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FULL PAPER

Synthesis and structural characterization of ruthenium carbonyl clusters containing acetylenic fluorene moieties derived from 9-ethynylfluoren-9-ol

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Five new ruthenium fluorene clusters, $[\mathrm{Ru_3(CO)_9(\mu\text{-}H)\{\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}CC(C_{13}H_9)\}}]$ **1** (8%), $[\mathrm{Ru_3(CO)_7(\mu\text{-}CO)\{\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^4\text{-}(HOC_{13}H_8)CCHC(C_{13}H_8OH)CH\}}]$ **2** (15%), $[\mathrm{Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_3\text{-}OH)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}C_{13}H_8CCH)}]$ **3** (12%), $[\mathrm{Ru_5(CO)_{11}(\mu\text{-}H)(\mu\text{-}CO)(\mu_3\text{-}OH)(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^6\text{-}C_{13}H_7CHC)}]$ **4** (10%) and $[\mathrm{Ru_6(CO)_{15}(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^3{:}\eta^6\text{-}C_{13}H_7CHC)}]$ **5** (9%), have been synthesized by a reaction of 9-ethynylfluoren-9-ol with triruthenium dodecacarbonyl in tetrahydrofuran under reflux. All these compounds have been fully characterized by spectroscopic and X-ray diffraction methods. The structure of **1** consists of a fluorene ring bound to the triruthenium cluster unit *via* a typical μ_3-(η^2-$\perp$) co-ordination mode. Cluster **2** is based on a Ru_3 triangle containing a C_4 chain which arises from the coupling of two ligand molecules with the formation of a metallacyclopentadiene ring. An interesting structural feature observed in cluster **3** is the formation of a Ru_4O square pyramidal framework in which the hydroxy group, originating from the ligand, is bound to the cluster in a triply bridging manner. The bonding modes of the organic fragments in **4** and **5** are very similar. They both interact with five ruthenium metal centres but with a novel Ru_5 bent chain in **4** and a spiked butterfly in **5**.

Introduction

The interaction of arene ligands with clusters has been an active area of study for some years.[1] Arene-containing clusters with metal nuclearities ranging from three to eight have been reported. The analogy between arenes bound to metal clusters and the interaction of arenes with metal surfaces may allow us to understand the chemisorption of organic molecules to metal surfaces.[2,3] In general, arenes tend to co-ordinate to the metal centres *via* two bonding modes, either terminal[4–6] or face-capping.[7–9] These bonding modes are known to undergo interconversion in some systems but the factors affecting the choice of the bonding modes have only partly been elucidated. Polycyclic aromatics, by virtue of the fact that they possess multiple ring sites and π-orbital electrons, appear to be interesting in the study of interaction between π systems and metal centres. However, the study of polymetallic polyaromatic compounds is usually hindered by the difficulty of introducing the polyaromatic component into the co-ordination sphere of the metal centre. As a result, very few mononuclear compounds or metal clusters of this kind have been reported. The polyaromatic ligands in these structures exhibit a variety of bonding modes, *e.g.* metallacyclization in $[\mathrm{Ru_2(CO)_5(\mu\text{-}CO)\{\mu\text{-}\eta^2{:}\eta^4\text{-}(C_6H_4)_2\}}]$,[10] face capping in $[\mathrm{Ru_3(CO)_7(\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^5\text{-}C_{12}H_8)}]$,[11] $[\mathrm{Ru_7C(CO)_{16}(C_9H_8)}]$ and $[\mathrm{Ru_7C(CO)_{16}(C_{12}H_{12})}]$,[12] a phenylphosphido anthracene moiety with a bow-tie geometry in $[\mathrm{Ru_5(CO)_{13}(\mu_5\text{-}\eta^1{:}\eta^2{:}\eta^3{:}\eta^3\text{-}C_{14}H_8\text{-}\eta^1\text{-}PPh)}]$,[13] a naphthyne ligand lying vertical to the Ru_4 metal plane in $[\mathrm{Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_{10}H_6)}]$[14] and a chelating diphenylmethane moiety in $[\mathrm{Ru_7C(CO)_{14}(\mu_3\text{-}\eta^1{:}\eta^6{:}\eta^6\text{-}C_6H_4CH_2C_6H_4)}]$.[15] Compared to these polyaromatic ligands, the fluorenyl group which can be considered as a dibenzocyclopentadienyl system, has attracted relatively more attention from co-ordination chemists. To our knowledge, the co-ordination chemistry of fluorene centred on mononuclear[16–21] and binuclear[22,23] metal complexes has previously been reported. However, that of functionalized acetylenic fluorene ligands with metal clusters has received less attention. It is also interesting to observe some systematic chemistry of functionalized acetylene groups bound to transition-metal carbonyl clusters.[24–26] Presented in this work is the reaction of $[\mathrm{Ru_3(CO)_{12}}]$ with 9-ethynylfluoren-9-ol, which leads to several new clusters containing metallacycles and novel fluorene moieties.

Results and discussion

The reaction of $[\mathrm{Ru_3(CO)_{12}}]$ with 9-ethynylfluoren-9-ol in refluxing tetrahydrofuran (68 °C) under a dinitrogen atmosphere gave a mixture of products in low yields which were separated by TLC (Scheme 1). Five new compounds were observed and identified as $[\mathrm{Ru_3(CO)_9(\mu\text{-}H)\{\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}CC(C_{13}H_9)\}}]$ **1**, $[\mathrm{Ru_3(CO)_7(\mu\text{-}CO)\{\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^4\text{-}(HOC_{13}H_8)CCHC(C_{13}H_8OH)CH\}}]$ **2**, $[\mathrm{Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_3\text{-}OH)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}C_{13}H_8CCH)}]$ **3**, $[\mathrm{Ru_5(CO)_{11}(\mu\text{-}H)(\mu\text{-}CO)(\mu_3\text{-}OH)(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^6\text{-}C_{13}H_7CHC)}]$ **4** and $[\mathrm{Ru_6(CO)_{15}(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^3{:}\eta^6\text{-}C_{13}H_7CHC)}]$ **5**, in 8, 15, 12, 10 and 9% yields respectively {based on $[\mathrm{Ru_3(CO)_{12}}]$}. Another side product isolated was found to be $[\mathrm{Ru_4H_2(CO)_{13}}]$ (5%). All the compounds were fully characterized by FAB mass spectrometry, IR, ^{1}H NMR spectroscopies and single-crystal X-ray crystallography.

