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Synthesis, characterization and crystal structures of a series of ruthenium μ_4-nitrene carbonyl clusters

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Methylation of $[Ru_3(CO)_{10}(NO)]^-$ anion has led to the isolation of $[Ru_6(\mu\text{-}H)(CO)_{16}(\mu\text{-}CO)(\mu_4\text{-}NH)\{\mu_3\text{-}\eta^2\text{-}C(O)OMe\}]$ **1** in addition to the major product $[Ru_3(CO)_{10}(NOMe)]$ **2**. Hydrogenation of **2** in refluxing hexane gave $[Ru_3(\mu\text{-}H)_2(CO)_9(NH)]$ **3** and $[Ru_3(\mu\text{-}H)_2(CO)_9(NOMe)]$ **4** in moderate yields, but in the presence of $[Ru_3(CO)_{12}]$ it gave $[Ru_6(\mu\text{-}H)(CO)_{16}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)]$ **5** and $[Ru_5(\mu\text{-}H)_3(CO)_{13}(\mu_4\text{-}NH)(\mu_3\text{-}OMe)]$ **6** in addition. Thermolysis of **2** in toluene at 90 °C for 3 h yielded $[Ru_4(CO)_{12}(\mu_4\text{-}N)(\mu\text{-}OMe)]$ **7** and $[Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)_2]$ **8**. Pyrolysis of **4** at 140 °C for 2 h afforded $[Ru_6(CO)_{15}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)\{\mu_3\text{-}\eta^2\text{-}N(H)C(O)OMe\}]$ **9**, $[Ru_6(\mu\text{-}H)_2(CO)_{14}(\mu\text{-}CO)_2\{\mu_5\text{-}\eta^2\text{-}NC(O)OMe\}]$ **10** and $[Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)(\mu\text{-}NCO)]$ **11** together with the known clusters $[Ru_4H_2(CO)_{13}]$ and $[Ru_3(\mu\text{-}H)(CO)_{10}(NH_2)]$. The crystal structures of **1** and **3**–**11** have been determined. Clusters **1**, **5**, **6**, **8**, **9** and **11** consist of a square-pyramidal '$Ru_4(CO)_8(\mu_4\text{-}NH)$' moiety with four ruthenium atoms forming a square-planar base which is capped by a quadruply bridging nitrene ligand. For **1**, **5**, **8**, **9** and **11**, two additional ruthenium fragments bridge the opposite edges of the $Ru_4(CO)_8(\mu_4\text{-}NH)$ metal core to give 'boat' form hexaruthenium nitrene compounds. Compound **6** also has a $Ru_4(CO)_8(\mu_4\text{-}NH)$ moiety, but with only one bridging $Ru(CO)_4$ fragment at one of the Ru–Ru edges of the tetraruthenium plane while the remaining three are bridged by hydrides. Compound **10** comprises a square-pyramidal array of five ruthenium atoms with a $Ru(CO)_3$ unit bridging one of the Ru–Ru edges of the base. The other side of the square plane is quadruply capped by the nitrogen atom of a NC(O)OMe ligand with the oxygen atom of the acyl group bonded to the apical $Ru(CO)_3$ unit. Compound **7** possesses a butterfly arrangement of four Ru atoms with the methoxy group bridging the hinge.

The chemistry of nitrido and nitrene clusters is of current interest.[1–5] Metal–surface-bound nitrido and nitrene species are believed to be the key intermediates in a number of chemical processes such as nitrogen oxide reduction and the Haber process.[2] Cluster compounds containing a μ_3-nitrene have been known for a long time, for example $[Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)]$,[3] $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)][BPh_4]$,[3] $[Fe_3(CO)_8(NO)(NH)]^-$[4] and $[FeCo_2(CO)_9(\mu_3\text{-}NH)]$.[5] However, μ_4-nitrene species are very rare. An obvious attempt to synthesize a μ_4-nitrene cluster is by protonation of μ_4-nitrido clusters with a 'semi-open' environment. However, this reaction usually leads to the formation of a hydrido cluster rather than a nitrene species as in the protonation of $[Fe_4(CO)_{12}N]^-$ anion.[6] Blohm and Gladfelter[7] have shown that protonation of $[N(PPh_3)_2][Ru_4(CO)_{12}N]$ in the presence of diphenylacetylene gives $[Ru_4(PhCCPh)(CO)_{11}(NH)]$ which is the only structurally characterized μ_4-NH-containing compound that we are aware of. We present in this article the isolation of a series of ruthenium μ_4-nitrene carbonyl clusters synthesized by thermolysis or pyrolysis of nitrosyl clusters.

Results and Discussion

Methylation of $[N(PPh_3)_2][Ru_3(CO)_{10}(NO)]$ with CF_3SO_3Me

Dropwise addition of 1.5 equivalents of CF_3SO_3Me to $[N(PPh_3)_2][Ru_3(CO)_{10}(NO)]$ in CH_2Cl_2 gives $[Ru_3(CO)_{10}(NOMe)]$[8] as the major product. In addition, a minor blue compound $[Ru_6(\mu\text{-}H)(CO)_{16}(\mu\text{-}CO)(\mu_4\text{-}NH)\{\mu_3\text{-}\eta^2\text{-}C(O)OMe\}]$ **1** was also isolated which was characterized by various spectroscopic methods. The spectroscopic data are given in Table 1. The positive FAB mass spectrum exhibits a peak envelope at *m/z* 1157 with an isotopic distribution of six ruthenium atoms. The ^1H NMR spectrum shows a triplet centred at δ 6.18 with a coupling constant of 54 Hz which may be attributable to the NH proton.[9] Besides, there are also two singlets with relative intensity of three to one located at δ 4.03 and −17.32 due to the methoxy proton and hydride ligand respectively. Furthermore, the IR spectrum shows the presence of both terminal and bridging carbonyl ligands. In order to elucidate the structure of **1**, an X-ray analysis was carried out on a dark blue crystal grown by slow evaporation of a hexane–dichloromethane solution at −20 °C. The molecular structure is depicted in Fig. 1 and relevant structural parameters are listed in Table 2.

The metal framework of complex **1** consists of a '$Ru_4(CO)_8(\mu_4\text{-}NH)$' moiety similar to that of $[Ru_4(PhCCPh)(CO)_{11}(NH)]$.[7] The tetraruthenium plane, Ru(2)–Ru(3)–Ru(4)–Ru(5) is twisted with a maximum deviation from the least-squares plane of 0.225 Å. The Ru–Ru bond distances range from

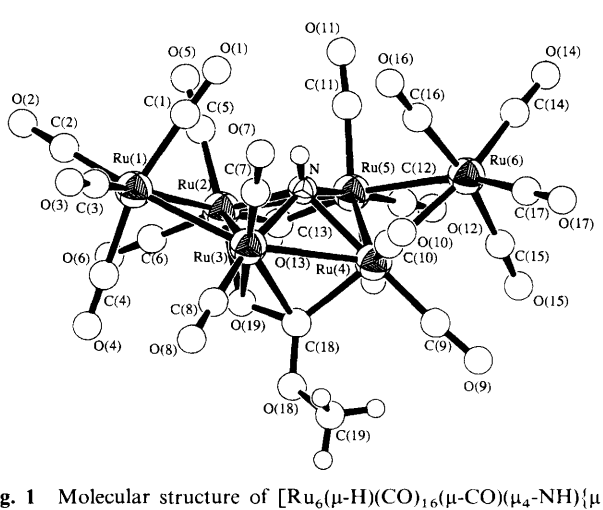


Fig. 1 Molecular structure of $[Ru_6(\mu\text{-}H)(CO)_{16}(\mu\text{-}CO)(\mu_4\text{-}NH)\{\mu_3\text{-}\eta^2\text{-}C(O)OMe\}]$ **1**, showing the atomic labelling scheme

Table 1 Spectroscopic data for compounds **1** and **3–11**

Compound	$\tilde{\nu}$(CO)/cm^{-1} (hexane)	Mass spectrum, m/z[a]	^{1}H NMR (δ, J/Hz)[b]
1	2103w, 2078vs, 2044vs, 2029s, 2023s, 2003m, 1976 (sh), 1970w, 1954w, 1890w	1157 (1157)	6.18 (t, J_{NH} = 54), 4.03 (s), −17.32 (s)
3	2114m, 2079s, 2055vs, 2045s, 2011vs, 2000s, 1987m	572 (572)	6.33 (t, J_{NH} = 48.6), −17.55(s)
4	2116m, 2078s, 2057vs, 2048s, 2036 (sh), 2010vs, 2005s, 1988m	602 (602)	3.46 (s), −17.22 (s)
5	2111w, 2082vs, 2051vs, 2042s, 2027s, 2012m, 1968w, 1888w	1157 (1157)	5.92 (t, J_{NH} = 48.6), 2.95 (s), −18.03 (s)
6	2109w, 2082vs, 2047vs, 2037s, 2022vs, 2012s, 1983m, 1952m	918 (918)	5.00 (br), 3.10 (s), −6.26 (d, J_{HH} = 6.8), −9.04 (d, J_{HH} = 2.7), −11.42 (dd, J_{HH} = 6.5, 2.4)
7	2096w, 2061vs, 2047s, 2015vs, 2007 (sh), 1988s, 1959w	786 (786)	2.08(s)
8	2077vs, 2045s, 2038m, 2026m, 1983w	1187 (1187)	5.75 (t, J_{NH} = 44.5), 2.90 (s)
9	2095w, 2087 (sh), 2077s, 2064vs, 2044vs, 2033 (sh), 2023s, 2010s, 2000m, 1980w, 1866m	1202 (1202)	5.55 (t, J_{NH} = 46), 3.75 (s), 2.83 (s), −0.82 (s)
10	2098w, 2075s, 2056s, 2039vs, 2030 (sh), 2017m, 2009w, 1984m, 1874m, 1846m	1101 (1129)[c]	[d]3.24 (s), −12.97 (s), −16.23 (s)
11	2099w, 2071vs, 2056s, 2049s, 2039vs, 2012m, 1984w, 1875w, 1847w	1170 (1198)[c]	5.70 (t, J_{NH} = 43), 2.83 (s)

[a] Calculated values in parentheses. [b] In $CDCl_3$. [c] Only $[M - CO]^+$ is observed. [d] In CD_2Cl_2.

Table 2 Selected bond lengths (Å) and angles (°) for compound **1**

Ru(1)–Ru(2)	2.797(2)	Ru(5)–N	2.123(9)
Ru(2)–Ru(3)	2.878(1)	Ru(4)–H(7)	1.81
Ru(4)–Ru(6)	2.802(2)	Ru(5)–H(7)	2.01
Ru(5)–Ru(6)	2.812(1)	Ru(2)–O(19)	2.174(10)
Ru(1)–Ru(3)	2.723(2)	Ru(3)–O(19)	2.188(9)
Ru(2)–Ru(5)	2.799(2)	Ru(3)–C(18)	2.28(1)
Ru(3)–Ru(4)	2.815(2)	Ru(4)–C(18)	2.07(1)
Ru(4)–Ru(5)	2.761(1)	O(19)–C(18)	1.35(1)
Ru(2)–N	2.161(9)	O(18)–C(18)	1.37(1)
Ru(3)–N	2.199(9)	O(18)–C(19)	1.42(2)
Ru(4)–N	2.157(9)	N–H(1)	0.87
Ru(2)–Ru(1)–Ru(3)	62.85(4)	Ru(2)–Ru(5)–Ru(4)	84.87(4)
Ru(1)–Ru(2)–Ru(5)	139.77(5)	Ru(4)–Ru(6)–Ru(5)	58.94(3)
Ru(3)–Ru(2)–Ru(5)	92.84(4)	Ru(2)–O(19)–Ru(3)	82.6(3)
Ru(1)–Ru(3)–Ru(4)	140.39(5)	Ru(3)–C(18)–Ru(4)	80.5(4)
Ru(1)–Ru(2)–Ru(3)	57.31(4)	Ru(2)–N–Ru(3)	82.6(3)
Ru(1)–Ru(3)–Ru(2)	59.84(4)	Ru(2)–N–Ru(5)	81.6(3)
Ru(2)–Ru(3)–Ru(4)	82.44(4)	Ru(3)–N–Ru(4)	80.5(3)
Ru(3)–Ru(4)–Ru(6)	132.81(5)	Ru(2)–N–Ru(4)	120.6(4)
Ru(5)–Ru(4)–Ru(6)	60.71(4)	Ru(3)–N–Ru(5)	144.2(4)
Ru(3)–Ru(4)–Ru(5)	95.04(4)	Ru(4)–N–Ru(5)	80.4(3)
Ru(2)–Ru(5)–Ru(6)	137.22(5)	O(18)–C(18)–O(19)	108(1)
Ru(4)–Ru(5)–Ru(6)	60.35(4)	C(18)–O(18)–C(19)	119(1)

Dihedral angles between planes

Plane	A	B	C
B	158.3		124.1
C	145.6	124.1	
D	62.4	82.0	38.6

Planes: A, Ru(2)–Ru(3)–Ru(4)–Ru(5); B, Ru(1)–Ru(2)–Ru(3); C, Ru(4)–Ru(5)–Ru(6); D, O(18)–O(19)–C(18).

Table 3 Selected bond lengths (Å) and angles (°) for compound **3**

Ru(1)–Ru(2)	2.6840(7)	Ru(1)–H(2)	1.84
Ru(1)–Ru(3)	2.8146(7)	Ru(2)–H(3)	1.75
Ru(2)–Ru(3)	2.821(1)	Ru(3)–H(3)	1.96
Ru(1)–N	2.036(5)	Ru(3)–H(2)	1.80
Ru(2)–N	2.056(5)	N–H(1)	0.93(7)
Ru(3)–N	2.053(5)	Mean C–O	1.133
Ru(2)–Ru(1)–Ru(3)	61.68(2)	Ru(1)–N–Ru(2)	82.0(2)
Ru(1)–Ru(3)–Ru(2)	56.88(2)	Ru(1)–N–Ru(3)	87.0(2)
Ru(1)–Ru(2)–Ru(3)	61.44(2)	Ru(2)–N–Ru(3)	86.7(2)

2.723(2) to 2.878(1) Å. The four ruthenium atoms are capped slightly asymmetrically above the basal plane by a quadruply bridging nitrene ligand (μ_4-NH) such that the N atom is displaced towards Ru(5) [Ru(5)–N(1) 2.123(9) *vs.* Ru(3)–N(1) 2.199(9) Å] and lies 0.876 Å above the least-squares plane. The edges Ru(2)–Ru(3) [2.878(1) Å] and Ru(4)–Ru(5) [2.761(1) Å] are each bridged by a $Ru(CO)_4$ fragment such that they both flap above the basal plane to form a distorted 'boat' form metal core similar to that of $[Ru_6(CO)_{14}(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_3\text{-}\eta^2\text{-}EtNCSNHEt)(\mu_3\text{-}\eta^2\text{-}EtNCNHEt)]$[10] and $[Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu\text{-}OH)_2(\mu_4\text{-}S)]$.[11] The two planes Ru(1)–Ru(2)–Ru(3) and Ru(4)–Ru(5)–Ru(6) form dihedral angles of 158.3 and 145.6° with the basal plane Ru(2)–Ru(3)–Ru(4)–Ru(5) respectively. Besides, there is a bridging carbonyl across the edge Ru(2)–Ru(5). The hydride ligand revealed by the ^{1}H NMR spectrum cannot be located directly from X-ray diffraction analysis. However, potential-energy calculations suggested it bridges the edge Ru(4)–Ru(5). Below the tetraruthenium plane, there is a μ_3-η^2-C(O)OMe ligand with its acyl group [C(18)–O(19)] acting as a five-electron donor to the cluster.

