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Reactivity of Indene, Fluorene, Azulene, and Acenaphthylene with a Basal-Edge-Bridged Square-Pyramidal Hexaruthenium Dihydride

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The basal-edge-bridged square-pyramidal hexanuclear cluster $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$ (**1**; H_2ampy = 2-amino-6-methylpyridine) reacts with indene in refluxing chlorobenzene to give $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}\eta^9\text{-}C_9H_7)(\mu\text{-}CO)_3(CO)_{11}]$ (**2**), $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^5\text{-}C_9H_7)(\mu_3\text{-}CO)(\mu\text{-}CO)_2(CO)_{11}]$ (**3**), and the known dimer $[Ru_2(\eta^5\text{-}C_9H_7)_2(\mu\text{-}CO)_2(CO)_2]$. While the indenyl ligand of complex **2** is $\eta^5{:}\eta^6$ edge bridging, complex **3** has a terminal η^5-indenyl ligand. The hexanuclear η^6-fluorene derivative $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^6\text{-}C_{13}H_{10})(\mu\text{-}CO)_2(CO)_{11}]$ (**4**) has been isolated from a reaction of compound **1** with fluorene in decane at reflux temperature. Under analogous conditions, azulene reacts with **1** to give $[Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_3\text{-}\eta^{10}\text{-}C_{10}H_8)(\mu\text{-}CO)_2(CO)_{10}]$ (**5**) and $[Ru_4(\mu_3\text{-}\eta^{10}\text{-}C_{10}H_8)(CO)_9]$ (**6**). In both complexes, the azulene ligand is attached to three Ru atoms through its ten C atoms. Four complexes have been isolated from reactions of acenaphthylene with complex **1** in refluxing decane: $[Ru_4(\mu_4\text{-}\kappa^2\text{-ampy})(\mu\text{-}\eta^6\text{-}C_{12}H_8)(\mu\text{-}\eta^4\text{-}C_{12}H_8)(\mu\text{-}CO)_2(CO)_5]$ (**7**), $[Ru_6(\mu_4\text{-}\kappa^2\text{-ampy})(\mu_3\text{-}\eta^{10}\text{-}C_{12}H_8)(CO)_{12}]$ (**8**), $[Ru_7(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_4\text{-}\eta^{12}\text{-}C_{12}H_8)(\mu\text{-}CO)(CO)_{12}]$ (**9**), and $[Ru_6(\mu_4\text{-}\kappa^1\text{-ampy})(\mu_4\text{-}\eta^{12}\text{-}C_{12}H_8)(\mu\text{-}CO)_2(CO)_9]$ (**10**). These compounds do not maintain the metallic skeleton of the starting complex **1** and contain acenaphthylene ligands that display unprecedented coordination modes, such as $\eta^5{:}\eta^1$ edge bridging (**7**), $\eta^2{:}\eta^2$ edge bridging (**7**), $\eta^6{:}\eta^5{:}\eta^1$ triangular face capping (**8**), and $\eta^5{:}\eta^3{:}\eta^2{:}\eta^2$ quadruply bridging (**9** and **10**). The coordination mode of the ampy ligand of compound **10**, which has a μ_4-imido fragment and an uncoordinated pyridyl group, is also unprecedented. The high temperatures required by all these reactions promote cluster decarbonylation processes. This accounts for the observation that, with few exceptions (**3**, **4**, **7**), most of the reaction products contain the polycyclic hydrocarbon ligands attached to various metal atoms through many carbon atoms.

Introduction

We have recently reported that $[Ru_3(CO)_{12}]$ reacts with triruthenium clusters of the type $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-HapyR})(CO)_9]$ (H_2apyR = a generic 2-aminopyridine) to give the hexanuclear derivatives $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-apyR})(\mu\text{-}CO)_2(CO)_{14}]$, which have a basal-edge-bridged square-pyramidal metallic skeleton.[1,2] In these compounds, five metal atoms are bridged by the N-donor ligand in such a way that the edge-bridging Ru atom is attached to the pyridine N atom, while the four basal Ru atoms of the square pyramid are capped by an imido fragment that arises from the activation of both N−H bonds of the original NH_2 group (Figure 1).