Spectroscopic and structural characterization of compound 1

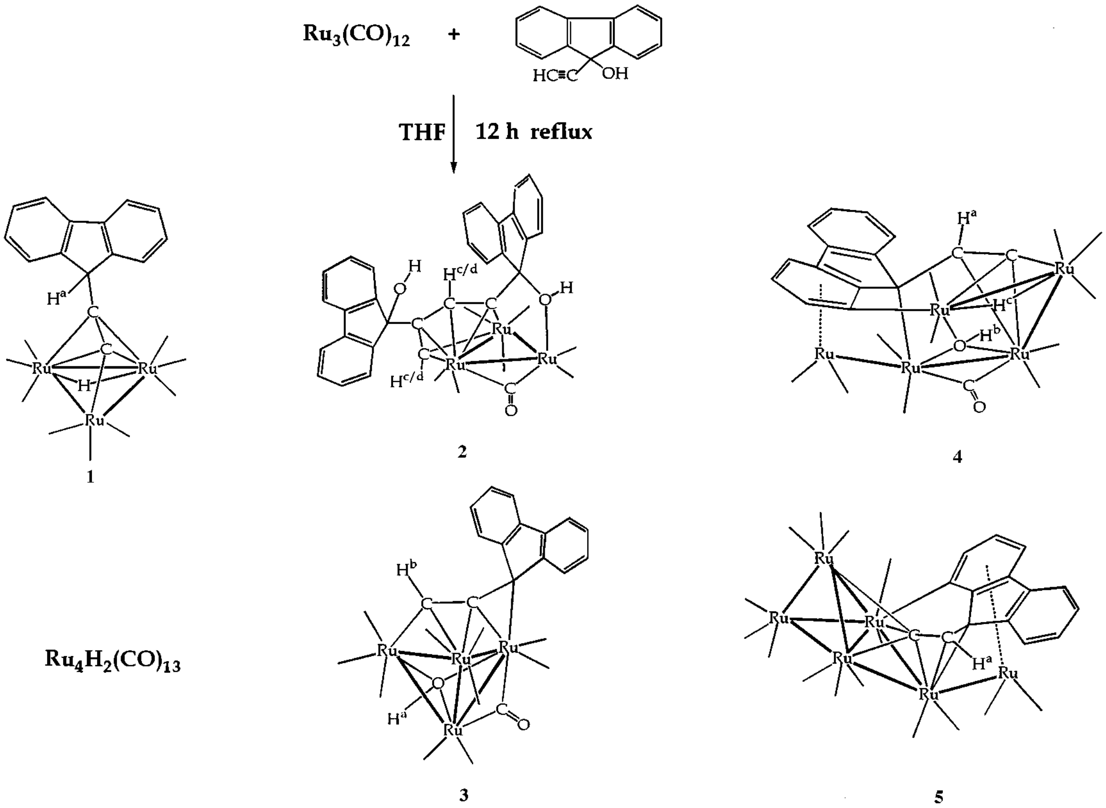
The first product was isolated near the top of the plate as an orange band that yields an oily material. Its positive FAB mass spectrum shows two molecular ions peaks at *m/z* 770 and 747 respectively, as well as peaks corresponding to the sequential loss of carbonyl ligands. The ^{1}H NMR spectrum in $CDCl_3$ shows two singlets at δ −20.33 and −18.65 which indicate the presence of metal hydrides. Two multiplets centred at δ 7.75 and 7.34 are due to the protons on the two phenyl rings, and a downfield singlet at δ 6.08 is assigned to the proton on C(32).

A single crystal X-ray analysis was carried out on an orange crystal grown from a dichloromethane–hexane solution at −10 °C. The asymmetric unit in the crystal structure consists of two molecules of compound **1** with a rather similar geometry

Table 1 Spectroscopic data for clusters **1**–**5**

Cluster	IR, $\tilde{\nu}(CO)^a/cm^{-1}$	^1H NMR, $\delta(J/Hz)^b$	MS, m/z^c
1	*d*: 2080w, 2045s, 2003s, 1986s *e*: 2078vs, 2068vs, 2052vs, 2032 (sh), 2020m	7.34–7.75 (16 H, m, Ph) 6.08 (2 H, s, H^a) −18.65 (2 H, s, RuH)[e] −20.33 (2 H, s, RuH)[d]	770 (770)[e] 747 (747)[d]
2	2066s, 2039vs, 2010vs, 1954 (sh), 1765w	7.73–6.94 (16 H, m, Ph) 7.80 (1 H, d, $J = 2.2$, H^c or H^d) 5.71 (1 H, d, $J = 2.2$, H^c or H^d)	941 (941)
3	2070s, 2058s, 2006m	9.28 (1 H, s, H^b) 6.70–7.98 (8 H, m, Ph) 4.30 (2 H, t, $J = 8.9$, L)[f] 2.47 (2 H, t, $J = 8.9$, L) 2.23 (2 H, m, $J = 8.9$, L) −2.00 (1 H, s, H^a)	920 (920)
4	2070s, 2044vs, 2035w, 2010s, 1993w	6.30–7.60 (7 H, m, Ph) 6.18 (1 H, s, H^a) −3.00 (1 H, s, H^b) −10.00 (1 H, s, H^c)	1048 (1048)
5	2078s, 2047s, 2023vs, 2014s, 1989w, 1948 (sh)	7.30–8.00 (7 H, m, Ph) 6.50 (1 H, s, H^a)	1215 (1215)

[a] In CH_2Cl_2. [b] In $CDCl_3$. [c] Simulated values given in parentheses. [d] For $[Ru_3(CO)_9(\mu\text{-}H)\{\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}CC(C_{13}H_9)\}]$. [e] For $[Ru_4H_2(CO)_{13}]$. [f] L = Lactone.