A similar co-ordination mode of an acyl group has been observed in $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}COPh)]$[12] and $[NEt_4][Fe_3(CO)_9(\mu_3\text{-}MeCO)]$.[13] The C–O bond length of the μ_3-η^2-bonded acyl fragment in compound **1** [1.35(1) Å] is similar to that observed in $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}COPh)]$ [1.368(5) Å] and $[NEt_4][Fe_3(CO)_9(\mu_3\text{-}MeCO)]$ [1.32(2) Å]. The co-ordination sphere is completed by terminal carbonyls to give a cluster valence electron (c.v.e.) count of 92 which is consistent with hexaruthenium clusters with eight metal–metal bonds. Complex **1** is a rare example of a cluster containing a μ_3-η^2-methoxycarbonyl group. The formation of this ligand seems to involve the methoxy moiety cleaved from an intermediate and carbonyl ligands bound on the cluster surface although the detailed mechanism remains uncertain.

Hydrogenation of $[Ru_3(CO)_{10}(NOMe)]$ 2

Compound **2** was hydrogenated in refluxing hexane until complete consumption was observed by IR monitoring. Two products identified as $[Ru_3(\mu\text{-}H)_2(CO)_9(NH)]$ **3** and $[Ru_3(\mu\text{-}H)_2(CO)_9(NOMe)]$ **4** were isolated in 5 and 50% yields respectively. Both **3** and **4** have been reported elsewhere. According to Gladfelter and co-workers,[14] hydrogenation of **2** gives **4** as the major product. Further hydrogenation gives **3** with the elimination of methanol (Scheme 1). However, the crystal structures of **3** and **4** have not been reported. Their molecular structures are depicted in Figs. 2 and 3 respectively and selected bond parameters are in Tables 3 and 4.

Compound **3** comprises a triruthenium metal core symmetrically capped by a μ_3-nitrene with an average Ru–N

Table 4 Selected bond lengths (Å) and angles (°) for compound **4**

Ru(1)–Ru(2)	2.819(2)	Ru(1)–H(1)	1.80
Ru(1)–Ru(3)	2.698(2)	Ru(2)–H(1)	1.82
Ru(2)–Ru(3)	2.828(2)	Ru(3)–H(2)	1.82
Ru(1)–N	2.01(1)	Ru(2)–H(2)	1.81
Ru(2)–N	2.07(1)	N–O(10)	1.43(1)
Ru(3)–N	2.04(1)	C(10)–O(10)	1.42(2)
Mean C–O	1.113		
Ru(2)–Ru(1)–Ru(3)	61.62(4)	Ru(1)–N–Ru(3)	83.4(5)
Ru(1)–Ru(3)–Ru(2)	61.31(4)	Ru(2)–N–Ru(3)	86.9(5)
Ru(1)–Ru(2)–Ru(3)	57.07(4)	N–O(10)–C(10)	115(1)
Ru(1)–N–Ru(2)	87.3(5)		

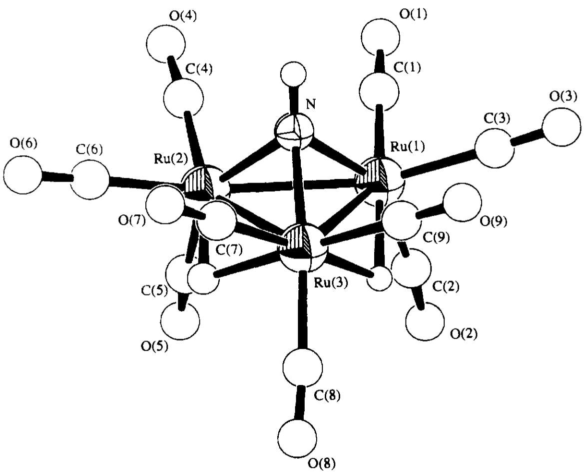


Fig. 2 Molecular structure of $[Ru_3(\mu\text{-}H)_2(CO)_9(NH)]$ **3**, showing the atomic labelling scheme

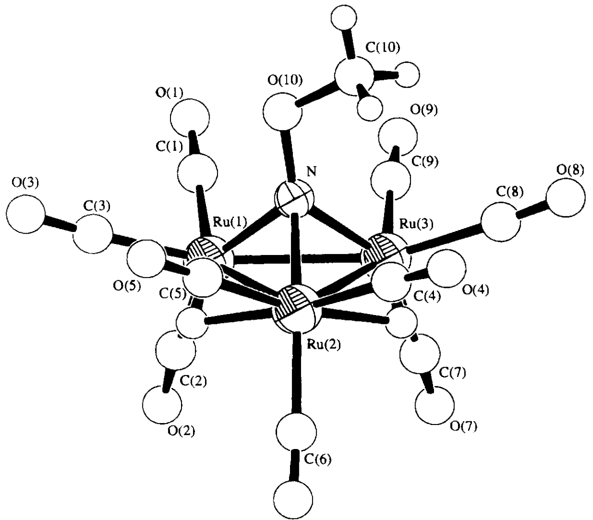


Fig. 3 Molecular structure of $[Ru_3(\mu\text{-}H)_2(CO)_9(NOMe)]$ **4**, showing the atomic labelling scheme

$$[Ru_3(CO)_{10}(NOMe)] \xrightarrow{H_2} [Ru_3(\mu\text{-}H)_2(CO)_9(NOMe)] \xrightarrow[-MeOH]{H_2} [Ru_3(\mu\text{-}H)_2(CO)_9(NH)]$$

Scheme 1

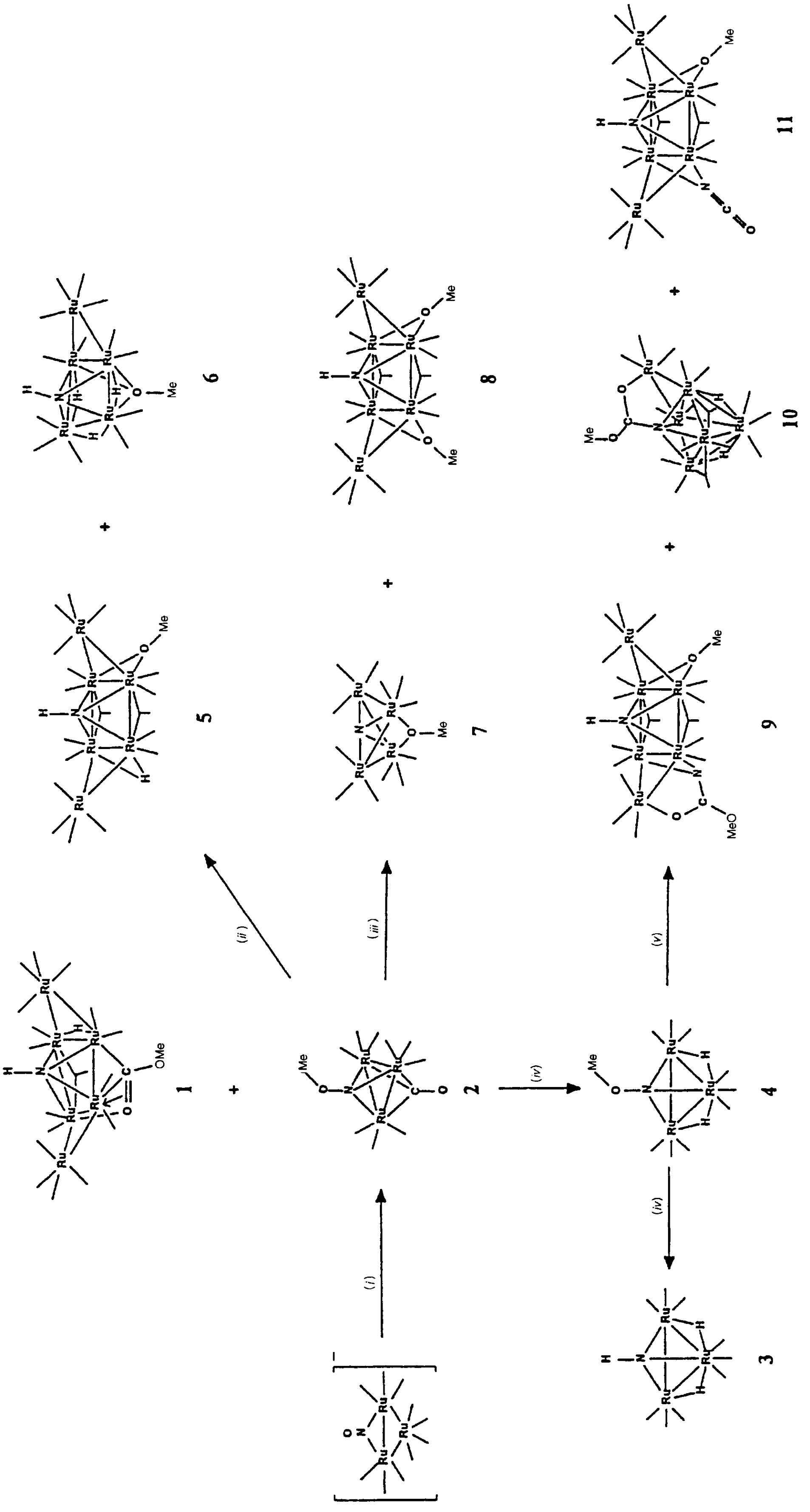
distance of 2.048(11) Å. Each metal centre is bonded by three terminal carbonyls. The edges Ru(1)–Ru(3) [2.8146(7) Å] and Ru(2)–Ru(3) [2.821(1) Å] are significantly longer than the Ru(1)–Ru(2) bond [2.684(1) Å] since the former two bonds are bridged by two equivalent hydride ligands as revealed from the ^1H NMR spectrum. The spectrum is consistent with the solid-state structure, exhibiting a triplet at δ 6.33 (J_{NH} 48.6 Hz) for the amido proton and a singlet at δ −17.55 for the bridging hydrides.

The structure of compound **4** consists of a ruthenium triangle symmetrically capped by a μ_3-methoxyimide ligand and the Ru–N distances range from 2.01(1) to 2.07(1) Å. The N–O distance in the NOMe ligand is 1.43(1) Å which is similar to that observed in **2** (1.433 Å).[8b,c] The nine carbonyls are all terminal, with three bonded to each metal atom. One of the Ru–Ru bonds [2.698(2) Å] is significantly shorter than the others [average 2.824(6) Å]. From ^1H NMR spectroscopy, a methoxy signal is observed at δ 3.46, and a singlet at δ −17.22 with an integral of two-thirds that of the methoxy group, indicating that two bridging hydrides are present which occupy positions across the two long Ru–Ru bonds. The whole structure as well as the bond parameters are similar to those observed in $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NPh)]$.[15] The structure is similar to that of **3** and they only differ by the substituents attached to the nitrogen atom. Instead of a μ_3-NOMe group in **4**, compound **3** is triply bridged by a μ_3-nitrene with a N–H distance of 0.93(7) Å. The IR spectrum of **3** shows a similar CO stretching frequency to that of **4** which indicates that both adopt the same symmetry C_s.

Hydrogenation of compound 2 in the presence of $[Ru_3(CO)_{12}]$

Hydrogenation of compound **2** in hexane gives **3** and **4** in 5 and 50% yields respectively. However, two new compounds $[Ru_6(\mu\text{-}H)(CO)_{16}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)]$ **5** and $[Ru_5(\mu\text{-}H)_3(CO)_{13}(\mu_4\text{-}NH)(\mu_3\text{-}OMe)]$ **6** are also obtained if this hydrogenation is carried out in the presence of $[Ru_3(CO)_{12}]$ (Scheme 2). The spectroscopic data for **5** and **6** are summarized in Table 1. The ^1H NMR spectra are consistent with their molecular structures. For compound **6** a singlet at δ 3.10 with a relative intensity of three is assigned to the methoxy group. A broad peak centred at δ 5.00 is due to the resonance of the μ_4-NH proton. There are three types of hydride signals in the negative region, two are doublets at δ −6.26 (J_{HH} 6.8) and −9.04 (J_{HH} 2.7 Hz) and a double doublet centred at δ −11.42 (J_{HH} 6.5, 2.4 Hz). The mass and IR spectra show that **6** contains five ruthenium atoms and only terminal carbonyls. In contrast, **5** is a hexaruthenium cluster containing both terminal and bridging carbonyls as shown by its mass and IR spectra. The ^1H NMR spectrum shows a triplet proton signal for NH centred at δ 5.92 (J_{NH} 48.6 Hz), a methoxy singlet at δ 2.95 and a hydride signal at δ −18.03.

The molecular structures of compounds **5** and **6** have been established by single-crystal X-ray analyses which are depicted in Figs. 4 and 5. Selected bond lengths and angles are listed in Tables 5 and 6. Both **5** and **6** also consist of a '$Ru_4(CO)_8(\mu_4\text{-}NH)$' unit similar to that of **1**. In **5** two additional $Ru(CO)_4$ units are found to bridge the opposite edges of the square-pyramidal '$Ru_4(CO)_8(\mu_4\text{-}NH)$' moiety. The basal plane Ru(2)–Ru(3)–Ru(4)–Ru(5) adopts an approximately trapezoidal geometry with a maximum deviation of 0.009 Å from the least-squares plane. The bond lengths of the opposite edges Ru(3)–Ru(4) and Ru(2)–Ru(5) are almost the same [average 2.801(7) Å] and both are bridged by carbonyl ligands. The edge Ru(4)–Ru(5) with a bridging methoxy group is significantly longer than the opposite edge Ru(2)–Ru(3) [2.894(1) *vs.* 2.774(1) Å]. The edge Ru(2)–Ru(3) is bridged by a hydride as revealed by the ^1H NMR signal at δ −18.03. The nitrene N atom lies 0.895 Å above the basal plane and towards the edge Ru(2)–Ru(3). The edges Ru(2)–Ru(3) and Ru(4)–Ru(5) are bridged by Ru(1) and Ru(6) atoms respectively which flap above the square base to give dihedral angles of 146.7 and 154.9° respectively. The co-ordination sphere is completed with terminal carbonyls to give a c.v.e. count of 92 similar to that in **1**.