Prior to our work, hexaruthenium cluster complexes with this metallic framework were very scarce, all being byproducts of processes that generally involve various steps from $[Ru_3(CO)_{12}]$.[3−5] Their reactivity has not been studied in detail, probably because of their low-yield preparations.

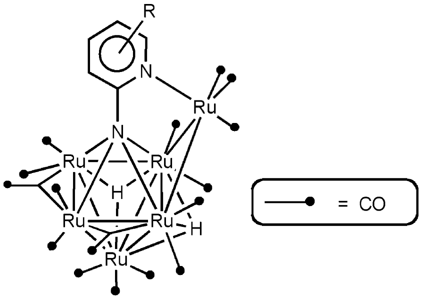

Figure 1. Schematic structure of compounds of the type $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-apyR})(\mu\text{-}CO)_2(CO)_{14}]$.

Our successful preparation of this type of cluster complexes opened up the possibility of exploring their reactivity. We have recently reported the reactions of tertiary phosphines,[1] diphenylacetylene,[6] diphenylbutadiyne,[7] and $[PPN][BH_4]$[8] with $[Ru_6$-

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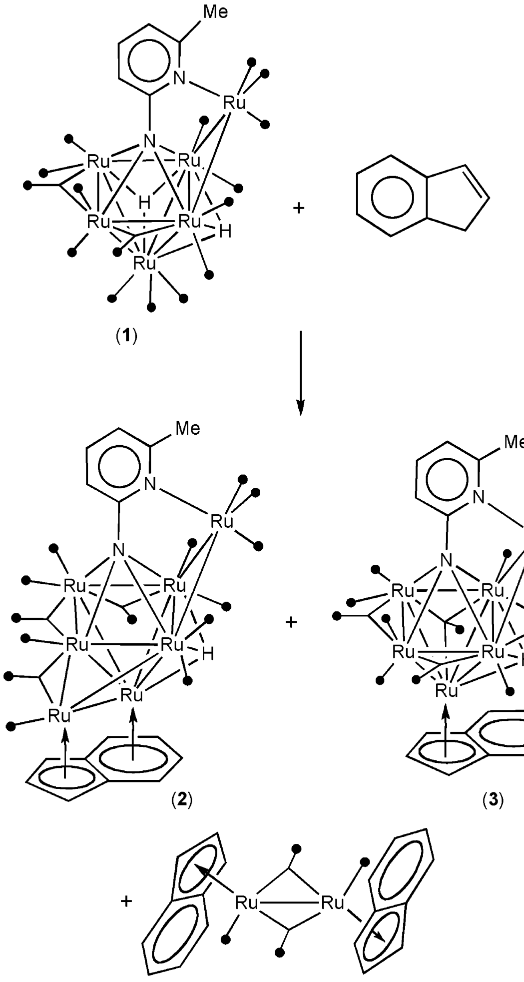
10.1021/om061078c CCC: $37.00

Scheme 1



(μ_3-H)$_2$(μ_5-κ^2-ampy)(μ-CO)$_2$(CO)$_{14}$] (**1**; H_2ampy = 2-amino-6-methylpyridine), a complex that can be prepared in almost quantitative yield in a one-pot reaction from [$Ru_3(CO)_{12}$] and 2-amino-6-methylpyridine.[1]

Studying the aforementioned reactions in toluene and xylenes at reflux temperature, we observed in some cases the presence of small amounts of solvent-containing species among the reaction products. This fact led us to investigate the reactivity of compound **1** with arenes and with other unsaturated cyclic hydrocarbons. We have already reported the reactivity of compound **1** with benzene and methylated benzenes, cycloheptatriene, and cyclopentadiene dimer (dicyclopentadiene). These reactions allowed the isolation of η^6-arene, η^5-cycloheptadienyl, μ_2- and μ_3-η^7-cycloheptatrienyl, and η^5-cyclopentadienyl derivatives, as well as a product containing an unprecedented enyne ligand derived from dicyclopentadiene.[9] We now report the reactivity of compound **1** with unsaturated bi- and tricyclic hydrocarbons. The isolated products comprise η^5- and μ-η^9-indenyl, η^6-fluorene, μ_3-η^{10}-azulene, and μ-η^4-, μ-η^6-, μ_3-η^{10}-, and μ_4-η^{12}-acenaphthylene derivatives. The coordination modes observed for some of these hydrocarbon ligands are unprecedented.