Scheme 1

and one of the known cluster $[Ru_4H_2(CO)_{13}]$.[27] The spectroscopic data (Table 1) are fully consistent with the solid-state structure. The molecular structure of cluster **1** is depicted in Fig. 1, together with the atomic numbering scheme. Selected interatomic distances and angles are given in Table 2. The three ruthenium atoms define an irregular triangle with the Ru(2)–Ru(3) bond [2.788(6) Å] [Ru(5)–Ru(6) 2.784(6) Å, in the second molecule] bridged by a hydride ligand. The fluorenyl acetylenic ligand undergoes a loss of the hydroxyl group and interacts with the three Ru atoms forming one σ bond with Ru(1) and two π bonds with Ru(2) and Ru(3). Such a bonding mode of the acetylenic ligand towards a metal cluster is very similar to that found in $[Ru_3(CO)_9(\mu\text{-}H)\{\mu_3\text{-}C_2C(CH_3)_3\}]$[28] and $[Ru_3(CO)_9(\mu\text{-}H)(C_6H_9)]$.[29] Regarding the acetylenic ligand as a 5-electron donor, the valence electron count is 48 for **1**, which is in agreement with the EAN rule.

Spectroscopic and structural characterization of compound 2

The trinuclear cluster **2** is a yellow solid which displays a characteristic band at 1765 cm^{-1} in the IR spectrum due to the presence of a bridging carbonyl ligand (Table 1). The positive FAB mass spectrum shows an envelope with a molecular ion peak at *m*/*z* 941. Its ^1H NMR spectrum in $CDCl_3$ shows multiplets due to the phenyl protons in the range δ 6.94–7.73. The proton on C(11) is spin coupled to that on C(13) to give two equally intense methylene doublets, one centred at δ 5.71 and another centred at δ 7.80 with J_{HH} 2.2 Hz. However, signals of

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

Ru(1)–Ru(2)	2.806(5) [2.794(4)]	Ru(1)–Ru(3)	2.798(3) [2.820(5)]
Ru(2)–Ru(3)	2.788(6) [2.784(6)]	Ru(1)–C(32)	1.945(6) [1.954(5)]
Ru(2)–C(32)	2.213(5) [2.218(5)]	Ru(2)–C(33)	2.258(5) [2.260(5)]
Ru(3)–C(32)	2.212(5) [2.208(5)]	Ru(3)–C(33)	2.258(5) [2.261(5)]
C(32)–C(33)	1.318(7) [1.312(7)]	C(33)–C(34)	1.502(7) [1.506(7)]
C(34)–C(35)	1.525(8) [1.535(7)]	C(34)–C(46)	1.525(8) [1.536(7)]
C(35)–C(36)	1.380(8) [1.373(8)]	C(35)–C(40)	1.394(8) [1.393(8)]
C(36)–C(37)	1.394(8) [1.393(8)]	C(37)–C(38)	1.36(1) [1.38(1)]
C(38)–C(39)	1.38(1) [1.38(1)]	C(39)–C(40)	1.382(9) [1.382(9)]
C(40)–C(41)	1.470(8) [1.471(8)]	C(41)–C(42)	1.393(8) [1.382(9)]
C(41)–C(46)	1.398(8) [1.390(7)]	C(42)–C(43)	1.35(1) [1.366(9)]
C(43)–C(44)	1.37(1) [1.378(9)]	C(44)–C(45)	1.421(9) [1.382(8)]
C(45)–C(46)	1.385(8) [1.383(7)]		
Ru(2)–Ru(1)–Ru(3)	59.69(10) [59.5(1)]	Ru(1)–Ru(3)–Ru(2)	60.29(8) [59.79(3)]
Ru(1)–C(32)–C(33)	153.1(4) [153.3(4)]	Ru(1)–Ru(2)–Ru(3)	60.02(2) [60.74(8)]
		C(32)–C(33)–C(34)	144.3(5) [144.9(5)]

The values of the second molecule are given in square brackets.

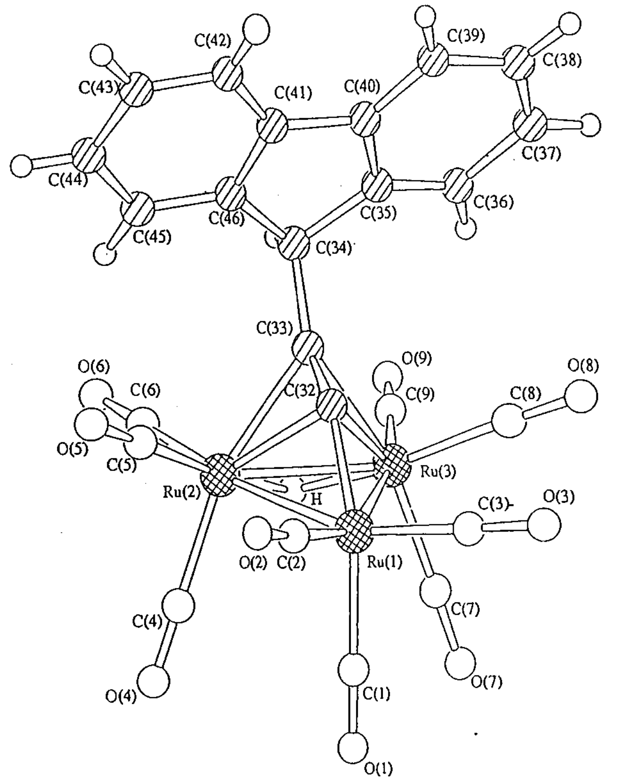


Fig. 1 Molecular structure of $[Ru_3(CO)_9(\mu-H)\{\mu_3-\eta^1:\eta^2:\eta^2-CC(C_{13}H_9)\}]$ **1**.