Scheme 2 (*i*) CF_3SO_3Me, CH_2Cl_2; (*ii*) $[Ru_3(CO)_{12}]$, H_2; (*iii*) toluene, 90 °C; (*iv*) H_2; (*v*) pyrolysis, 140 °C

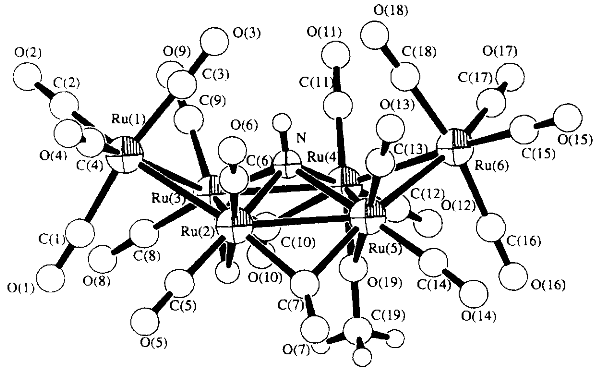


Fig. 4 Molecular structure of $[Ru_6(\mu\text{-H})(CO)_{16}(\mu\text{-CO})_2(\mu_4\text{-NH})(\mu\text{-OMe})]$ **5**, showing the atomic labelling scheme

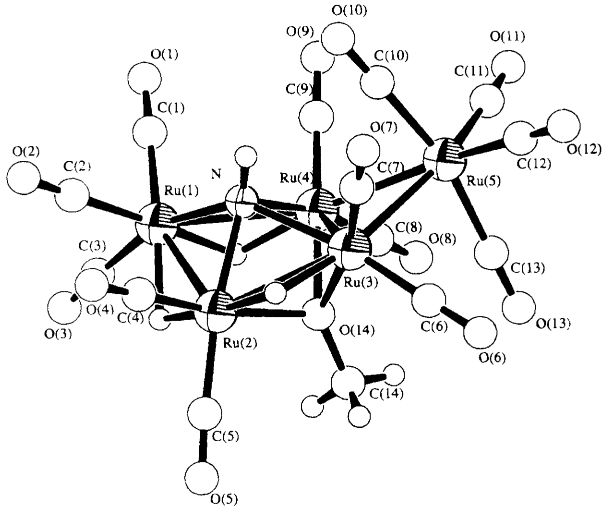


Fig. 5 Molecular structure of $[Ru_5(\mu\text{-H})_3(CO)_{13}(\mu_4\text{-NH})(\mu_3\text{-OMe})]$ **6**, showing the atomic labelling scheme

Table 5 Selected bond lengths (Å) and angles (°) for compound **5**

Ru(1)–Ru(2)	2.807(2)	Ru(3)–H(2)	1.93
Ru(2)–Ru(3)	2.774(1)	Ru(2)–N	2.158(9)
Ru(4)–Ru(6)	2.772(2)	Ru(3)–N	2.152(9)
Ru(5)–Ru(6)	2.779(2)	Ru(4)–N	2.203(9)
Ru(1)–Ru(3)	2.809(2)	Ru(5)–N	2.223(9)
Ru(2)–Ru(5)	2.806(2)	Ru(4)–O(19)	2.059(8)
Ru(3)–Ru(4)	2.796(2)	Ru(5)–O(19)	2.070(8)
Ru(4)–Ru(5)	2.894(1)	C(19)–O(19)	1.38(2)
Ru(2)–H(2)	1.99	N–H(1)	0.91
Ru(2)–Ru(1)–Ru(3)	59.21(4)	Ru(4)–Ru(5)–Ru(6)	58.46(4)
Ru(1)–Ru(2)–Ru(5)	137.51(5)	Ru(2)–Ru(5)–Ru(4)	88.24(4)
Ru(3)–Ru(2)–Ru(5)	91.58(4)	Ru(4)–Ru(6)–Ru(5)	62.84(4)
Ru(1)–Ru(3)–Ru(4)	137.48(5)	Ru(2)–N–Ru(4)	131.0(4)
Ru(1)–Ru(2)–Ru(3)	60.43(4)	Ru(3)–N–Ru(5)	132.2(4)
Ru(1)–Ru(3)–Ru(2)	60.36(4)	Ru(4)–N–Ru(5)	81.6(3)
Ru(2)–Ru(3)–Ru(4)	90.86(4)	Ru(3)–N–Ru(4)	79.9(3)
Ru(3)–Ru(4)–Ru(6)	139.92(5)	Ru(2)–N–Ru(5)	79.6(3)
Ru(5)–Ru(4)–Ru(6)	58.70(4)	Ru(2)–N–Ru(3)	80.1(3)
Ru(3)–Ru(4)–Ru(5)	89.31(4)	Ru(4)–O(19)–Ru(5)	89.0(3)
Ru(2)–Ru(5)–Ru(6)	139.26(5)		

Dihedral angles between planes

Plane	A	B
B	146.7	
C	154.9	121.6

Planes: A, Ru(2)–Ru(3)–Ru(4)–Ru(5); B, Ru(1)–Ru(2)–Ru(3); C, Ru(4)–Ru(5)–Ru(6).

Table 6 Selected bond lengths (Å) and angles (°) for compound **6**

Ru(1)–Ru(2)	2.805(1)	Ru(4)–O(14)	2.180(6)
Ru(2)–Ru(3)	2.683(1)	Ru(2)–O(14)	2.157(6)
Ru(3)–Ru(5)	2.727(1)	Ru(3)–O(14)	2.133(6)
Ru(1)–Ru(4)	2.845(2)	Ru(1)–H(5)	1.79
Ru(3)–Ru(4)	2.938(1)	Ru(2)–H(5)	1.84
Ru(4)–Ru(5)	2.804(1)	Ru(3)–H(6)	1.77
Ru(1)–N	2.154(7)	Ru(1)–H(7)	1.83
Ru(2)–N	2.117(7)	Ru(2)–H(6)	1.78
Ru(3)–N	2.365(7)	Ru(4)–H(7)	1.88
Ru(4)–N	2.148(7)	N–H(1)	0.92
Ru(3)–Ru(5)–Ru(4)	64.16(3)	Ru(2)–O(14)–Ru(4)	104.3(2)
Ru(2)–Ru(1)–Ru(4)	74.65(3)	Ru(3)–O(14)–Ru(4)	85.9(2)
Ru(2)–Ru(3)–Ru(4)	74.96(3)	Ru(2)–O(14)–Ru(3)	77.4(2)
Ru(4)–Ru(3)–Ru(5)	59.20(3)	Ru(1)–N–Ru(3)	145.0(3)
Ru(1)–Ru(2)–Ru(3)	103.52(4)	Ru(1)–N–Ru(2)	82.1(2)
Ru(2)–Ru(3)–Ru(5)	134.07(4)	Ru(1)–N–Ru(4)	82.8(3)
Ru(1)–Ru(4)–Ru(5)	143.25(4)	Ru(2)–N–Ru(3)	73.3(2)
Ru(1)–Ru(4)–Ru(3)	96.38(3)	Ru(3)–N–Ru(4)	81.1(2)
Ru(3)–Ru(4)–Ru(5)	56.64(3)	Ru(2)–N–Ru(4)	106.9(3)

Dihedral angles between planes

Plane	A	B
B	177.1	
C	149.2	147.2

Planes: A, Ru(2)–Ru(3)–Ru(4); B, Ru(3)–Ru(4)–Ru(5); C, Ru(1)–Ru(2)–Ru(4).

In compound **6** a $Ru(CO)_4$ fragment bridges at one edge of the tetraruthenium '$Ru_4(CO)_8(\mu_4\text{-NH})$' base whilst the remaining three Ru–Ru edges are occupied by bridging hydrides. This metal framework is similar to that in $[Ru_5(CO)_{14}(\mu_4\text{-S})_2]$.[16] The Ru–Ru distances range from 2.683(1) to 2.938(1) Å. The square base Ru(1)–Ru(2)–Ru(3)–Ru(4) is significantly distorted (maximum deviation 0.34 Å) by the triply bridging methoxy group bonded to Ru(2), Ru(3) and Ru(4). The Ru(1) atom lies 1.928 Å above the plane described by Ru(2)–Ru(3)–Ru(4) such that the dihedral angle between the planes Ru(1)–Ru(2)–Ru(4) and Ru(2)–Ru(3)–Ru(4) is 149.2°. The nitrene N atom caps the tetraruthenium base asymmetrically [Ru(1)–N 2.154(7), Ru(2)–N 2.117(7), Ru(3)–N 2.365(7) and Ru(4)–N 2.148(7) Å]. The N atom is displaced towards Ru(2) and away from Ru(3). However, atoms Ru(2)–Ru(5) are nearly coplanar as evidenced by the dihedral angle of 177.1° between the planes Ru(2)–Ru(3)–Ru(4) and Ru(3)–Ru(4)–Ru(5). If the μ_4-nitrene and the triply bridging methoxy group are assumed to be four- and five-electron donors to the cluster respectively, a c.v.e. count of 78 results which is consistent with a pentaruthenium cluster with six metal–metal bonds.

Since only compounds **3** and **4** are obtained by hydrogenation of **2**, the occurrence of **5** and **6** should involve the participation of $[Ru_3(CO)_{12}]$. In order to clarify this, the reaction was repeated under the same conditions except that either **3** or **4** was used instead of **2**. However, neither **3** nor **4** can give **5** or **6** under the same reaction conditions. Hydrogenation of **4** with $[Ru_3(CO)_{12}]$ in stoichiometric quantity affords $[Ru_3(CO)_{12}]$ and **3** as the only isolated products. However, hydrogenation in the presence of both $[Ru_3(CO)_{12}]$ and **3** results in no chemical reaction other than decomposition of the reactants. We are interested in the metal skeleton of **6** as its formation seems to be different from that of **1** and **5**. Therefore, $[Fe_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ were used instead of $[Ru_3(CO)_{12}]$ to see whether any heterometallic nitrene clusters possessing structures similar to that of **5** and **6** are formed. Unfortunately, no such clusters were isolated under the same conditions.

Thermolysis of compound 2

Heating compound **2** in toluene at 90 °C for 3 h gives $[Ru_4(CO)_{12}(\mu_4\text{-N})(\mu\text{-OMe})]$ **7** and $[Ru_6(CO)_{16}(\mu\text{-CO})_2(\mu_4\text{-}$

NH)(μ-OMe)$_2$] **8** as the only isolated products, see Scheme 2. The mass and IR spectra of **7** show that it is a tetraruthenium compound with terminal carbonyls only. In the ^{1}H NMR spectrum only a singlet at δ 2.08 for the methoxy ligand is observed. On the contrary, compound **8** is a hexaruthenium compound with both terminal and bridging carbonyls as revealed by the mass and IR spectra. The ^{1}H NMR spectrum shows two signals at δ 5.75 (triplet, coupling constant 44.5 Hz) and 2.90 attributed to the NH and methoxy resonances respectively. The relative intensity of these two signals is 1 : 6 indicating the existence of two equivalent resonances for the methoxy groups. Single crystals of **7** and **8** suitable for X-ray diffraction analyses were obtained by slow evaporation of their hexane–dichloromethane solutions at −20 °C and the molecular structures are depicted in Figs. 6 and 7. Selected bond parameters are presented in Tables 7 and 8.

Compound **7** adopts a butterfly arrangement of four Ru atoms with a nitride ligand bonded to each metal atom. This metal-core geometry is similar to that observed in [N(PPh$_3$)$_2$][Fe$_4$(CO)$_{12}$N] (62 c.v.e.s).[17] However, in contrast, **7** is a 64-electron system since there is no direct metal–metal bond between the hinge of the butterfly structure [Ru(2) ··· Ru(3) 3.22 Å]. Atoms Ru(2) and Ru(3) are bridged by a methoxy group [average Ru–O 2.094(1) Å]. The metal core can be viewed as a diagonal-folded square-planar array of 'Ru$_4$(μ$_4$-N)' such that the hinge metal atoms [Ru(2) and Ru(3)] are bridged by the methoxy moiety. The metal–metal bonds span a narrow range, average Ru–Ru 2.822(4) Å which is longer than that in [Ru$_4$(μ-H)$_3$(CO)$_{11}$(μ$_4$-N)] [2.792(6) Å].[18] The bond distances Ru(2)–N and Ru(3)–N are the same [average 2.133(2) Å], significantly longer than Ru(1)–N and Ru(4)–N. The angle Ru(1)–N–Ru(4) is almost linear [175.5(3)°], similar to that in [N(PPh$_3$)$_2$]-[Fe$_4$(CO)$_{12}$N]. The dihedral angle between the planes Ru(1)–Ru(2)–Ru(3) and Ru(2)–Ru(3)–Ru(4) is 110.3°.