Results and Discussion

Reactivity of Compound 1 with Indene. The reaction of compound **1** with indene (1:5 molar ratio) in chlorobenzene at reflux temperature (132 °C) was slow. A reaction time of 6 h was necessary to observe the complete consumption of complex **1** (IR and spot TLC monitoring). After this time, a chromatographic workup of the reaction mixture allowed the isolation of the novel heptanuclear derivative [Ru_7(μ_3-H)(μ_5-κ^2-ampy)(μ-η^9-C_9H_7)(μ-CO)$_3$(CO)$_{11}$] (**2**) and a small amount of the known[10] dimeric complex [Ru_2(η^5-C_9H_7)$_2$(μ-CO)$_2$(CO)$_2$] (Scheme 1).

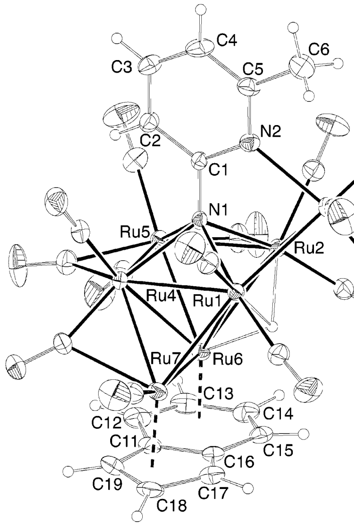


Figure 2. Molecular structure of compound **2**.

In an alternative reaction, a small amount of complex **1** (50 mg) was treated with a large excess of indene (1 mL) in chlorobenzene at 110 °C. After 4 h, this reaction allowed the isolation of the hexanuclear derivative [Ru_6(μ_3-H)(μ_5-κ^2-ampy)(η^5-C_9H_7)(μ_3-CO)(μ-CO)$_2$(CO)$_{11}$] (**3**) (Scheme 1), but the major product was the binuclear complex [Ru_2(η^5-C_9H_7)$_2$(μ-CO)$_2$(CO)$_2$]. Complex **2** was not observed in the reaction mixture.

The structure of complex **2** was determined by X-ray diffraction (Figure 2, Table 1). Its Ru_7(μ_5-ampy) fragment can be described as resulting from the formal attachment of an additional Ru atom, Ru(7), to a triangular face of the Ru_6(μ_5-ampy) fragment of compound **1**, thus having a basal-edge-bridged and triangular-face-capped square-pyramidal heptametallic skeleton. An indenyl ligand spans the Ru(6)−Ru(7) edge in such a way that all the atoms of the six-membered ring are attached to Ru(6), while all the carbon atoms of the five-membered ring are attached to Ru(7). The cluster shell is completed by a hydride ligand, which caps the Ru(1)−Ru(2)−Ru(6) face, and by 3 edge-bridging and 11 terminal CO ligands.

The heptaruthenium skeleton of complex **2** has only two precedents, namely, [Ru_7(μ_3-H)(μ_5-κ^2-L)(μ-CO)$_2$(CO)$_{16}$] (L = CbipyMe, CphenMe), which arise from the ruthenium-cluster-mediated activation of the three C−H bonds of one of the methyl groups of 6,6′-dimethyl-2,2′-bipyridine and 2,9-dimethyl-1,10-phenanhroline.[11] The η^5:η^6 edge-bridging coordination mode of the indenyl ligand is unprecedented in cluster chemistry, although a few binuclear complexes having μ-η^5:η^6-indenyl ligands have been reported.[12]

The most relevant feature of the ^{1}H NMR spectrum of **2** is that the indenyl resonances (seven) appear at low chemical shifts