the metallated hydroxy group and the free hydroxy group were not observed. A perspective view of the molecular structure of cluster **2** together with the atomic numbering scheme is illustrated in Fig. 2. Selected bond distances and angles are listed in Table 3. Within the triangular ruthenium framework of **2** the edge Ru(1)–Ru(3) 2.879(9) Å is significantly longer than the other two M–M bonds due to the steric effect. The resulting ligand, derived from the head-to-tail coupling of two 9-ethynylfluoren-9-ol units, is co-ordinated in a novel $\mu_3-\eta^1:\eta^2:\eta^4$ fashion to the Ru_3 triangle. This gives rise to a ruthenole unit formed from the π co-ordination of the ruthenacyclopentadiene ring Ru(2)–C(10)–C(11)–C(12)–C(13) to Ru(3), which contains one long and two short C–C bonds [C(10)–C(11) 1.396(9), C(11)–C(12) 1.425(8), C(12)–C(13) 1.386(8) Å] in common with other crystallographically characterized examples containing Group VIII metals.[30–33] The hydroxy group in one of the fluorenyl fragments is bonded to Ru(1) [Ru(1)–O(9) 2.181(4) Å]. One of the fluorenyl fragments lies almost perpendicular to the triruthenium plane and the other fluorenyl moiety is skewed. However, no interactions of the π systems with the metal centres are observed. The organic moiety and the bridging hydroxyl group count as a 6 electron and 2 electron donor respectively to achieve 48 CVEs (cluster valence electrons) for cluster **2**.

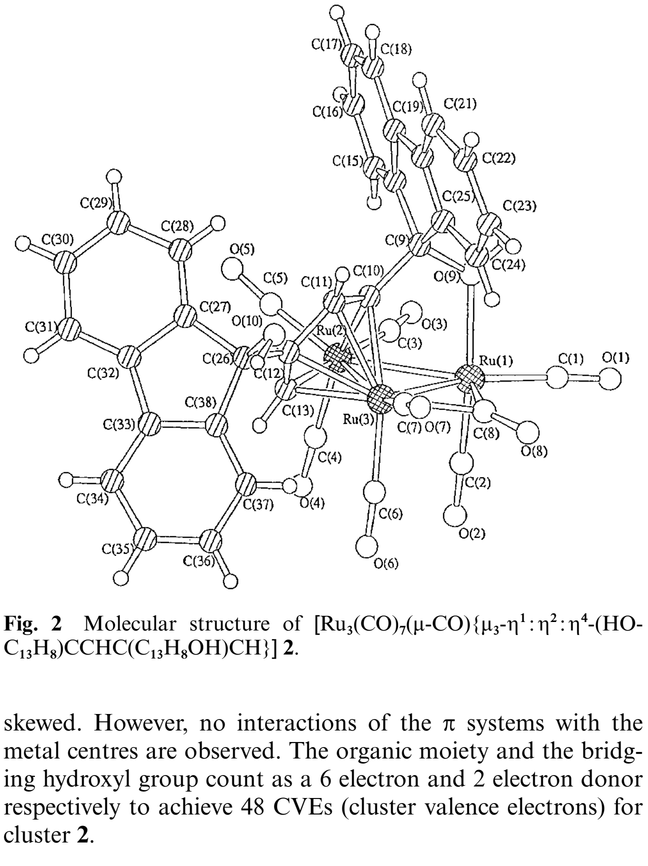


Fig. 2 Molecular structure of $[Ru_3(CO)_7(\mu-CO)\{\mu_3-\eta^1:\eta^2:\eta^4-(HOC_{13}H_8)CCHC(C_{13}H_8OH)CH\}]$ **2**.

Spectroscopic and structural characterization of compound 3

Isolation by preparative TLC afforded the third fraction which gave slightly air-sensitive red crystals of compound **3**. The ^1H NMR spectrum **3** in $CDCl_3$ displays a singlet signal at δ 9.28 due to the proton on the alkynyl unit, and multiplets due to the eight phenyl protons in the range δ 6.70–7.98 (Table 1). Resonances of the two triplets centred at δ 4.30 and 2.47, as well as one quartet centred at δ 2.23 with J_{HH} 8.9 Hz, were assigned as a lactone solvent molecule. Furthermore, a singlet signal at δ −2.00 is observed which arises from the μ_3-bridging hydroxyl group. A labelling experiment using D_2O indicated that the hydroxyl proton is exchangeable in solution. The positive FAB mass spectrum of **3** shows a molecular ion peak at *m/z* 920 which is also consistent with its solid-state structure.

Single crystals of compound **3** suitable for X-ray analysis were obtained from slow evaporation of a CH_2Cl_2 solution contaminated with lactone at −10 °C. The stoichiometry $\mathbf{3}\cdot CH_2Cl_2\cdot C_4H_6O_2$ in the asymmetric unit was established by X-ray dif-

Table 3 Selected bond lengths (Å) and angles (°) for cluster **2**

Ru(1)–Ru(2)	2.833(9)	Ru(1)–Ru(3)	2.879(9)
Ru(2)–Ru(3)	2.776(8)	Ru(1)–O(9)	2.181(4)
Ru(2)–C(10)	2.110(6)	Ru(2)–C(13)	2.069(7)
Ru(3)–C(10)	2.302(6)	Ru(3)–C(11)	2.251(6)
Ru(3)–C(12)	2.238(7)	C(9)–O(9)	1.441(7)
C(9)–C(10)	1.513(9)	C(9)–C(14)	1.541(9)
C(10)–C(11)	1.396(9)	C(11)–C(12)	1.425(8)
C(12)–C(13)	1.386(8)	C(12)–C(26)	1.526(9)
C(14)–C(15)	1.356(10)	C(15)–C(16)	1.396(10)
C(16)–C(17)	1.34(1)	C(17)–C(18)	1.38(1)
C(18)–C(19)	1.39(1)	C(19)–C(20)	1.47(1)
C(20)–C(21)	1.37(1)	C(21)–C(22)	1.37(1)
C(22)–C(23)	1.40(1)	C(23)–C(24)	1.41(1)
C(26)–O(10)	1.446(7)	C(26)–C(27)	1.523(9)
C(26)–C(38)	1.320(9)	C(27)–C(28)	1.362(10)
C(28)–C(29)	1.39(1)	C(29)–C(30)	1.36(1)
C(30)–C(31)	1.38(1)	C(31)–C(32)	1.38(1)
C(32)–C(33)	1.46(1)	C(33)–C(34)	1.39(1)
C(34)–C(35)	1.39(1)	C(35)–C(36)	1.36(1)
C(36)–C(37)	1.39(1)	C(37)–C(38)	1.383(10)
Ru(1)–Ru(2)–Ru(3)	61.76(2)	Ru(1)–Ru(3)–Ru(2)	60.08(2)
Ru(2)–Ru(1)–Ru(3)	58.16(2)	Ru(1)–O(9)–C(9)	119.6(4)
O(9)–C(9)–C(10)	105.3(5)	C(10)–Ru(2)–C(13)	76.9(3)
Ru(2)–C(10)–C(11)	114.0(4)	C(10)–C(11)–C(12)	116.9(6)
C(11)–C(12)–C(13)	112.9(6)	Ru(2)–C(13)–C(12)	118.0(5)