Compound **8** is a hexaruthenium cluster with a metal skeleton resembling that of **5**. The tetraruthenium base, Ru(2)–Ru(3)–Ru(4)–Ru(5), adopts a square-planar geometry (maximum deviation from least-squares plane 0.024 Å). The bond distances of the opposite edges of the base are very similar. The Ru–N distances span a narrow range from 2.19(1) to 2.22(1) Å so that the nitrene N atom caps almost symmetrically above the basal square plane (out-of-plane distance 0.818 Å) while the edges Ru(2)–Ru(3) and Ru(4)–Ru(5) are bridged by two Ru(CO)$_4$ fragments which flap above the square plane towards the side of the nitrene such that the dihedral angles between the square plane and Ru(4)–Ru(5)–Ru(6) as well as Ru(1)–Ru(2)–Ru(3) are 150.2 and 149.7° respectively. The edges Ru(2)–Ru(5) and Ru(3)–Ru(4) are

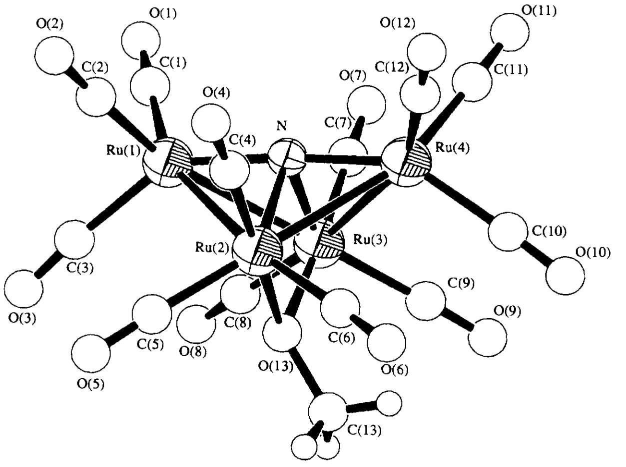


Fig. 6 Molecular structure of [Ru$_4$(CO)$_{12}$(μ$_4$-N)(μ-OMe)] **7**, showing the atomic labelling scheme

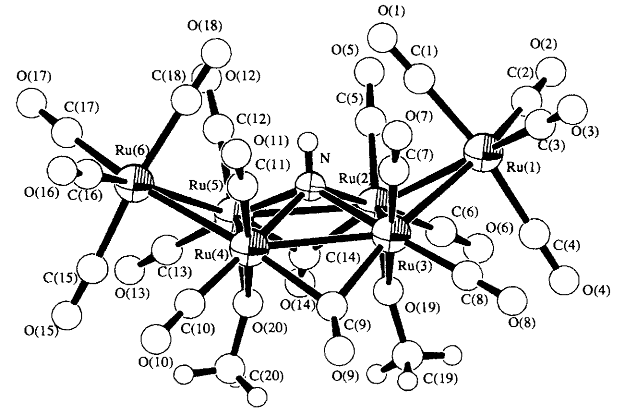


Fig. 7 Molecular structure of [Ru$_6$(CO)$_{16}$(μ-CO)$_2$(μ$_4$-NH)(μ-OMe)$_2$] **8**, showing the atomic labelling scheme

Table 7 Selected bond lengths (Å) and angles (°) for compound **7**

Ru(1)–Ru(2)	2.8172(7)	Ru(3)–N	2.134(5)
Ru(2)–Ru(4)	2.8258(7)	Ru(4)–N	1.903(5)
Ru(3)–Ru(4)	2.8249(7)	Ru(2)–O(13)	2.095(4)
Ru(1)–Ru(3)	2.8214(7)	Ru(3)–O(13)	2.093(4)
Ru(1)–N	1.906(5)	C(13)–O(13)	1.430(7)
Ru(2)–N	2.131(4)	mean C–O	1.132
Ru(2)–Ru(1)–Ru(3)	69.64(2)	Ru(2)–N–Ru(3)	98.0(2)
Ru(1)–Ru(3)–Ru(4)	84.74(2)	Ru(3)–N–Ru(4)	88.6(2)
Ru(1)–Ru(2)–Ru(4)	84.81(2)	Ru(1)–N–Ru(2)	88.3(2)
Ru(2)–Ru(4)–Ru(3)	69.47(2)	Ru(1)–N–Ru(4)	175.5(3)
Ru(2)–O(13)–Ru(3)	100.5(2)	Ru(2)–N–Ru(4)	88.8(2)
Ru(1)–N–Ru(3)	88.4(2)		

Dihedral angles between planes

Plane	A	B	C
B	176.6		82.0
C	81.9	82.0	
D	82.0	81.9	176.6

Planes: A, Ru(1)–Ru(2)–N; B, Ru(2)–Ru(4)–N; C, Ru(1)–Ru(3)–N; D, Ru(3)–Ru(4)–N.

Table 8 Selected bond lengths (Å) and angles (°) for compound **8**

Ru(1)–Ru(2)	2.814(2)	Ru(4)–N	2.22(1)
Ru(2)–Ru(3)	2.962(2)	Ru(5)–N	2.20(1)
Ru(4)–Ru(6)	2.802(2)	Ru(2)–O(19)	2.09(1)
Ru(5)–Ru(6)	2.803(2)	Ru(3)–O(19)	2.10(1)
Ru(1)–Ru(3)	2.813(2)	Ru(4)–O(20)	2.10(1)
Ru(2)–Ru(5)	2.825(2)	Ru(5)–O(20)	2.11(1)
Ru(3)–Ru(4)	2.832(2)	O(20)–C(20)	1.40(2)
Ru(4)–Ru(5)	2.947(2)	O(19)–C(19)	1.40(2)
Ru(2)–N	2.20(1)	N–H(7)	0.91
Ru(3)–N	2.19(1)		
Ru(2)–Ru(1)–Ru(3)	63.53(6)	Ru(4)–Ru(5)–Ru(6)	58.27(5)
Ru(1)–Ru(2)–Ru(5)	136.65(7)	Ru(2)–Ru(5)–Ru(4)	90.14(6)
Ru(3)–Ru(2)–Ru(5)	89.97(6)	Ru(4)–Ru(6)–Ru(5)	63.44(6)
Ru(1)–Ru(3)–Ru(4)	137.61(7)	Ru(2)–N–Ru(3)	84.7(4)
Ru(1)–Ru(2)–Ru(3)	58.22(5)	Ru(2)–N–Ru(5)	79.9(4)
Ru(1)–Ru(3)–Ru(2)	58.25(6)	Ru(3)–N–Ru(4)	79.9(4)
Ru(2)–Ru(3)–Ru(4)	89.69(6)	Ru(2)–N–Ru(4)	135.3(6)
Ru(3)–Ru(4)–Ru(6)	137.10(7)	Ru(3)–N–Ru(5)	137.6(6)
Ru(5)–Ru(4)–Ru(6)	58.29(6)	Ru(4)–N–Ru(5)	83.8(5)
Ru(3)–Ru(4)–Ru(5)	90.14(6)	Ru(2)–O(19)–Ru(3)	90.0(4)
Ru(2)–Ru(5)–Ru(6)	138.25(7)	Ru(4)–O(20)–Ru(5)	88.8(4)

Dihedral angles between planes

Plane	A	B
B	149.7	
C	150.2	119.9

Planes: A, Ru(2)–Ru(3)–Ru(4)–Ru(5); B, Ru(1)–Ru(2)–Ru(3); C, Ru(4)–Ru(5)–Ru(6).

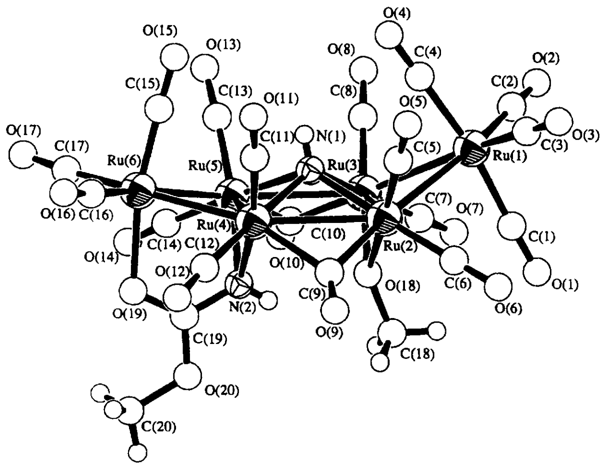


Fig. 8 Molecular structure of $[Ru_6(CO)_{15}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)\{\mu_3\text{-}\eta^2\text{-}N(H)C(O)OMe\}]$ **9**, showing the atomic labelling scheme

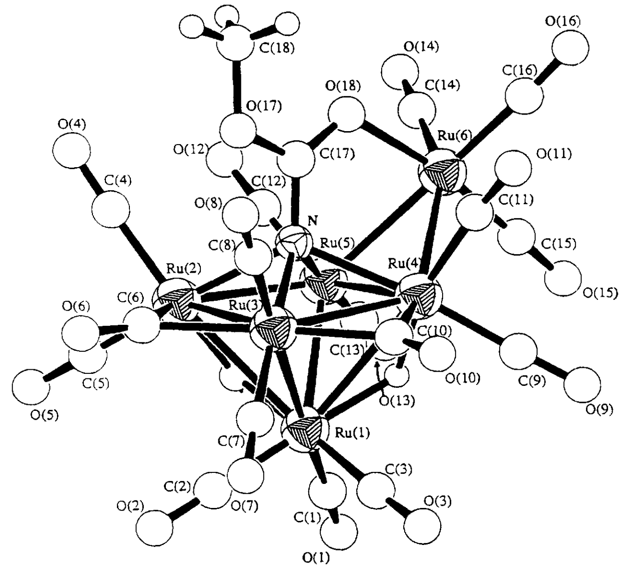


Fig. 9 Molecular structure of $[Ru_6(\mu\text{-}H)_2(CO)_{14}(\mu\text{-}CO)_2\{\mu_5\text{-}\eta^2\text{-}NC(O)OMe\}]$ **10**, showing the atomic labelling scheme

bridged by carbonyls while both Ru(2)–Ru(3) and Ru(4)–Ru(5) edges are bridged by methoxy groups with an average Ru–O distance of 2.10(8) Å and bond angle (Ru–O–Ru) of 89.4(8)°. Although the molecular structure of **8** differs from that of **5** only by replacement of the bridging hydride with a bridging methoxy group over the edge Ru(2)–Ru(3), electron counting indicates that **8** has 94 valence electrons rather than the expected 92, as the bridging methoxy group acts as a three-electron donor while the bridging hydride donates only one electron.

Pyrolysis of $[Ru_3(\mu\text{-}H)_2(CO)_9(NOMe)]$ 4

Solid state pyrolysis of compound **4**[19] at 140 °C for 2 h yields a complex mixture from which three new hexanuclear clusters, $[Ru_6(CO)_{15}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)\{\mu_3\text{-}\eta^2\text{-}N(H)C(O)OMe\}]$ **9**, $[Ru_6(\mu\text{-}H)_2(CO)_{14}(\mu\text{-}CO)_2\{\mu_5\text{-}\eta^2\text{-}NC(O)OMe\}]$ **10** and $[Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)(\mu\text{-}NCO)]$ **11**, can be isolated, along with the known clusters $[Ru_4H_2(CO)_{13}]$ and $[Ru_3(\mu\text{-}H)(CO)_{10}(NH_2)]$,[14,20] see Scheme 2. Compounds **9**–**11** contain six ruthenium atoms as evidenced by both the molecular ion peaks and isotopic distributions from their mass spectra. Their IR spectra show CO stretching frequencies corresponding to both terminal and bridging carbonyls. In order to establish their molecular structures the compounds have been characterized by X-ray crystallographic analyses and their molecular structures are depicted in Figs. 8, 9 and 10 respectively. Selected bond parameters are in Tables 9–11.

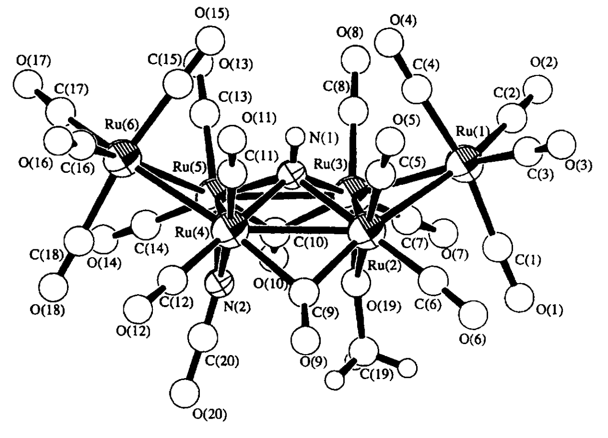


Fig. 10 Molecular structure of $[Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)(\mu\text{-}NCO)]$ **11**, showing the atomic labelling scheme

Table 9 Selected bond lengths (Å) and angles (°) for compound **9**

Ru(1)–Ru(2)	2.8330(9)	Ru(6)–O(19)	2.193(5)
Ru(2)–Ru(3)	2.969(1)	Ru(2)–N(1)	2.172(6)
Ru(4)–Ru(6)	2.719(1)	Ru(3)–N(1)	2.175(6)
Ru(5)–Ru(6)	2.7327(9)	Ru(4)–N(1)	2.192(6)
Ru(1)–Ru(3)	2.839(1)	Ru(5)–N(1)	2.201(6)
Ru(2)–Ru(4)	2.811(1)	O(19)–C(19)	1.248(9)
Ru(3)–Ru(5)	2.826(1)	O(20)–C(20)	1.45(1)
Ru(4)–Ru(5)	2.878(1)	C(18)–O(18)	1.418(10)
Ru(2)–O(18)	2.092(5)	C(19)–O(20)	1.328(9)
Ru(3)–O(18)	2.101(5)	N(2)–C(19)	1.35(1)
Ru(4)–N(2)	2.187(7)	N(1)–H(1)	0.78
Ru(5)–N(2)	2.179(7)	N(2)–H(8)	0.73(8)
Ru(2)–Ru(1)–Ru(3)	63.13(2)	Ru(2)–N(1)–Ru(4)	80.2(2)
Ru(1)–Ru(2)–Ru(4)	137.30(3)	Ru(3)–N(1)–Ru(4)	136.4(3)
Ru(3)–Ru(2)–Ru(4)	89.06(3)	Ru(4)–N(1)–Ru(5)	81.9(2)
Ru(1)–Ru(3)–Ru(5)	137.04(3)	Ru(2)–N(1)–Ru(3)	86.2(2)
Ru(1)–Ru(2)–Ru(3)	58.53(2)	Ru(2)–N(1)–Ru(5)	136.8(3)
Ru(1)–Ru(3)–Ru(2)	58.34(2)	Ru(3)–N(1)–Ru(5)	80.4(2)
Ru(2)–Ru(3)–Ru(5)	89.09(3)	Ru(4)–N(2)–Ru(5)	82.5(2)
Ru(2)–Ru(4)–Ru(6)	147.63(3)	Ru(4)–N(2)–C(19)	113.7(5)
Ru(5)–Ru(4)–Ru(6)	58.37(3)	Ru(5)–N(2)–C(19)	113.6(5)
Ru(2)–Ru(4)–Ru(5)	91.23(3)	Ru(6)–O(19)–C(19)	114.5(5)
Ru(3)–Ru(5)–Ru(6)	146.68(3)	O(19)–C(19)–N(2)	123.5(8)
Ru(4)–Ru(5)–Ru(6)	57.90(3)	O(19)–C(19)–O(20)	120.8(7)
Ru(3)–Ru(5)–Ru(4)	90.62(3)	O(20)–C(19)–N(2)	115.7(7)
Ru(4)–Ru(6)–Ru(5)	63.73(2)	C(19)–O(20)–C(20)	117.1(7)
Ru(2)–O(18)–Ru(3)	90.2(2)	C(19)–N(2)–H(8)	121(7)

Dihedral angles between planes

Plane	A	B	C
B	150.6		138.9
C	168.3	138.9	
D	91.7	87.8	91.4

Planes: A, Ru(2)–Ru(3)–Ru(4)–Ru(5); B, Ru(1)–Ru(2)–Ru(3); C, Ru(4)–Ru(5)–Ru(6); D, O(19)–O(20)–N(2)–C(19).