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Table 1. Selected Interatomic Distances (Å) in Compounds 2, 4, and 5

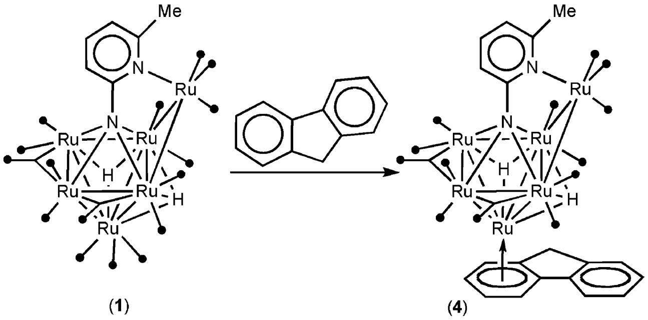
	2	4	5
Ru(1)−Ru(2)	2.7355(7)	2.7462(8)	2.7327(7)
Ru(1)−Ru(3)	2.7178(8)	2.7546(9)	2.7412(7)
Ru(1)−Ru(4)	2.6879(8)	2.7521(9)	2.6787(7)
Ru(1)−Ru(6)	2.7826(8)	2.8700(10)	2.8685(7)
Ru(1)−Ru(7)	2.7735(7)		
Ru(2)−Ru(3)	2.7732(8)	2.7132(10)	2.7222(7)
Ru(2)−Ru(5)	2.7336(8)	2.7761(9)	2.6790(7)
Ru(2)−Ru(6)	2.8163(8)	2.8809(8)	2.8275(7)
Ru(4)−Ru(5)	2.7043(7)	2.7153(9)	2.7775(7)
Ru(4)−Ru(6)	2.7837(8)	2.8465(9)	2.8101(7)
Ru(4)−Ru(7)	2.7280(7)		
Ru(5)−Ru(6)	2.7776(8)	2.8699(9)	2.8313(6)
Ru(6)−Ru(7)	2.7314(7)		
N(1)−Ru(1)	2.144(4)	2.177(5)	2.156(4)
N(1)−Ru(2)	2.149(4)	2.162(5)	2.180(4)
N(1)−Ru(4)	2.215(4)	2.234(5)	2.247(4)
N(1)−Ru(5)	2.263(4)	2.244(5)	2.176(4)
N(2)−Ru(3)	2.203(5)	2.228(6)	2.214(4)
C(11)−Ru(6)	2.332(5)	2.239(7)	2.229(5)
C(11)−Ru(7)	2.548(6)		
C(12)−Ru(6)	2.250(6)	2.219(7)	2.211(5)
C(13)−Ru(6)	2.242(6)	2.219(8)	2.213(5)
C(14)−Ru(6)	2.246(6)	2.240(7)	2.224(5)
C(15)−Ru(6)	2.255(6)	2.257(7)	2.223(5)
C(16)−Ru(4)			2.183(5)
C(16)−Ru(6)	2.340(6)	2.265(7)	
C(16)−Ru(7)	2.493(6)		2.174(5)
C(17)−Ru(4)			2.174(5)
C(17)−Ru(7)	2.181(6)		
C(18)−Ru(4)			2.614(5)
C(18)−Ru(5)			2.514(5)
C(18)−Ru(7)	2.155(6)		
C(19)−Ru(5)			2.173(5)
C(19)−Ru(7)	2.224(6)		
C(20)−Ru(5)			2.201(5)

(5.77−3.77 ppm), thus confirming the coordination of all the H-containing C atoms[12a,b,d,g] and that the asymmetry observed for this complex in the solid state is maintained in solution.

