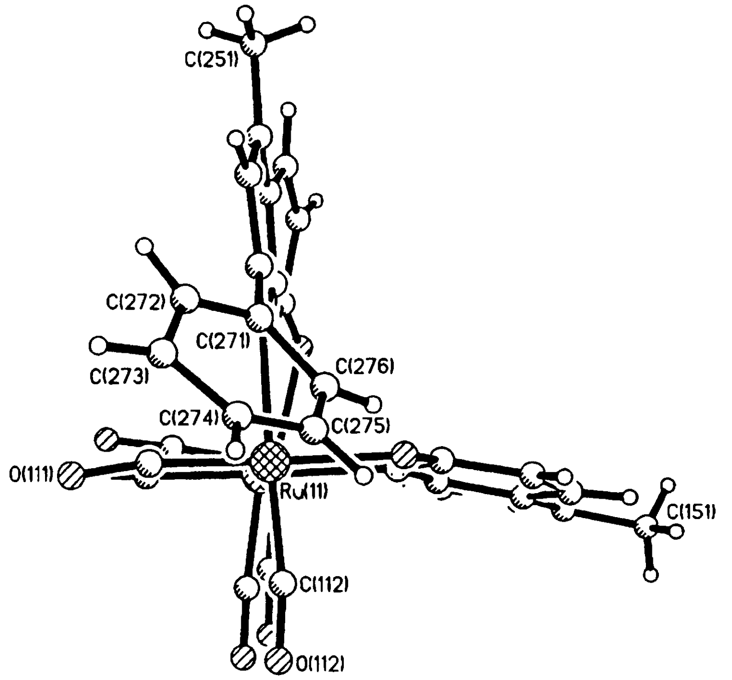

Fig. 3 Projection of complex **3** parallel to the axis of the Ru_3 chain

(41 electrons),[17] all examples of three-atom chains with less than 50 valence electrons contain at least one metal atom belonging to the platinum group.[15] For metals which conform to the 16-electron rule, a linear three-atom sequence will be expected to be associated with 44 valence electrons. Only one cluster [$Ni_3(C_{12}H_{17})_2$]$^{2-}$ has previously been reported[18] which exhibits an electron count of 46 similar to those of **2** and **3**. The unusually low number of valence electrons in the trimetallic compounds presented in this work prompts the question as to whether agostic[19] C–H ··· Ru interactions between the 7-methyl or 7-phenyl substituents and the terminal ruthenium atoms might provide axial electron pairs. Perusal of the molecular structure of **3** in the direction of the Ru_3 chain (Fig. 3) suggests that this is not the case. Distances of 2.49 and 2.54 Å are observed for Ru(11) ··· H(276) and Ru(13) ··· H(176), with the hydrogen atoms markedly displaced from the respective axes of the Ru–Ru bonds. Corroboration for this interpretation is provided by the absence of pronounced ^1H NMR high-field shifts for the protons involved.[19] The phenyl rings are twisted at respective angles of

56.9 and 52.7° relative to the planes of their naphthyridine ring systems.

A formal description as an Ru^{I}–Ru^{0}–Ru^{I} chain is reasonable for cluster **3**. It is interesting that the Ru–Ru single bond lengths [2.701(2), 2.702(3) Å] in this 46-electron cluster are much shorter than in the 50-electron triruthenium cluster $[\mathrm{Ru_3}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CO})_8]$[16] [2.889(1) Å], presumably as a result of the absence of axially co-ordinated ligands in the former compound. The adoption of a trinucleating function by the bridging naphthyridine derivative in **3** leads to marked changes in the X(2)–Ru–Ru (X = N or O) and N(1)–Ru–Ru angles in comparison to those of the dinuclear complex **1**. For instance N(2a)–Ru(1)–Ru(1a) displays a value of 88.0(2)° in the latter compound, which is much larger than the average value of 82.5(6)° in **3**. At the same time the N(1)–Ru–Ru [X(2)] angle increases from 79.6(2) to 83.9(7)° on going from **1** to **3**. This means that the [N(1)] Ru–Ru [X(2)] bond shifts towards N(8) in **1** to allow for axial co-ordination of this nitrogen and away from N(8) in **3** to accommodate the third ruthenium atom in the Ru$_3$ chain. Significant increases are also observed for the angles N(1)–C(2)–X(2) [115.4(7) in **1**, 123(3)° in **3**], N(1)–C(9)–N(8) [110.5(7) in **1**, 119(3)° in **3**] and C(2)–X(2)–Ru [121.0(4) in **1**, 129(2)° in **3**]. The adoption of a very large C(2)–X(2)–Ru angle, which is necessary for a trinucleating co-ordination mode, will be associated with a relatively small energy disadvantage for an exocyclic oxygen O(2), as in mopnapy$^-$ or monapy$^-$. In contrast such an angle would be energetically very unfavourable for the trigonal nitrogen atom N(2) in bmnapy$^-$, with the apparent consequence that this ligand is incapable of bridging a Ru$_3$ chain. The angle changes discussed above are also associated with pronounced increases in the distances X(2)···N(1) [2.27(1) in **1**, 2.37(3) Å in **3**] and N(1)···N(8) [2.20(1) in **1**, 2.35(3) Å in **3**] on going from the di- to the trinuclear complex. The analogous distances in $[\mathrm{H_2mopnapy}]\mathrm{Cl}$[5] are 2.257(5) and 2.297(5) Å. In this context, it is interesting that, despite the flexibility of the naphthyridine derivative in **3**, the N–Ru–Ru–N and N–Ru–Ru–O torsion angles in this cluster are relatively small (2.0–8.2°), as is also observed for **1** [N(1)–Ru(1)–Ru(1a)–N(2) 2.7°].

This work has demonstrated, for the first time, a trinucleating capability of substituted naphthyridine ligands for three-atom metal chains. The employment of asymmetrically 2,7-disubstituted derivatives with bulky groups such as methyl or phenyl appears to be essential to prevent polymerization. For instance, the analogous reaction of $[\mathrm{Ru_3(CO)_{12}}]$ with Honapy leads to the formation of a precipitate, which cannot be dissolved in conventional organic solvents.

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