The metal frameworks of compounds **9** and **11** are similar to those of **1**, **5** and **8**, comprising a square-planar '$Ru_4(CO)_8(\mu_4\text{-}NH)$' moiety with two additional ruthenium fragments bridging the opposite edges of the square base to form a 'boat' form metal core. The square tetraruthenium basal plane Ru(2)–Ru(3)–Ru(4)–Ru(5) is coplanar with a deviation from the least-squares plane less than 0.003 Å for **9** and 0.018 Å for **11**. The nitrene N atom symmetrically caps the square base with average Ru–N distances of 2.185(14) and 2.190(8) Å for **9** and **11** respectively and it lies 0.806 Å for **9** and 0.818 Å for **11** above the basal plane. The edges Ru(2)–Ru(3) and Ru(4)–Ru(5) are bridged by two ruthenium carbonyl fragments such that the

Table 10 Selected bond lengths (Å) and angles (°) for compound **10**

Ru(1)–Ru(2)	2.971(2)	Ru(2)–N	2.20(1)
Ru(1)–Ru(4)	2.997(2)	Ru(4)–N	2.186(10)
Ru(2)–Ru(5)	2.806(2)	Ru(6)–O(18)	2.174(9)
Ru(4)–Ru(6)	2.796(2)	Ru(1)–H(6)	1.88
Ru(1)–Ru(3)	2.862(2)	Ru(2)–H(6)	1.99
Ru(1)–Ru(5)	2.886(2)	Ru(1)–H(7)	1.75
Ru(2)–Ru(3)	2.753(2)	Ru(4)–H(7)	1.78
Ru(3)–Ru(4)	2.791(2)	N–C(17)	1.40(2)
Ru(4)–Ru(5)	2.757(2)	O(18)–C(17)	1.24(1)
Ru(5)–Ru(6)	2.680(2)	C(17)–O(17)	1.32(1)
Ru(3)–N	2.239(10)	C(18)–O(17)	1.47(2)
Ru(5)–N	2.19(1)		

Ru(2)–Ru(1)–Ru(3)	56.28(4)	Ru(1)–Ru(5)–Ru(6)	125.01(5)
Ru(2)–Ru(1)–Ru(5)	57.23(4)	Ru(2)–Ru(5)–Ru(4)	90.66(5)
Ru(3)–Ru(1)–Ru(4)	56.83(4)	Ru(1)–Ru(5)–Ru(4)	64.12(4)
Ru(1)–Ru(2)–Ru(5)	59.87(4)	Ru(2)–Ru(5)–Ru(6)	126.19(5)
Ru(1)–Ru(3)–Ru(2)	63.86(4)	Ru(4)–Ru(5)–Ru(6)	61.88(4)
Ru(2)–Ru(1)–Ru(4)	83.05(4)	Ru(4)–Ru(6)–Ru(5)	60.41(4)
Ru(3)–Ru(1)–Ru(5)	85.17(4)	Ru(2)–N–Ru(3)	76.7(3)
Ru(4)–Ru(1)–Ru(5)	55.84(4)	Ru(2)–N–Ru(5)	79.6(4)
Ru(1)–Ru(2)–Ru(3)	59.86(4)	Ru(2)–N–Ru(4)	129.1(5)
Ru(3)–Ru(2)–Ru(5)	88.81(5)	Ru(3)–N–Ru(5)	122.9(5)
Ru(1)–Ru(3)–Ru(4)	64.03(4)	Ru(3)–N–Ru(4)	78.2(3)
Ru(1)–Ru(4)–Ru(3)	59.14(4)	Ru(4)–N–Ru(5)	78.1(3)
Ru(1)–Ru(4)–Ru(6)	116.92(5)	Ru(4)–Ru(6)–O(18)	81.8(3)
Ru(3)–Ru(4)–Ru(6)	127.09(5)	Ru(5)–Ru(6)–O(18)	83.8(3)
Ru(2)–Ru(3)–Ru(4)	91.08(5)	Ru(6)–O(18)–C(17)	116.5(8)
Ru(1)–Ru(4)–Ru(5)	60.04(4)	N–C(17)–O(18)	123(1)
Ru(3)–Ru(4)–Ru(5)	89.04(5)	N–C(17)–O(17)	114(1)
Ru(5)–Ru(4)–Ru(6)	57.71(4)	O(17)–C(17)–O(18)	121(1)
Ru(1)–Ru(5)–Ru(2)	62.90(4)	C(18)–O(17)–C(17)	116(1)

Dihedral angles between planes

Plane	A	B	C
B	56.8		169.2
C	134.0	169.2	
D	91.7	92.6	87.6

Planes: A, Ru(2)–Ru(3)–Ru(4)–Ru(5); B, Ru(1)–Ru(4)–Ru(5); C, Ru(4)–Ru(5)–Ru(6); D, Ru(6)–O(18)–N–C(17).

Table 11 Selected bond lengths (Å) and angles (°) for compound **11**

Ru(1)–Ru(2)	2.786(3)	Ru(4)–N(1)	2.19(2)
Ru(2)–Ru(3)	2.922(2)	Ru(5)–N(1)	2.20(2)
Ru(4)–Ru(6)	2.800(2)	Ru(2)–O(19)	2.10(1)
Ru(5)–Ru(6)	2.812(2)	Ru(3)–O(19)	2.08(1)
Ru(1)–Ru(3)	2.792(3)	Ru(4)–N(2)	2.09(1)
Ru(2)–Ru(4)	2.813(2)	Ru(5)–N(2)	2.09(1)
Ru(3)–Ru(5)	2.818(3)	N(2)–C(20)	1.19(2)
Ru(4)–Ru(5)	2.941(3)	C(20)–O(20)	1.21(3)
Ru(2)–N(1)	2.19(1)	C(19)–O(19)	1.47(2)
Ru(3)–N(1)	2.18(1)	N(1)–H(1)	0.9(2)

Ru(2)–Ru(1)–Ru(3)	63.18(7)	Ru(3)–Ru(5)–Ru(4)	89.90(6)
Ru(1)–Ru(2)–Ru(4)	139.73(7)	Ru(4)–Ru(6)–Ru(5)	63.20(6)
Ru(3)–Ru(2)–Ru(4)	90.38(7)	Ru(2)–N(1)–Ru(4)	79.8(5)
Ru(1)–Ru(3)–Ru(5)	140.09(7)	Ru(3)–N(1)–Ru(5)	80.1(5)
Ru(1)–Ru(2)–Ru(3)	58.50(6)	Ru(4)–N(1)–Ru(5)	84.2(5)
Ru(1)–Ru(3)–Ru(2)	58.31(6)	Ru(2)–N(1)–Ru(3)	83.7(5)
Ru(2)–Ru(3)–Ru(5)	89.99(7)	Ru(2)–N(1)–Ru(5)	135.3(6)
Ru(2)–Ru(4)–Ru(6)	138.46(7)	Ru(3)–N(1)–Ru(4)	137.0(7)
Ru(5)–Ru(4)–Ru(6)	58.61(6)	Ru(4)–N(2)–Ru(5)	89.4(6)
Ru(2)–Ru(4)–Ru(5)	89.70(6)	Ru(2)–O(19)–Ru(3)	88.6(5)
Ru(3)–Ru(5)–Ru(6)	137.48(8)	O(20)–C(20)–N(2)	173(3)
Ru(4)–Ru(5)–Ru(6)	58.19(5)		

Dihedral angles between planes

Plane	A	B
B	153.7	
C	151.0	124.6

Planes: A, Ru(2)–Ru(3)–Ru(4)–Ru(5); B, Ru(1)–Ru(2)–Ru(3); C, Ru(4)–Ru(5)–Ru(6).

apical Ru atoms, Ru(1) and Ru(6), are displaced above the square plane with the dihedral angles between the planes Ru(2)–Ru(3)–Ru(4)–Ru(5) and Ru(1)–Ru(2)–Ru(3) as well as Ru(4)–Ru(5)–Ru(6) being 150.6 and 168.3° for **9** and 153.7 and 151.0° for **11** respectively. The triangle Ru(4)–Ru(5)–Ru(6) in **9** is bridged by a μ_3-η^2-N(H)C(O)OMe ligand, while in **11** there is only a μ-cyanate ligand with a bond angle of N(2)–C(20)–O(20) 173(3)° bridging the edge Ru(4)–Ru(5). Both **9** and **11** have a bridging methoxy group at the edge Ru(2)–Ru(3) and two bridging carbonyls at Ru(2)–Ru(4) and Ru(3)–Ru(5). Their coordination spheres are completed by terminal carbonyls to give a c.v.e. count of 94. The divergence in dihedral angle between the base and the atoms defining the plane Ru(4)–Ru(5)–Ru(6) may be due to the clamping effect of the μ_3-η^2-N(H)C(O)OMe ligand. The N(H)C(O)OMe moiety in **9** can be regarded as a carbamate derivative, essentially coplanar (maximum deviation 0.023 Å), which is located mutually perpendicular to the metal plane as is evident from the dihedral angle of 91.4° between the planes N(2)–C(19)–O(19)–O(20) and Ru(4)–Ru(5)–Ru(6).

The ^{1}H NMR spectra can be interpreted with reference to the solid-state structures of compounds **9** and **11**. The spectrum of **9** exhibits two singlets at δ 3.75 and 2.83 due to the methoxy resonance in the carbamate and the bridging methoxide ligand while the triplet at δ 5.55 (J_{NH} 46 Hz) and the broad peak at δ −0.82 are assigned to the μ_4-NH and the amido hydrogen respectively. For **11** there is only a triplet at δ 5.70 (J_{NH} 43 Hz) for the nitrene hydrogen and a singlet at δ 2.83 for the bridging methoxy group.

For a 'boat' form metal cluster with eight metal–metal bonds, 92 valence electrons are expected as in **1** and **5**. However, only species containing 94 electrons have been reported[10,11] as in **8**, **9** and **11**. According to Adams *et al.*,[11] the two surplus electrons are supposed to occupy a delocalized antibonding orbital of the tetraruthenium plane which results in a weakening of the corresponding metal–metal bonds within the Ru_4 square base. Focusing on the unprecedented 92-electron 'boat' form clusters **1** and **5**, their hydride-bridged edges Ru(4)–Ru(5) (for **1**) and Ru(2)–Ru(3) (for **5**) within the square bases are remarkably short with bond distances of 2.761(1) and 2.774(1) Å respectively.

The molecular structure of compound **10** comprises a square-pyramidal cluster of five ruthenium atoms, with an additional $Ru(CO)_3$ group bridging one edge of the square base which is similar to that found in $[Ru_6(CO)_{15}(\mu_4\text{-}S)(\mu\text{-}H)(\mu\text{-}1,5\text{-}Me_2C_5H_5)]$.[21] The atoms defining the plane Ru(2)–Ru(3)–Ru(4)–Ru(5) are essentially coplanar with a maximum deviation of 0.063 Å. The Ru–Ru bond lengths in the square base span a narrow range [2.753(2)–2.806(2) Å] while the $Ru(CO)_3$ unit caps symmetrically over the square base with an average Ru–Ru distance of 2.929 Å. The other side of the square base contains a μ_5-η^2-NC(O)OMe ligand of which the nitrogen atom caps symmetrically (average Ru–N 2.204 Å) and lies 1.003 Å above the square base of Ru(2)–Ru(3)–Ru(4)–Ru(5). The oxygen atom of the ligand is bonded in a terminal fashion to the apical $Ru(CO)_3$ unit. The dihedral angle between the square base and the plane Ru(4)–Ru(5)–Ru(6) is 134.0° which is smaller than that observed in **6**, **8**, **9** and **11**. The reduction in dihedral angle similar to that in **9** is believed to be caused by the bridging effect of the μ_5-η^2-NC(O)OMe ligand similar to that in **9** so that the apical bridging $Ru(CO)_3$ fragment tends to be located at the hindered side of the molecule.

The NC(O)OMe moiety in compound **10** can also be regarded as a carbamate derivative similar to that of **9**. The coplanar carbamate ligand (maximum deviation 0.026 Å) is situated perpendicular to the planes Ru(2)–Ru(3)–Ru(4)–Ru(5) and Ru(4)–Ru(5)–Ru(6) and the dihedral angles between them are 91.7 and 87.6° respectively. The bonds Ru(2)–Ru(3) and Ru(3)–Ru(4) are bridged by carbonyl ligands while the edges Ru(1)–Ru(2) and Ru(1)–Ru(4) are bridged by hydrides. The ^{1}H NMR spectrum reveals two types of hydride signals at δ −12.97 and −16.23. The μ_5-η^2-NC(O)OMe moiety donates six electrons to the cluster to give a c.v.e. count of 88.