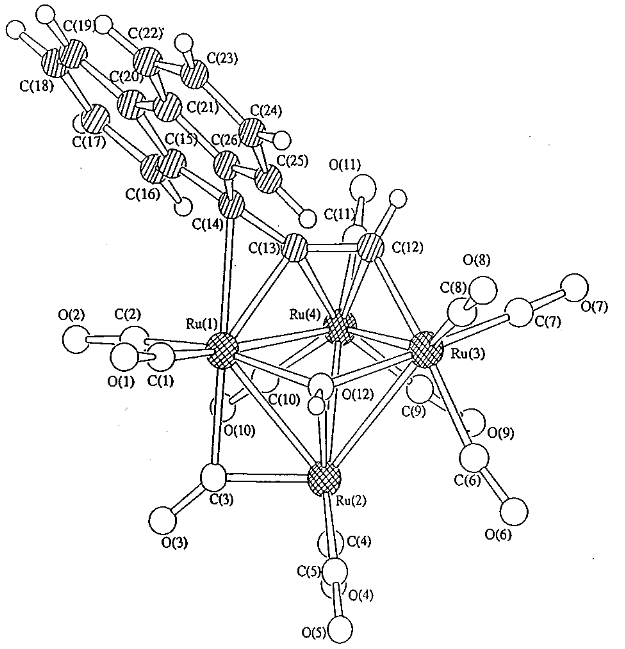


Fig. 3 Molecular structure of $[Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_3\text{-}OH)(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_{13}H_8CCH)]$ **3**.

Table 4 Selected bond lengths (Å) and angles (°) for cluster **3**

Ru(1)–Ru(2)	2.808(5)	Ru(1)–Ru(4)	2.916(5)
Ru(2)–Ru(3)	2.896(6)	Ru(2)–Ru(4)	2.975(5)
Ru(3)–Ru(4)	2.835(5)	Ru(1)–O(12)	2.159(3)
Ru(1)–C(13)	2.188(4)	Ru(1)–C(14)	2.421(4)
Ru(2)–O(12)	2.117(3)	Ru(3)–O(12)	2.121(3)
Ru(3)–C(12)	2.064(5)	Ru(4)–C(12)	2.236(5)
C(12)–C(13)	1.379(7)	C(13)–C(14)	1.389(6)
C(14)–C(15)	1.485(6)	C(14)–C(26)	1.480(6)
C(15)–C(16)	1.384(7)	C(15)–C(20)	1.414(7)
C(16)–C(17)	1.375(8)	C(17)–C(18)	1.367(10)
C(18)–C(19)	1.377(10)	C(19)–C(20)	1.398(8)
C(20)–C(21)	1.445(7)	C(21)–C(22)	1.395(8)
C(21)–C(26)	1.391(7)	C(22)–C(23)	1.411(9)
C(23)–C(24)	1.386(9)	C(24)–C(25)	1.388(8)
C(25)–C(26)	1.385(7)		
Ru(1)–Ru(4)–Ru(3)	79.47(1)	Ru(1)–Ru(2)–Ru(4)	60.49(1)
Ru(1)–O(12)–Ru(3)	60.49(1)	Ru(1)–O(12)–Ru(2)	82.13(10)

fraction studies. The molecular structure of **3** is shown in Fig. 3. Some important interatomic bond distances and angles are given in Table 4. The structure shows that the unprecedented "Ru_4O" framework may be described as a square based pyramid, with the four ruthenium atoms in a butterfly arrangement and the oxygen atom of the bridging hydroxyl group occupying the remaining vertex of the square pyramid. The Ru–O bond distances [average 2.159(5) Å] are comparable to those observed in $[Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu\text{-}OH)_2(\mu_4\text{-}S)]$[34] (average 2.123 Å). A μ_3-hydroxide ligand bridging across three centres [Ru(1), Ru(2) and Ru(3)] is believed to originate from the hydroxyl group of 9-ethynylfluoren-9-ol. Ten carbonyl ligands in **3** are terminally bound to the Ru atoms, and the C(3)–O(3) is found to bridge Ru(1)–Ru(2) which is consistent with the band at 1805 cm^{-1} observed in the IR spectrum. The principal structural feature in **3** is the co-ordinated acetylenic fragment, C(12)–C(26), attached to the open Ru_3 [Ru(1)–Ru(4)–Ru(3)] triangle of the Ru_3O [Ru(1)–Ru(4)–Ru(3)–O(12)] square plane. The atom Ru(3) is σ-bound to the acetylenic carbon atom C(12), while Ru(4) is involved in a π interaction [Ru(4)–C(12) 2.236(5), Ru(4)–C(13) 2.180(4) Å] based upon the C≡C bond activation. Another π-bonding interaction is also observed from C(13)–C(14) to Ru(1) arising from the loss of the OH group. These two π-bonding interactions are twisted and the dihedral angle between the planes Ru(1)–C(13)–C(14) and Ru(4)–C(12)–C(13) is 55.3°. Both the C(12)–C(13) [1.379(7) Å] and C(13)–C(14) [1.389(6) Å] bond lengths are consistent with a reduction in the bond order expected upon co-ordination of the acetylenic triple bond. Several related clusters, such as $[Ru_4(CO)_{10}(\mu\text{-}CO)_2\{\mu_4\text{-}\eta^1:\eta^1:\eta^2\text{-}P(Ph)C(C{\equiv}CMe)CMe\}]$,[35] $[Ru_4(CO)_{10}(\mu\text{-}H)(\mu\text{-}PPh_2)\{\mu_4\text{-}\eta^1(P):\eta^1(P):\eta^1(P):\eta^1:\eta^2\text{-}(C_6H_4)PPh\}]$[36] and $[Os_4(CO)_{12}\{\mu_4\text{-}\eta^3\text{-}SC(Ph){=}CH\}]$,[37] have been studied for the activation of small molecules at a square M_3X face where M = Ru or Os and X = P or S. In total, the organic ligand and the bridging hydroxyl group behave as a five and a three electron donor respectively so that cluster **3** possesses 62 CVEs which is consistent with five metal–metal bonds observed as suggested by the EAN rule.

Spectroscopic and structural characterization of compound 4

The chromatographic separation of the reaction mixture yielded the fourth fraction which gave slightly air-sensitive black crystals of compound **4** after recrystallization from a solution of chloroform–ethanol by slow evaporation at −10 °C. Cluster **4** exhibits five absorptions at 2070s, 2044vs, 2035w, 2010s and 1993w cm^{-1} in the IR spectrum (Table 1). Its ^1H NMR spectrum in $CDCl_3$ shows multiplets in the range δ 6.30–7.60 due to the seven protons on the phenyl rings and a singlet at δ 6.18 attributed to the methylene proton on C(14). Two upfield singlets at δ −3.00 and −10.00 were observed and assigned to the proton on the bridging hydroxyl group and the bridging hydride, respectively. The positive FAB mass spectrum displays a parent ion peak at *m*/*z* 1048.

The asymmetric unit consists of two independent but structurally similar molecules of compound **4** and solvates $CHCl_3$·2EtOH. A perspective drawing of cluster **4** with the atomic numbering scheme is shown in Fig. 4. Selected interatomic bonds and angles are in Table 5. The metal framework consists of a bent open chain of five metal atoms which is rarely observed.[38,39] The Ru–Ru bond lengths range from 2.757(5) to 2.894(4) Å [2.785(5) to 2.876(5) Å, in the second molecule], with Ru(4)–Ru(5) being the shortest due to the steric requirements of the bridging ring system. The ethynylfluorenyl fragment is found to co-ordinate to the metal core in an unprecedented mode. One of the phenyl rings of the fluorenyl unit is bonded to Ru(5) in a η^6 fashion while C–H bond activation results in a σ interaction between one of the ring carbon atoms C(26) and

Table 5 Selected bond lengths (Å) and angles (°) for cluster **4**

Ru(1)–Ru(2)	2.894(4) [2.876(5)]	Ru(2)–Ru(3)	2.777(5) [2.785(4)]
Ru(3)–C(4)	2.780(4) [2.794(4)]	Ru(4)–Ru(5)	2.757(5) [2.785(5)]
Ru(1)–C(13)	1.97(3) [2.02(3)]	Ru(1)–C(26)	2.11(3) [2.10(4)]
Ru(1)–O(13)	2.18(3) [2.15(2)]	Ru(2)–C(13)	2.07(3) [2.01(3)]
Ru(3)–C(13)	2.42(4) [2.33(3)]	Ru(3)–C(14)	2.42(4) [2.37(4)]
Ru(3)–O(13)	2.13(3) [2.11(2)]	Ru(4)–C(15)	2.37(3) [2.39(4)]
Ru(4)–O(13)	2.10(2) [2.16(2)]	Ru(5)–C(22)	2.29(3) [2.49(4)]
Ru(5)–C(23)	2.26(4) [2.38(4)]	Ru(5)–C(24)	2.30(5) [2.40(5)]
Ru(5)–C(25)	2.25(5) [2.29(4)]	Ru(5)–C(26)	2.34(3) [2.36(3)]
Ru(5)–C(27)	2.27(3) [2.35(3)]	C(13)–C(14)	1.46(5) [1.39(4)]
C(14)–C(15)	1.46(4) [1.45(4)]	C(15)–C(16)	1.48(4) [1.55(4)]
C(15)–C(27)	1.46(5) [1.51(5)]	C(16)–C(21)	1.43(4) [1.43(5)]
C(21)–C(22)	1.53(5) [1.52(4)]	C(22)–C(27)	1.39(4) [1.55(5)]
C(26)–C(27)	1.35(4) [1.48(4)]		
Ru(2)–Ru(3)–Ru(4)	130.1(2) [128.9(2)]	Ru(1)–Ru(2)–Ru(3)	71.6(1) [72.8(1)]
Ru(3)–O(13)–Ru(4)	82.3(9) [81.9(8)]	Ru(3)–Ru(4)–Ru(5)	132.6(2) [132.9(1)]
		Ru(4)–C(15)–C(14)	100(2) [104(2)]

The values of the second molecule are given in square brackets.

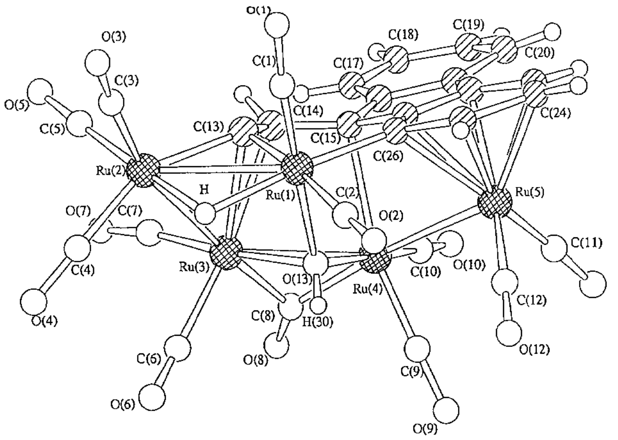


Fig. 4 Molecular structure of $[Ru_5(CO)_{11}(\mu\text{-}H)(\mu\text{-}CO)(\mu_3\text{-}OH)(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^6\text{-}C_{13}H_7CHC)]$ **4**.