From a structural point of view, the formation of a 'boat'

Table 12 Crystal data and data collection parameters for clusters **1** and **3**–**11** [a]

	1	**3**	**4**	**5**	**6**
Formula	$C_{19}H_5NO_{19}Ru_6\cdot CH_2Cl_2$	$C_9H_3NO_9Ru_3$	$C_{10}H_5NO_{10}Ru_3$	$C_{19}H_5NO_{19}Ru_6$	$C_{14}H_7NO_{14}Ru_5$
M	1242.60	572.33	602.36	1157.66	918.56
Crystal colour, habit	Blue, plates	Yellow, blocks	Yellow, needles	Blue, needles	Dark blue, blocks
Crystal size/mm	0.10 × 0.34 × 0.36	0.18 × 0.21 × 0.26	0.12 × 0.22 × 0.44	0.11 × 0.11 × 0.25	0.17 × 0.19 × 0.22
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	11.616(4)	9.645(2)	8.772(2)	15.190(3)	11.166(4)
b/Å	10.448(3)	9.756(2)	13.548(3)	9.375(2)	14.703(3)
c/Å	28.030(2)	9.484(2)	14.398(1)	22.026(2)	8.540(3)
α/°		94.81(2)			99.62(2)
β/°	91.38(1)	93.48(2)	91.63(1)	100.21(1)	111.35(3)
γ/°		62.68(2)			70.36(2)
U/Å^3	3401(1)	789.9(3)	1710.3(5)	3087.0(9)	1228.2(7)
Z	4	2	4	4	2
D_c/g cm^{-3}	2.427	2.406	2.339	2.491	2.484
F(000)	2336	536	1136	2168	860
μ(Mo-Kα)/cm^{-1}	28.31	28.72	26.63	29.42	30.69
Scan width/°	0.84 + 0.35 tan θ	1.73 + 0.35 tan θ	1.78 + 0.35 tan θ	1.10 + 0.35 tan θ	1.10 + 0.35 tan θ
Transmission factors	0.644–1.000	0.727–1.000	0.688–1.000	0.896–1.000	0.913–1.000
p Factor [b]	0.004	0.002	0.004	0.024	0.001
Reflections collected	5028	2965	2535	4521	3399
Unique reflections	4751	2782	2357	4331	3200
Observed reflections [$I > 3\sigma(I)$]	3357	2621	1807	2638	2525
R	0.046	0.028	0.046	0.042	0.035
R'	0.048	0.034	0.061	0.049	0.039
Goodness of fit	2.36	5.29	4.66	1.56	2.05
Largest Δ/σ	0.00	0.00	0.01	0.00	0.01
No. parameters	233	202	217	216	172
Residual electron density/e Å^{-3}	1.31, −0.79	0.27, −0.60	0.72, −1.61	0.77, −1.00	0.90, −0.83

Table 12 (*continued*)

	7	**8**	**9**	**10**	**11**
Formula	$C_{13}H_3NO_{13}Ru_4$	$C_{20}H_7NO_{20}Ru_6$	$C_{20}H_8N_2O_{20}Ru_6$	$C_{18}H_5NO_{18}Ru_6\cdot CH_2Cl_2$	$C_{20}H_4N_2O_{20}Ru_6$
M	785.45	1187.69	1202.7	1214.59	1198.67
Crystal colour, habit	Yellow, blocks	Green, blocks	Dark green, blocks	Brown, blocks	Dark blue, blocks
Crystal size/mm	0.20 × 0.23 × 0.24	0.10 × 0.15 × 0.24	0.22 × 0.26 × 0.30	0.20 × 0.20 × 0.25	0.12 × 0.14 × 0.34
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	9.7538(9)	15.83(3)	11.773(4)	17.619(2)	9.094(4)
b/Å	13.888(1)	9.24(2)	15.993(3)	9.323(1)	11.718(4)
c/Å	9.446(1)	22.81(3)	9.367(2)	20.864(2)	30.334(3)
α/°	105.693(9)		94.00(2)		
β/°	116.765(8)	106.5(1)	107.92(2)	110.47(1)	93.97(2)
γ/°	76.938(8)		104.22(2)		
U/Å^3	1091.8(2)	3200(9)	1606.5(7)	3210.5(7)	3224(1)
Z	2	4	2	4	4
D_c/g cm^{-3}	2.389	2.464	2.484	2.513	2.469
F(000)	736	2232	1130	2280	2248
μ(Mo-Kα)/cm^{-1}	27.77	28.43	28.35	29.94	28.24
Scan width/°	1.73 + 0.35 tan θ	1.10 + 0.35 tan θ	1.26 + 0.35 tan θ	0.55 + 0.35 tan θ	0.68 + 0.35 tan θ
Transmission factors	0.738–1.000	0.864–1.000	0.879–1.000	0.827–1.000	0.939–1.000
p Factor [b]	0.002	0.004	0.006	0.005	0.003
Reflections collected	3061	6233	4459	4663	4779
Unique reflections	2858	6004	4211	4542	4450
Observed reflections [$I > 3\sigma(I)$]	2463	3737	3362	2519	1896
R	0.023	0.046	0.031	0.039	0.041
R'	0.023	0.066	0.033	0.043	0.043
Goodness of fit	2.22	3.11	1.92	1.65	1.42
Largest Δ/σ	0.01	0.00	0.01	0.02	0.03
No. parameters	280	424	253	246	231
Residual electron density/e Å^{-3}	0.26, −0.36	0.88, −1.07	0.40, −0.35	0.71, −0.47	1.07, −0.62

[a] Details in common: 298 K; 2θ 4–45°; scan type ω–2θ; scan speed 16° min^{-1}; absorption correction by ψ scan and refinement by full-matrix least squares. [b] Weighting scheme: $w = 4F_o^2/[\sigma^2(F_o^2) + pF_o^2]^2$.

Table 13 Atomic coordinates for $[Ru_6(\mu\text{-}H)(CO)_{16}(\mu\text{-}CO)(\mu_4\text{-}NH)\{\mu_3\text{-}\eta^2\text{-}C(O)OMe\}]$ **1**

Atom	*x*	*y*	*z*
Ru(1)	0.730 78(10)	−0.036 6(1)	0.355 04(4)
Ru(2)	0.949 39(9)	−0.002 23(9)	0.397 08(3)
Ru(3)	0.808 08(9)	0.208 27(9)	0.364 67(4)
Ru(4)	1.014 78(9)	0.345 55(9)	0.378 30(3)
Ru(5)	1.153 90(9)	0.131 25(9)	0.381 41(3)
Ru(6)	1.222 57(9)	0.347 46(9)	0.329 59(4)
Cl(1)	0.610 7(6)	0.230 8(6)	0.607 6(2)
Cl(2)	0.478 0(8)	0.324 1(7)	0.530 7(3)
O(1)	0.868 2(9)	−0.016 8(10)	0.262 5(4)
O(2)	0.710(1)	−0.329(1)	0.355 0(4)
O(3)	0.497(1)	0.006(1)	0.306 2(4)
O(4)	0.635 8(9)	0.004 2(9)	0.455 3(4)
O(5)	1.018 7(9)	−0.223 1(10)	0.335 1(3)
O(6)	0.883 0(9)	−0.196 7(10)	0.470 8(4)
O(7)	0.738 8(10)	0.251(1)	0.262 4(4)
O(8)	0.582(1)	0.318(1)	0.392 6(4)
O(9)	1.089 5(9)	0.593(1)	0.424 1(4)
O(10)	0.897 5(8)	0.504 7(9)	0.301 1(3)
O(11)	1.240 8(8)	−0.045 8(9)	0.304 8(3)
O(12)	1.390 2(10)	0.132(1)	0.428 7(4)
O(13)	1.161 4(8)	−0.056 8(9)	0.463 7(3)
O(14)	1.453(1)	0.288(1)	0.284 1(4)
O(15)	1.332 0(9)	0.439 8(10)	0.424 4(4)
O(16)	1.072 0(8)	0.241 1(9)	0.247 7(3)
O(17)	1.200 5(9)	0.618(1)	0.290 5(4)
O(18)	0.855 4(8)	0.351 0(8)	0.467 1(3)
O(19)	0.879 2(8)	0.159 8(9)	0.435 4(3)
N	0.987 1(7)	0.155 6(8)	0.350 1(3)
C(1)	0.816(1)	−0.026(1)	0.296 7(5)
C(2)	0.716(2)	−0.218(2)	0.354 2(6)
C(3)	0.588(1)	−0.011(1)	0.324 2(5)
C(4)	0.671(1)	−0.013(1)	0.418 5(5)
C(5)	0.993(1)	−0.136(1)	0.358 9(5)
C(6)	0.906(1)	−0.121(1)	0.442 4(5)
C(7)	0.763(1)	0.238(1)	0.303 1(5)
C(8)	0.671(1)	0.273(1)	0.381 3(5)
C(9)	1.057(1)	0.496(1)	0.407 1(5)
C(10)	0.939(1)	0.442(1)	0.330 9(5)
C(11)	1.211(1)	0.022(1)	0.334 3(5)
C(12)	1.299(1)	0.136(1)	0.409 9(5)
C(13)	1.116(1)	0.000(1)	0.431 9(4)
C(14)	1.367(1)	0.307(1)	0.301 9(5)
C(15)	1.292(1)	0.406(1)	0.388 4(5)
C(16)	1.127(1)	0.279(1)	0.278 5(4)
C(17)	1.211(1)	0.516(1)	0.305 6(5)
C(18)	0.904(1)	0.286(1)	0.430 6(4)
C(19)	0.830(1)	0.483(1)	0.461 2(5)
C(20)	0.599(2)	0.244(2)	0.547 4(8)

Table 14 Atomic coordinates for $[Ru_3(\mu\text{-}H)_2(CO)_9(NH)]$ **3**

Atom	*x*	*y*	*z*
Ru(1)	0.711 87(6)	0.021 47(6)	0.769 63(5)
Ru(2)	0.497 58(6)	0.319 58(6)	0.774 41(6)
Ru(3)	0.815 65(6)	0.247 68(6)	0.765 34(6)
O(1)	0.488 9(7)	−0.097 7(6)	0.643 7(6)
O(2)	0.702 1(7)	−0.066 5(7)	1.069 4(5)
O(3)	0.989 9(7)	−0.271 5(6)	0.648 7(7)
O(4)	0.229 8(7)	0.270 6(7)	0.639 6(7)
O(5)	0.375 1(7)	0.338 2(6)	1.068 8(6)
O(6)	0.344 2(7)	0.656 6(7)	0.692 5(8)
O(7)	0.764 7(8)	0.527 9(7)	0.605 8(7)
O(8)	0.961 5(7)	0.348 7(7)	1.021 4(6)
O(9)	1.120 4(6)	0.019 0(6)	0.625 4(6)
N	0.671 6(6)	0.188 2(6)	0.634 7(5)
C(1)	0.572 6(8)	−0.050 8(7)	0.691 4(7)
C(2)	0.706 8(8)	−0.040 3(8)	0.957 1(8)
C(3)	0.888 9(9)	−0.162 6(8)	0.694 4(8)
C(4)	0.334 4(9)	0.284 4(8)	0.689 9(8)
C(5)	0.417 7(9)	0.338 9(8)	0.961 3(8)
C(6)	0.400 1(8)	0.532 5(9)	0.721 2(9)
C(7)	0.784 8(9)	0.423 7(9)	0.664 4(8)
C(8)	0.913 3(8)	0.306 4(8)	0.925 7(8)
C(9)	1.009 6(8)	0.108 2(8)	0.676 8(7)

Table 15 Atomic coordinates for $[Ru_3(\mu\text{-}H)_2(CO)_9(NOMe)]$ **4**

Atom	*x*	*y*	*z*
Ru(1)	0.809 3(1)	0.331 85(10)	0.113 99(8)
Ru(2)	0.900 9(1)	0.420 44(9)	0.283 77(8)
Ru(3)	0.596 7(1)	0.425 25(10)	0.213 33(9)
O(1)	0.589(2)	0.187(1)	0.025 3(9)
O(2)	0.840(2)	0.457(1)	−0.059 9(9)
O(3)	1.067(2)	0.182(1)	0.087(1)
O(4)	0.825(1)	0.454 1(10)	0.488 4(8)
O(5)	1.170(1)	0.281(1)	0.321 1(9)
O(6)	1.104(2)	0.605 2(10)	0.280 1(9)
O(7)	0.519(2)	0.606(1)	0.094(1)
O(8)	0.411(2)	0.460(1)	0.390(1)
O(9)	0.331(1)	0.320(1)	0.115 5(10)
O(10)	0.725(1)	0.218 0(8)	0.287 6(7)
N	0.744(1)	0.312 7(9)	0.245 6(8)
C(1)	0.670(2)	0.243(1)	0.056(1)
C(2)	0.833(2)	0.408(1)	0.003(1)
C(3)	0.975(2)	0.240(1)	0.097(1)
C(4)	0.855(2)	0.440(1)	0.416(1)
C(5)	1.072(2)	0.333(1)	0.309(1)
C(6)	1.030(2)	0.541(1)	0.283(1)
C(7)	0.545(2)	0.544(1)	0.138(1)
C(8)	0.480(2)	0.450(1)	0.325(1)
C(9)	0.432(2)	0.356(1)	0.151(1)
C(10)	0.660(2)	0.219(1)	0.377(1)

form metal framework in compounds **1**, **5**, **8**, **9** and **11** is supposed to involve the coupling of two triangular Ru_3 units with two direct metal–metal bonds between one of the edges of each Ru_3 moiety such that the two apical Ru atoms are far apart. Although **10** may also be formed by coupling of two Ru_3 units, one of the apical Ru atoms tends to interact with the bridging edge of another Ru_3 unit. As mentioned before, the first structurally characterized μ_4-NH cluster was synthesized by protonation of $[N(PPh_3)_2][Ru_4(CO)_{12}N]$ in the presence of diphenylacetylene to stabilize the metal framework. Similarly, each of the μ_4-nitrene clusters in this work contains a bridging methoxy group which is situated on the other side of the square base opposite to the nitrene ligand so as to stabilize the molecular geometry. The nitrene hydrogen atoms of the μ_4-nitrene clusters are probably derived from a variety of sources such as protons during the formation of **1** and **8**. Moreover, the nitrene hydrogen atoms in **5** and **6** as well as **9** and **11** probably originate from molecular hydrogen and hydride respectively. However, the mechanism of the synthesis of the μ_4-nitrene moiety from the O-alkylated nitrosyl compound under various conditions remains uncertain. It is believed that the facile cleavage of the N–O bond in the methoxyimide moiety probably accounts for the characteristic reactivity of **2** and **4**.