Ru(1), while the second phenyl group remains unco-ordinated. The C(15) atom of the fluorenyl group is bonded to Ru(4) in a σ fashion arising from the loss of the OH group. The ethynyl side chain [C(13)–C(14)] is activated to form two σ interactions with Ru(1) and Ru(2), and one π interaction with Ru(3). Moreover, as observed in **3**, a μ_3-hydroxide ligand bridging across Ru(1), Ru(3) and Ru(4) is observed and it is also believed to originate from the hydroxyl group of 9-ethynylfluoren-9-ol. The fluorenyl ring system is essentially planar with a maximum deviation of 0.08 Å [0.10 Å in the second molecule], and it interacts with the Ru(1)–Ru(2)–Ru(3)–Ru(4)–Ru(5) chain in a μ_5-$\eta^1{:}\eta^1{:}\eta^2{:}\eta^2{:}\eta^6$ manner. The ligand as a whole donates twelve electrons to the cluster framework which, together with a μ_3-bridging hydroxide group, a bridging hydride, and the CO ligands, gives the cluster an electron count of 82, which is consistent with a Ru_5 chain cluster according to the EAN rule.

Table 6 Selected bond lengths (Å) and angles (°) for cluster **5**

Ru(1)–Ru(2)	2.780(1)	Ru(1)–Ru(3)	2.780(1)
Ru(1)–Ru(4)	2.871(1)	Ru(2)–Ru(3)	2.819(1)
Ru(2)–Ru(4)	2.835(1)	Ru(3)–Ru(4)	2.756(1)
Ru(3)–Ru(5)	2.835(1)	Ru(3)–C(20)	2.124(9)
Ru(4)–Ru(5)	2.884(1)	Ru(5)–Ru(6)	2.914(1)
Ru(5)–C(16)	2.363(10)	Ru(5)–C(17)	2.243(9)
Ru(5)–C(18)	2.347(9)	Ru(6)–C(19)	2.335(9)
Ru(6)–C(20)	2.344(9)	Ru(6)–C(21)	2.29(1)
Ru(6)–C(22)	2.24(1)	Ru(6)–C(23)	2.286(9)
Ru(6)–C(24)	2.307(9)	C(16)–C(17)	1.42(1)
C(17)–C(18)	1.39(1)	C(18)–C(19)	1.46(1)
C(18)–C(30)	1.49(1)	C(19)–C(24)	1.46(1)
Ru(4)–Ru(5)–Ru(6)	140.95(4)	Ru(3)–C(16)–C(17)	130.1(7)
Ru(3)–C(20)–C(19)	71.9(5)	C(20)–Ru(3)–C(16)	89.9(4)
C(16)–C(17)–C(18)	122.6(8)	C(17)–C(18)–C(19)	124.5(9)
C(18)–C(19)–C(20)	130.2(8)		

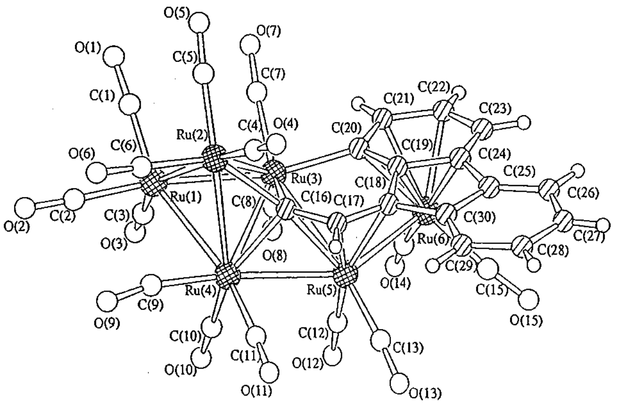


Fig. 5 Molecular structure of $[Ru_6(CO)_{15}(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^3{:}\eta^6\text{-}C_{13}H_7\text{-}CHC)]$ **5**.

Spectroscopic and structural characterization of compound 5

The spectroscopic data (Table 1) for cluster **5** are fully consistent with its solid-state structure. An intense molecular ion peak at *m*/*z* 1215 was observed in the positive FAB mass spectrum. The ^1H NMR spectrum in $CDCl_3$ shows multiplets between δ 8.00 and 7.30 assigned to the seven phenyl protons, and a singlet signal at δ 6.50 for a proton on an allyl unit. A perspective drawing of cluster **5** is shown in Fig. 5, and some important bonding parameters are given in Table 6. The metal core consists of a spiked edge-bridged tetrahedron which is seldom observed.[40] The Ru–Ru bond distances range from 2.756(1) to 2.914(1) Å. The ethynylfluorenyl moiety interacts with five ruthenium atoms of the hexaruthenium unit in a μ_5-$\eta^1{:}\eta^1{:}\eta^2{:}\eta^3{:}\eta^6$ manner. Although some examples of such step site geometry, $[Os_5H_3(CO)_{14}(C_5H_4N)]$[41] and $[Ru_5(CO)_{11}(\mu_4\text{-}C_6H_6)(\mu\text{-}PPh_2)_2]$,[42] containing a small unsaturated hydrocarbyl ring are known, the structural characterization of **5** provides a rare example of the interaction between a fluorene ring and step site metal atoms *via* a quadruply bridging carbide. The co-ordination mode is very similar to that observed in cluster **4** except that a η^3-allyl bonding mode to Ru(5) is apparent for the side chain C(16)–C(17)–C(18). However, the same fragment is bonded to the cluster core in a $\sigma{:}\eta^2$-olefin fashion to the two metal centres [Ru(2) and Ru(3)] in **4**. The terminal allyl carbon atom C(16) is quadruply bridging across a distorted

Table 7 Summary of crystal data and data collection parameters for clusters **1**–**5**