Experimental

All operations were carried out under argon using standard Schlenk techniques, except for the chromatographic separations. All chemicals, unless otherwise stated, were from commercial sources and used as received. Solvents were dried according to standard methods and distilled prior to use. Products were separated by thin-layer chromatography on plates coated with silica (Merck Kieselgel 60 GF_{254}). Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer using 0.5 mm solution cells, ^1H NMR spectra on a JEOL GSX 270FT-NMR spectrometer using deuteriated solvents as lock and reference, and positive and negative ionisation fast atom bombardment (FAB) mass spectra on a Finnigan MAT 95 mass

Table 16 Atomic coordinates for [$Ru_6(\mu$-H)(CO)$_{16}(\mu$-CO)$_2(\mu_4$-NH)(μ-OMe)] **5**

Atom	*x*	*y*	*z*
Ru(1)	0.214 50(7)	0.382 4(1)	1.147 20(5)
Ru(2)	0.290 05(7)	0.433 8(1)	1.041 86(5)
Ru(3)	0.264 10(7)	0.155 2(1)	1.077 27(5)
Ru(4)	0.231 15(7)	0.067 1(1)	0.954 03(5)
Ru(5)	0.255 72(7)	0.358 2(1)	0.916 64(5)
Ru(6)	0.151 91(7)	0.166 0(1)	0.838 65(5)
O(1)	0.403 2(7)	0.378(1)	1.225 6(5)
O(2)	0.131 0(8)	0.229(1)	1.245 6(5)
O(3)	0.038 5(7)	0.379(1)	1.054 9(4)
O(4)	0.179 8(8)	0.688(1)	1.184 0(5)
O(5)	0.435 2(7)	0.598(1)	1.124 6(5)
O(6)	0.172 0(7)	0.696(1)	1.026 0(5)
O(7)	0.415 4(7)	0.561(1)	0.962 6(4)
O(8)	0.383 5(8)	0.045(1)	1.192 4(6)
O(9)	0.113 8(7)	−0.007(1)	1.119 3(5)
O(10)	0.355 1(7)	−0.121(1)	1.047 9(5)
O(11)	0.057 8(6)	−0.077(1)	0.962 7(4)
O(12)	0.282 4(7)	−0.194(1)	0.888 4(5)
O(13)	0.116 4(7)	0.582(1)	0.877 6(5)
O(14)	0.340 1(7)	0.462(1)	0.812 5(5)
O(15)	0.080 6(9)	0.326(1)	0.719 6(6)
O(16)	0.326 3(9)	0.098(1)	0.793 1(6)
O(17)	0.057 2(8)	−0.114(1)	0.796 9(5)
O(18)	0.004 2(7)	0.274(1)	0.904 8(5)
O(19)	0.340 4(5)	0.187 4(9)	0.942 6(4)
N	0.202 0(6)	0.270 6(10)	0.996 5(4)
C(1)	0.333 2(9)	0.382(2)	1.194 5(6)
C(2)	0.162 4(10)	0.285(2)	1.208 5(7)
C(3)	0.105 1(9)	0.378(1)	1.088 4(6)
C(4)	0.194(1)	0.574(2)	1.169 5(7)
C(5)	0.377 6(9)	0.535(1)	1.092 9(6)
C(6)	0.216 8(9)	0.596(1)	1.031 4(6)
C(7)	0.357 0(9)	0.494(1)	0.973 9(6)
C(8)	0.336 7(10)	0.089(2)	1.148 4(7)
C(9)	0.170 3(9)	0.054(1)	1.101 6(6)
C(10)	0.309 1(9)	−0.019(1)	1.036 2(6)
C(11)	0.125 6(9)	−0.020(1)	0.960 2(6)
C(12)	0.261 7(10)	−0.093(2)	0.913 4(7)
C(13)	0.170 4(9)	0.494(2)	0.894 2(6)
C(14)	0.305 3(9)	0.419(2)	0.851 9(6)
C(15)	0.109(1)	0.266(2)	0.765 5(8)
C(16)	0.260(1)	0.122(2)	0.810 6(7)
C(17)	0.091 4(10)	−0.007(2)	0.810 8(7)
C(18)	0.058 8(9)	0.230(1)	0.879 7(6)
C(19)	0.430(1)	0.159(2)	0.943 2(7)

Table 17 Atomic coordinates for [$Ru_5(\mu$-H)$_3$(CO)$_{13}(\mu_4$-NH)(μ_3-OMe)] **6**

Atom	*x*	*y*	*z*
Ru(1)	1.260 46(8)	0.248 26(6)	−0.206 3(1)
Ru(2)	1.180 89(8)	0.132 12(6)	−0.058 09(10)
Ru(3)	0.920 21(7)	0.159 49(6)	−0.242 15(10)
Ru(4)	0.977 92(8)	0.334 20(5)	−0.278 33(10)
Ru(5)	0.727 72(8)	0.300 91(6)	−0.445 1(1)
O(1)	1.235 4(8)	0.348 5(6)	−0.505(1)
O(2)	1.464 8(8)	0.067 6(6)	−0.301(1)
O(3)	1.465 9(10)	0.345 4(7)	0.036(1)
O(4)	1.374 9(8)	−0.057 6(6)	−0.113 3(10)
O(5)	1.266 6(8)	0.097 3(6)	0.312(1)
O(6)	0.718 4(8)	0.143 5(6)	−0.106(1)
O(7)	0.845 7(7)	0.006 8(6)	−0.499 4(10)
O(8)	0.836 4(8)	0.533 5(6)	−0.165(1)
O(9)	0.924 9(7)	0.419 0(5)	−0.601 3(9)
O(10)	0.861 8(8)	0.184 6(6)	−0.702(1)
O(11)	0.594 4(10)	0.488 1(7)	−0.636(1)
O(12)	0.496(1)	0.211 3(8)	−0.584(1)
O(13)	0.661 0(9)	0.393 0(6)	−0.121(1)
O(14)	1.009 8(6)	0.257 5(4)	−0.062 2(7)
N	1.096 1(7)	0.186 6(5)	−0.301 8(9)
C(1)	1.244(1)	0.309 8(8)	−0.395(1)
C(2)	1.392(1)	0.133 5(8)	−0.265(1)
C(3)	1.392(1)	0.308 3(9)	−0.058(2)
C(4)	1.301(1)	0.015 9(7)	−0.093(1)
C(5)	1.238(1)	0.107 6(8)	0.170(1)
C(6)	0.797 8(10)	0.147 7(7)	−0.159(1)
C(7)	0.876 3(10)	0.063 9(7)	−0.402(1)
C(8)	0.893(1)	0.458 2(8)	−0.207(1)
C(9)	0.947 6(10)	0.385 5(7)	−0.474(1)
C(10)	0.812(1)	0.228 9(8)	−0.609(1)
C(11)	0.640(1)	0.415 4(9)	−0.567(2)
C(12)	0.580(1)	0.246 6(10)	−0.533(2)
C(13)	0.686(1)	0.361 0(8)	−0.241(1)
C(14)	0.987(1)	0.303 3(8)	0.092(1)

Table 18 Atomic coordinates for [Ru_4(CO)$_{12}(\mu_4$-N)(μ-OMe)] **7**

Atom	*x*	*y*	*z*
Ru(1)	0.900 26(6)	0.279 16(4)	0.769 36(6)
Ru(2)	0.607 13(6)	0.226 51(4)	0.538 15(6)
Ru(3)	0.837 92(6)	0.321 28(4)	0.468 69(6)
Ru(4)	0.765 63(6)	0.121 11(4)	0.343 73(6)
O(1)	1.247 7(6)	0.287 8(4)	0.915 4(7)
O(2)	0.927 1(7)	0.162 9(5)	1.011 8(7)
O(3)	0.817 1(6)	0.484 5(4)	0.951 4(7)
O(4)	0.625 7(6)	0.048 6(4)	0.673 8(7)
O(5)	0.461 0(7)	0.366 1(5)	0.759 5(7)
O(6)	0.313 7(6)	0.165 3(5)	0.237 5(7)
O(7)	1.163 0(6)	0.264 5(4)	0.491 2(8)
O(8)	0.912 7(7)	0.534 4(4)	0.655 1(8)
O(9)	0.728 9(7)	0.353 0(5)	0.125 3(7)
O(10)	0.537 6(7)	0.121 3(5)	−0.008 3(7)
O(11)	1.040 2(6)	0.030 9(4)	0.259 4(7)
O(12)	0.719 5(7)	−0.086 8(4)	0.347 9(7)
O(13)	0.615 4(4)	0.353 0(3)	0.462 8(5)
N	0.839 1(5)	0.195 9(3)	0.559 4(6)
C(1)	1.119 4(8)	0.285 6(5)	0.862 9(8)
C(2)	0.916 3(9)	0.208 5(6)	0.922 6(9)
C(3)	0.853 3(8)	0.408 4(6)	0.890 4(8)
C(4)	0.618 7(7)	0.113 7(6)	0.621 5(9)
C(5)	0.517 0(8)	0.313 7(6)	0.679 5(9)
C(6)	0.423 5(8)	0.187 1(5)	0.347 2(9)
C(7)	1.041 8(9)	0.287 0(5)	0.484 2(9)
C(8)	0.883 7(8)	0.455 3(6)	0.588 4(9)
C(9)	0.770 4(8)	0.339 0(6)	0.252 4(10)
C(10)	0.623 8(9)	0.118 4(6)	0.120 3(9)
C(11)	0.936 4(9)	0.065 7(5)	0.288 4(8)
C(12)	0.734 4(8)	−0.009 2(6)	0.343 6(8)
C(13)	0.487 2(8)	0.392 5(5)	0.332 7(9)

spectrometer. The complex [N(PPh$_3$)$_2$][Ru_3(CO)$_{10}$(NO)] was prepared according to the published procedure.[8a]

Isolation of [$Ru_6(\mu$-H)(CO)$_{16}(\mu$-CO)(μ_4-NH){μ_3-η^2-C(O)OMe}] 1

The compound [N(PPh$_3$)$_2$][Ru_3(CO)$_{10}$(NO)] (1.80 g, 1.56 mmol) was dissolved in CH_2Cl_2 (50 cm^3) to give a dark yellowish green solution. A solution of CF_3SO_3Me (0.25 cm^3, 2.21 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise. The solution was allowed to stir for 1 h, the solvent was then removed *in vacuo* and the residue chromatographed by TLC using hexane–dichloromethane (4:1) as eluent. In order of elution, the products were characterized by IR spectroscopy as [Ru_3(CO)$_{12}$] (yellow, 5%), [Ru_4H_2(CO)$_{13}$] (red, 10%), [Ru_3(CO)$_{10}$(NOMe)] **2** (yellow, 50%), and [$Ru_6(\mu$-H)(CO)$_{16}(\mu$-CO)(μ_4-NH){μ_3-η^2-C(O)OMe}] **1** (blue, 5%).

Preparation of compounds 3 and 4

The compound [Ru_3(CO)$_{10}$(NOMe)] **2** (500 mg, 0.796 mmol) was dissolved in hexane (60 cm^3). The bright yellow solution was heated at 65 °C while hydrogen was bubbled through it.

Table 19 Atomic coordinates for $[Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)_2]$ **8**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.711 71(10)	0.330 9(2)	1.137 37(7)	O(19)	0.866 7(7)	0.245(1)	1.066 4(6)
Ru(2)	0.785 69(9)	0.427 5(2)	1.045 80(6)	O(20)	0.843 8(7)	0.199(1)	0.941 7(5)
Ru(3)	0.756 61(10)	0.116 2(2)	1.064 07(7)	N	0.705 8(8)	0.261(1)	0.985 8(6)
Ru(4)	0.734 61(9)	0.066 4(2)	0.938 12(7)	C(1)	0.599(1)	0.345(2)	1.072 8(8)
Ru(5)	0.757 67(9)	0.377 7(2)	0.919 53(6)	C(2)	0.692(2)	0.514(3)	1.170 3(10)
Ru(6)	0.651 0(1)	0.203 5(2)	0.827 30(7)	C(3)	0.657(1)	0.209(3)	1.187(1)
O(1)	0.535 6(8)	0.353(2)	1.035 6(6)	C(4)	0.833(1)	0.314(2)	1.191 7(8)
O(2)	0.681(1)	0.623(2)	1.188 7(8)	C(5)	0.702(1)	0.583(2)	1.031 8(8)
O(3)	0.627(1)	0.137(2)	1.214 4(8)	C(6)	0.864(1)	0.549(2)	1.106 2(9)
O(4)	0.902 7(9)	0.304(2)	1.223 1(6)	C(7)	0.646(1)	0.019(2)	1.061 0(9)
O(5)	0.655 1(9)	0.677(1)	1.025 3(7)	C(8)	0.808(2)	0.011(2)	1.136 9(10)
O(6)	0.911(1)	0.618(2)	1.140 7(7)	C(9)	0.808(1)	−0.055(2)	1.019 1(9)
O(7)	0.585 3(9)	−0.038(2)	1.060 9(8)	C(10)	0.768(1)	−0.080(2)	0.890 9(10)
O(8)	0.839(1)	−0.054(2)	1.180 4(8)	C(11)	0.624(1)	−0.036(2)	0.926 8(9)
O(9)	0.849(1)	−0.155(2)	1.030 6(7)	C(12)	0.666(1)	0.521(2)	0.895 9(8)
O(10)	0.791(1)	−0.168(2)	0.864 5(8)	C(13)	0.811(1)	0.459(2)	0.861 7(9)
O(11)	0.562 2(9)	−0.101(2)	0.918 2(7)	C(14)	0.858(1)	0.509(2)	0.985 9(8)
O(12)	0.612(1)	0.605(2)	0.879 8(7)	C(15)	0.756(1)	0.176(2)	0.798 6(9)
O(13)	0.843(1)	0.512(2)	0.830 0(7)	C(16)	0.588(1)	0.029(3)	0.785 5(9)
O(14)	0.913 4(8)	0.582(2)	0.984 1(6)	C(17)	0.599(1)	0.347(3)	0.761(1)
O(15)	0.815(1)	0.163(2)	0.780 5(8)	C(18)	0.556(1)	0.245(2)	0.866 0(9)
O(16)	0.555(1)	−0.071(2)	0.763 6(8)	C(19)	0.958(1)	0.226(2)	1.090(1)
O(17)	0.568(1)	0.426(2)	0.726 4(8)	C(20)	0.926(1)	0.170(2)	0.931 8(10)
O(18)	0.504 3(8)	0.276(2)	0.888 1(7)				

Table 20 Atomic coordinates for $[Ru_6(CO)_{15}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)\{\mu_3\text{-}\eta^2\text{-}N(H)C(O)OMe\}]$ **9**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	−0.054 09(6)	0.279 96(4)	0.563 46(8)	O(19)	0.503 5(5)	0.263 2(3)	1.274 8(6)
Ru(2)	0.025 22(6)	0.238 65(4)	0.860 79(7)	O(20)	0.467 7(5)	0.386 6(3)	1.353 5(6)
Ru(3)	0.203 12(6)	0.346 60(4)	0.734 08(7)	N(1)	0.190 3(5)	0.222 4(4)	0.818 1(7)
Ru(4)	0.219 37(6)	0.178 60(4)	1.039 76(7)	N(2)	0.346 9(6)	0.310 2(4)	1.120 4(8)
Ru(5)	0.392 58(6)	0.282 33(4)	0.916 92(7)	C(1)	−0.080 9(8)	0.381 5(6)	0.653(1)
Ru(6)	0.448 88(6)	0.156 26(4)	1.085 93(8)	C(2)	−0.054 6(8)	0.326 6(6)	0.381(1)
O(1)	−0.100 0(6)	0.441 0(4)	0.704 3(8)	C(3)	−0.222 7(9)	0.215 7(6)	0.514(1)
O(2)	−0.054 6(6)	0.356 6(4)	0.272 3(7)	C(4)	−0.010 4(8)	0.177 5(6)	0.502 5(10)
O(3)	−0.324 4(7)	0.174 9(5)	0.488 5(8)	C(5)	−0.080 5(8)	0.129 3(6)	0.778 6(10)
O(4)	0.014 3(6)	0.116 6(4)	0.468 3(7)	C(6)	−0.111 6(8)	0.269 2(6)	0.883(1)
O(5)	−0.148 4(7)	0.060 1(5)	0.727 5(8)	C(7)	0.185 0(7)	0.450 5(5)	0.668 5(9)
O(6)	−0.196 2(7)	0.290 5(5)	0.893 5(8)	C(8)	0.229 1(7)	0.319 4(5)	0.555 6(9)
O(7)	0.177 0(6)	0.515 6(4)	0.624 5(7)	C(9)	0.064 3(7)	0.209 3(5)	1.079 5(9)
O(8)	0.248 2(6)	0.307 6(4)	0.442 6(7)	C(10)	0.391 4(8)	0.403 6(5)	0.835 7(9)
O(9)	0.021 4(5)	0.204 9(4)	1.175 8(6)	C(11)	0.137 4(7)	0.062 8(5)	0.957 5(9)
O(10)	0.468 1(6)	0.466 3(4)	0.835 9(7)	C(12)	0.250 0(7)	0.146 5(5)	1.232 8(9)
O(11)	0.090 1(6)	−0.009 7(4)	0.906 8(7)	C(13)	0.430 7(8)	0.235 7(6)	0.757 8(10)
O(12)	0.263 3(6)	0.128 1(4)	1.351 2(7)	C(14)	0.561 4(8)	0.332 7(5)	1.013 5(9)
O(13)	0.459 7(6)	0.207 5(4)	0.662 8(8)	C(15)	0.380 7(8)	0.077 5(6)	0.910(1)
O(14)	0.664 9(6)	0.368 8(4)	1.072 9(7)	C(16)	0.442 4(9)	0.065 3(6)	1.208(1)
O(15)	0.334 5(6)	0.029 3(4)	0.796 4(8)	C(17)	0.614 9(9)	0.163 1(6)	1.095(1)
O(16)	0.435 3(7)	0.008 1(5)	1.273 6(9)	C(18)	0.145 2(8)	0.439 5(6)	1.005(1)
O(17)	0.711 5(7)	0.161 8(5)	1.096 8(8)	C(19)	0.441 0(7)	0.316 7(5)	1.251 1(9)
O(18)	0.153 5(4)	0.362 6(3)	0.929 2(5)	C(20)	0.567 9(9)	0.395 4(7)	1.495(1)

With the aid of IR spectroscopic monitoring, the reaction was stopped when the peak at 1741 cm^{-1} disappeared. The solvent was then removed *in vacuo* and the residue chromatographed on TLC plates using hexane–dichloromethane (6 : 1) as eluent. The first few bands contained $[Ru_3(CO)_{12}]$ and trace amounts of compounds which were not identified. A minor yellow band of $[Ru_3(\mu\text{-}H)_2(CO)_9(NH)]$ **3** ($R_f \approx 0.6$) and a major yellow band of $[Ru_3(\mu\text{-}H)_2(CO)_9(NOMe)]$ **4** ($R_f \approx 0.5$) were isolated in 5 and 50% yields respectively.

Hydrogenation of compound 2 with $[Ru_3(CO)_{12}]$

Compound **2** (126 mg, 0.2 mmol) and $[Ru_3(CO)_{12}]$ (128 mg, 0.2 mmol) were dissolved in hexane (60 cm^3). The orange solution was then hydrogenated under reflux. The reaction was monitored by spot TLC until complete consumption of **2**. The solvent was then removed and the residue chromatographed on TLC plates using hexane–dichloromethane (5 : 1) as eluent. A number of products were eluted in the sequence: $[Ru_3(CO)_{12}]$ (yellow, 50%), **3** (yellow, 10%), $[Ru_6(\mu\text{-}H)(CO)_{16}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)]$ **5** (blue, 5%), **4** (yellow, 30%) and $[Ru_5(\mu\text{-}H)_3(CO)_{13}(\mu_4\text{-}NH)(\mu_3\text{-}OMe)]$ **6** (dark blue, 5%).

Thermolysis of compound 2

Compound **2** (250 mg, 0.4 mmol) was dissolved in toluene (50 cm^3). The yellow solution was heated to 90 °C for 3 h which resulted in the formation of a deep reddish brown solution. The solvent was removed *in vacuo* and the products were separated by TLC using hexane–dichloromethane (4 : 1) as eluent. Three products were isolated in the following order of elution: $[Ru_3(CO)_{12}]$ (yellow, 5%), $[Ru_4(CO)_{12}(\mu_4\text{-}N)(\mu\text{-}OMe)]$ **7** (yellow, 10%) and $[Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)_2]$ **8** (green, 5%).

Table 21 Atomic coordinates for $[Ru_6(\mu\text{-}H)_2(CO)_{14}(\mu\text{-}CO)_2\{\mu_5\text{-}\eta^2\text{-}NC(O)OMe\}]$ **10**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.663 95(7)	0.306 7(1)	0.777 93(6)	O(16)	0.851 7(8)	−0.329(1)	0.652 1(6)
Ru(2)	0.836 23(7)	0.319 8(1)	0.869 58(6)	O(17)	0.929 2(5)	−0.002(1)	0.901 9(4)
Ru(3)	0.737 12(7)	0.104 0(1)	0.884 69(5)	O(18)	0.904 4(5)	−0.048(1)	0.791 5(5)
Ru(4)	0.709 02(7)	0.008 1(1)	0.751 63(5)	N	0.819 0(6)	0.105(1)	0.823 3(5)
Ru(5)	0.796 54(7)	0.238 7(1)	0.732 17(5)	C(1)	0.621(1)	0.441(2)	0.703 9(8)
Ru(6)	0.822 77(7)	−0.018 7(1)	0.686 65(5)	C(2)	0.654 2(10)	0.431(2)	0.845 1(8)
Cl(1)	0.360 4(4)	0.189 2(7)	0.973 6(4)	C(3)	0.564 1(9)	0.219(2)	0.767 8(7)
Cl(2)	0.517 0(6)	0.270(1)	1.060 1(5)	C(4)	0.948 0(9)	0.313(2)	0.912 4(7)
O(1)	0.592 2(8)	0.525(2)	0.660 9(7)	C(5)	0.844(1)	0.512(2)	0.891 6(9)
O(2)	0.648 5(8)	0.511(1)	0.885 4(7)	C(6)	0.811 1(9)	0.263(2)	0.951 8(8)
O(3)	0.502 9(8)	0.161(1)	0.759 0(6)	C(7)	0.658 1(10)	0.142(2)	0.923 0(8)
O(4)	1.017 5(8)	0.306(1)	0.937 5(6)	C(8)	0.790 8(8)	−0.031(2)	0.952 6(7)
O(5)	0.852 3(8)	0.636(2)	0.903 6(7)	C(9)	0.612 1(10)	−0.045(2)	0.685 1(8)
O(6)	0.826 8(6)	0.295(1)	1.009 4(5)	C(10)	0.663 5(10)	−0.049(2)	0.829 0(8)
O(7)	0.607 9(7)	0.165(1)	0.945 2(6)	C(11)	0.741 4(9)	−0.179(2)	0.752 5(8)
O(8)	0.820 9(7)	−0.115(1)	0.995 8(5)	C(12)	0.900 5(10)	0.293(2)	0.744 4(7)
O(9)	0.552 0(7)	−0.080(1)	0.642 2(6)	C(13)	0.765 9(9)	0.340(2)	0.650 7(8)
O(10)	0.616 3(7)	−0.138(1)	0.833 3(6)	C(14)	0.905 1(9)	0.044(2)	0.657 0(7)
O(11)	0.750 6(7)	−0.303(1)	0.756 0(6)	C(15)	0.742 7(9)	0.021(2)	0.603 1(7)
O(12)	0.966 4(7)	0.322(1)	0.753 2(6)	C(16)	0.838(1)	−0.214(2)	0.664 5(8)
O(13)	0.746 3(7)	0.397(1)	0.598 6(6)	C(17)	0.885 6(8)	0.014(2)	0.836 7(7)
O(14)	0.957 1(7)	0.085(1)	0.638 5(5)	C(18)	1.001 5(9)	−0.093(2)	0.917 8(8)
O(15)	0.691 4(7)	0.048(1)	0.551 2(6)	C(19)	0.453	0.189	1.003

Table 22 Atomic coordinates for $[Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)(\mu\text{-}NCO)]$ **11**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.706 6(2)	0.198 7(2)	0.165 40(5)	O(19)	0.695(1)	−0.074(1)	0.197 1(4)
Ru(2)	0.557 2(1)	−0.004 4(2)	0.145 32(5)	O(20)	0.661(3)	−0.430(2)	0.194 9(9)
Ru(3)	0.874 2(2)	−0.001 1(2)	0.168 79(5)	N(1)	0.746(2)	−0.066(1)	0.110 7(4)
Ru(4)	0.588 6(2)	−0.204 5(1)	0.095 60(5)	N(2)	0.721(1)	−0.276(1)	0.147 5(5)
Ru(5)	0.906 6(2)	−0.204 7(2)	0.120 95(5)	C(1)	0.673(2)	0.168(2)	0.226 6(6)
Ru(6)	0.791 2(2)	−0.300 7(2)	0.040 91(5)	C(2)	0.857(2)	0.308(2)	0.179 8(6)
O(1)	0.645(2)	0.153(1)	0.263 2(5)	C(3)	0.550(2)	0.308(2)	0.157 0(7)
O(2)	0.953(2)	0.370(1)	0.187 1(5)	C(4)	0.743(2)	0.199(2)	0.105 0(7)
O(3)	0.450(2)	0.367(2)	0.149 2(5)	C(5)	0.457(2)	0.073(2)	0.098 4(6)
O(4)	0.767(1)	0.202(1)	0.068 3(5)	C(6)	0.418(2)	0.050(2)	0.180 8(7)
O(5)	0.395(1)	0.121(1)	0.070 7(4)	C(7)	0.964(2)	0.053(2)	0.221 1(7)
O(6)	0.328(2)	0.078(1)	0.203 7(5)	C(8)	1.013(2)	0.077(2)	0.138 6(7)
O(7)	1.019(2)	0.092(1)	0.253 2(5)	C(9)	0.433(2)	−0.152(2)	0.140 0(6)
O(8)	1.097(2)	0.126(1)	0.120 3(5)	C(10)	1.000(2)	−0.154(2)	0.183 2(6)
O(9)	0.325(1)	−0.192(1)	0.153 5(4)	C(11)	0.498(2)	−0.145(2)	0.045 7(6)
O(10)	1.080(1)	−0.182(1)	0.211 9(4)	C(12)	0.472(2)	−0.334(2)	0.086 3(7)
O(11)	0.434(1)	−0.111(1)	0.013 7(4)	C(13)	1.056(2)	−0.145(2)	0.088 5(7)
O(12)	0.392(2)	−0.410(2)	0.078 3(5)	C(14)	1.016(2)	−0.337(2)	0.129 9(7)
O(13)	1.149(2)	−0.109(1)	0.068 7(5)	C(15)	0.810(2)	−0.148(2)	0.018 3(7)
O(14)	1.091(2)	−0.415(1)	0.134 7(5)	C(16)	0.659(3)	−0.344(2)	−0.005 5(8)
O(15)	0.831(2)	−0.060(1)	0.006 9(4)	C(17)	0.968(3)	−0.352(2)	0.016 3(8)
O(16)	0.565(2)	−0.370(2)	−0.032 6(6)	C(18)	0.769(2)	−0.442(2)	0.073 2(7)
O(17)	1.077(2)	−0.375(2)	0.003 1(6)	C(19)	0.667(3)	−0.127(2)	0.239 7(8)
O(18)	0.758(2)	−0.524(2)	0.091 0(5)	C(20)	0.698(3)	−0.351(2)	0.172 2(8)

Pyrolysis of compound 4

The compound $[Ru_3(\mu\text{-}H)_2(CO)_9(NOMe)]$ **4** (200 mg, 0.333 mmol) was sealed in a Carius tube under reduced pressure and placed in an oven at 140 °C for 2 h. The dark green residue was then extracted by dichloromethane until the extract became colourless. The solvent of the combined dark green extract was removed and the residue chromatographed on a silica gel TLC plate using hexane–dichloromethane (9:1) as eluent. Six distinct bands, in order of elution, were isolated: $[Ru_3(CO)_{12}]$ (yellow, 5%), $[Ru_4H_2(CO)_{13}]$ (red, 5%), $[Ru_3(\mu\text{-}H)(CO)_{10}(NH_2)]$ (yellow, 30%), $[Ru_6(CO)_{15}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)\{\mu_3\text{-}\eta^2\text{-}N(H)C(O)OMe\}]$ **9** (dark green, 5%), $[Ru_6(\mu\text{-}H)_2(CO)_{14}(\mu\text{-}CO)_2\{\mu_5\text{-}\eta^2\text{-}NC(O)OMe\}]$ **10** (brown, 5%) and $[Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)(\mu\text{-}NCO)]$ **11** (dark blue, 5%).

Crystallography

Crystals suitable for X-ray analyses were glued on glass fibres with epoxy resin and mounted on an Enraf-Nonius CAD4 (cluster **10**) or Rigaku-AFC7R diffractometer (clusters **1**, **3**–**9** and **11**) equipped with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) for unit-cell determination and data collection. Details of the intensity data collection and crystal data are given in Table 12. The intensity data were corrected for Lorentz-polarization effects and semiempirical absorption corrections (ψ-scan method)[22] were also applied. The positions of ruthenium atoms were determined by direct methods (SIR 88).[23] The molecular structures were determined by subsequent Fourier and Fourier-difference techniques.

Atomic coordinates and thermal parameters were refined by full-matrix least-squares analysis on *F*, with the ruthenium atoms and non-hydrogen atoms refined anisotropically. The hydrogen atoms of the nitrene moieties and metal hydrides were located by Fourier-difference synthesis while those of the organic moieties were generated in their ideal positions (C–H 0.95 Å). Calculations were performed on a Silicon-Graphics computer using the program package TEXSAN.[24] Final atomic coordinates are listed in Tables 13–22.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Acknowledgements

We gratefully acknowledge the Hong Kong Research Grants Council and the University of Hong Kong for financial support.

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Received 5th September 1995; *Paper* 5/05865A