	1	**2**	**3**	**4**	**5**
Empirical formula	$2C_{24}H_{11}O_9Ru_3{\cdot}C_{13}H_2O_{13}Ru_4$	$C_{40}H_{24}Cl_4O_{10}Ru_3$	$C_{31}H_{18}Cl_2O_{14}Ru_4$	$C_{59}H_{33}Cl_3O_{28}Ru_{10}$	$C_{30}H_8O_{15}Ru_6$
M	2261.53	1109.65	1089.66	2306.95	1214.80
Crystal colour, habit	Red, block	Yellow, block	Red, block	Dark green, block	Dark red, block
Crystal size/mm	0.12 × 0.25 × 0.26	0.14 × 0.22 × 0.34	0.12 × 0.14 × 0.22	0.11 × 0.18 × 0.19	0.13 × 0.19 × 0.20
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/a$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	9.54(2)	12.517(1)	10.281(1)	11.936(1)	10.338(1)
b/Å	18.98(2)	15.499(1)	13.107(1)	35.696(2)	12.852(1)
c/Å	21.40(2)	22.129(2)	14.187(1)	17.285(1)	13.118(1)
α/°	66.80(1)	—	76.32(2)	—	73.45(1)
β/°	85.83(1)	101.20(2)	82.76(2)	107.76(1)	83.33(1)
γ/°	77.33(1)	—	81.08(2)	—	84.58(1)
U/Å^3	3473(7)	4211.3(6)	1827.1(4)	7013.6(9)	1655.9(3)
Z	2	4	2	4	2
D_c/g cm^{-3}	2.162	1.750	1.981	2.185	2.436
F(000)	2156	2176	1052	4408	1144
μ(Mo-Kα)/cm^{-1}	21.96	13.71	18.33	22.84	27.40
2θ Range collected/°	2.0–51.2	2.0–51.2	2.0–51.2	2.0–51.2	2.0–51.2
No. reflections collected	28073	36351	16731	30060	17139
No. unique reflections	11810	7478	6315	5094	5347
No. observed reflections [$I > 3\sigma(I)$]	8371	4389	5201	2798	3025
R	0.029	0.045	0.038	0.072	0.037
R'	0.036	0.044	0.044	0.082	0.040
Goodness of fit, S	1.09	2.56	1.89	1.93	1.11
No. variables	919	504	455	442	460
Maximum, minimum density in ΔF map/e Å^{-3}, close to Ru	0.57, −0.78	1.05, −0.87	0.97, −1.00	0.51, −0.48	0.73, −0.84

butterfly face [Ru(2)–Ru(3)–Ru(4)–Ru(5)]. The fluorenyl group is almost planar within experimental error (maximum deviation 0.07 Å). It is also worth noting that Ru(3), C(16), C(17), C(18), C(19) and C(20) form another metallated six-membered ring (maximum deviation 0.14 Å) which is nearly coplanar with the fluorenyl ring (dihedral angle 6.0°). With the organic fragment donating a total of twelve electrons, **5** contains 90 CVEs and is consistent with the observed nine metal–metal bonds according to the EAN rule.

Experimental

All the reactions were performed under an atmosphere of high purity nitrogen using standard Schlenk techniques. Analytical grade solvents were purified by distillation over the appropriate drying agents and under an inert nitrogen atmosphere prior to use. Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer using a 0.5 mm solution cell, positive-ion fast atom bombardment mass spectra using a Finnigan MAT 95 spectrometer, ^1H and ^{13}C NMR spectra in $CDCl_3$ on a Bruker DPX 300 instrument, referenced to internal $SiMe_4$ (δ 0). The reactions were monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F_{254}, E. Merck) and the products separated on preparative thin-layer chromatographic plates coated with Merck Kieselgel 60 GF_{254}. The compound 9-ethynylfluoren-9-ol obtained from Lancaster was used without further purification.

Synthesis

The compound $[Ru_3(CO)_{12}]$ (0.5 g, 0.78 mmol) was refluxed with 9-ethynylfluoren-9-ol (0.16 g, 0.78 mmol) in tetrahydrofuran (60 ml) for 12 h. Infrared spectroscopy and TLC indicated complete consumption of the starting material. The solvent was removed *in vacuo* and the residue separated by TLC using dichloromethane–hexane (60:40 v/v) as eluent to afford five bands with R_f values of 0.35, 0.50, 0.65, 0.75 and 0.85 respectively. The clusters **1**–**5** were isolated as solids in 8, 15, 12, 10 and 9% yields respectively (Found for $2C_{24}H_{11}O_9Ru_3{\cdot}C_{13}H_2O_{13}Ru_4$ **1**: C, 32.63; H, 1.27. Calc.: C, 32.37; H, 1.07. Found for $C_{38}H_{20}O_{10}Ru_3$ **2**: C, 48.65; H, 2.30. Calc.: C, 48.56; H, 2.15. Found for $C_{26}H_{10}O_{12}Ru_4$ **3**: C, 34.21; H, 1.34. Calc.: C, 33.99; H, 1.10. Found for $C_{27}H_{10}O_{18}Ru_5$ **4**: C, 31.16; H, 1.15. Calc.: C, 30.95; H, 0.96. Found for $C_{30}H_8O_{15}Ru_6$ **5**: C, 29.91; H, 0.76. Calc.: C, 29.65; H, 0.66%).

X-Ray data collection and structural determination of complexes 1–5

Single crystals of compounds **1**, **2**, **3**, and **5** for X-ray analyses were obtained by slow evaporation of their respective dichloromethane–hexane solutions at −10 °C for 3 d, while **4** was obtained as described above. The air-sensitive crystals of clusters **3** and **4** were sealed in 0.3 mm Lindermann glass capillaries while complexes **1**, **2** and **5** were mounted on top of a glass fibre using epoxy resin. Data were collected at ambient temperature on a MAR Research image plate scanner with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using ω scan techniques. A summary of the crystallographic data and structure refinement is given in Table 7. All intensity data were corrected for Lorentz-polarization effects. An approximate absorption correction by interimage scaling was applied. Scattering factors were taken from ref. 43(*a*) and anomalous dispersion effects[43b] were included in F_c. The structures were solved by a combination of direct methods (SHELXS 86[44] for **1** and **3**, SIR 88[45] for **2**, **4** and **5**) and Fourier difference techniques and refined on F by full-matrix least-squares analysis. The hydrogen atoms of the organic moieties were generated in their ideal positions (C–H 0.95 Å) while the metal hydride positions in **1** and **4** were estimated by potential-energy calculations.[46] All calculations were performed on a Silicon-Graphics computer, using the program package TEXSAN.[47]

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