Although complex **3** could not be characterized by X-ray diffraction, its structure (Scheme 1) was inferred from a combination of analytical and spectroscopic techniques. Its FAB mass spectrum shows the appropriate molecular ion isotopomers. The carbonyl stretching region of its IR spectrum is nearly identical with that of $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^5\text{-}C_5H_5)(\mu_3\text{-}CO)(\mu\text{-}CO)_2(CO)_{11}]$, which has a terminal cyclopentadienyl ligand on the apical Ru atom.[9] The ^1H NMR resonances of the four protons of the six-membered ring of the indenyl ligand are observed as two multiplets at 7.33 and 7.21 ppm, whereas those of the five-membered ring appear at 5.18 (t, 1 H) and 4.73 (d, 2 H) ppm, confirming the η^5 coordination of the indenyl ligand.[13]

The observation that, at a low concentration of indene and at 132 °C, complex **2** (63% yield) and some $[Ru_2(\eta^5\text{-}C_9H_7)_2(\mu\text{-}CO)_2(CO)_2]$ (7%) were the only isolated products, whereas some **3** (12%) and $[Ru_2(\eta^5\text{-}C_9H_7)_2(\mu\text{-}CO)_2(CO)_2]$ (29%) were the products at high concentration of indene and at a lower temperature (110 °C), can be explained by assuming that complex **3** is the initial product of the reaction of **1** with indene and that it should decompose slowly at 110 °C in the presence of indene to give $[Ru_2(\eta^5\text{-}C_9H_7)_2(\mu\text{-}CO)_2(CO)_2]$ and rapidly at 132 °C in the absence of indene to give **2** and some $[Ru_2(\eta^5\text{-}C_9H_7)_2(\mu\text{-}CO)_2(CO)_2]$.

Scheme 2



$[Ru_3(CO)_{12}]$ is the only ruthenium carbonyl cluster whose reactivity with indenes has been studied. With indene itself, it gives a mixture of $[Ru_2(\eta^5\text{-}C_9H_7)_2(\mu\text{-}CO)_2(CO)_2]$ and $[Ru_4(\mu_3\text{-}\eta^5\text{:}\eta^2\text{:}\eta^2\text{-}C_9H_7)(\eta^5\text{-}C_9H_9)(\mu\text{-}CO)_2(CO)_7]$,[10b] whereas with [2.2]-*p*-benzoindenophane and *anti*-[2.2]indenophane, it gives tetranuclear derivatives having $\mu_3\text{-}\eta^5\text{:}\eta^2\text{:}\eta^2$-indenyl fragments.[14] It has also been reported that $[Ru_3(CO)_{12}]$ reacts with diazoindene to give a mixture of $[Ru_3(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_9H_6)_3(CO)_6]$ and $[Ru_3(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{18}H_{12})(CO)_8]$.[13c] E-bridged bis(indenyl) reagents (E = $SiMe_2$, $Me_2SiOSiMe_2$, $Me_2SiSiMe_2$) react with $[Ru_3(CO)_{12}]$ to give binuclear derivatives that contain bridging $E(\eta^5\text{-indenyl})_2$ ligands.[13d] A nonanuclear ruthenium cluster containing two $\mu_3\text{-}\eta^5\text{:}\eta^2\text{:}\eta^2$-indenyl ligands is the minor product of the reaction of $[Ru_3(CO)_{12}]$ with $(C_9H_7)Me_2SiSiMe_2(C_9H_7)$.[13d] Some additional indenylruthenium carbonyl clusters have been prepared from diphenylbutadiyne and phenylcumulene as indenyl ligand precursors.[15]

Reactivity of Compound 1 with Fluorene. Treatment of compound **1** with fluorene (1:3 mole ratio) in decane at reflux temperature (174 °C) for 8 h afforded a mixture of compounds along with a large amount of intractable decomposition products. Lower temperatures resulted in very slow reactions, even using a large excess of fluorene. Shorter reaction times resulted in incomplete consumption of complex **1**. The hexanuclear cluster $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^6\text{-}C_{13}H_9)(\mu\text{-}CO)_2(CO)_{11}]$ (**4**) was isolated in low yield after column chromatography (Scheme 2).

The molecular structure of compound **4** is shown in Figure 3. A selection of interatomic distances is given in Table 1. Its $Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})$ fragment is similar to that of complex **1**. The fluorene ligand is attached to the axial Ru(6) atom through the six C atoms of one of its six-membered rings. Two hydrides

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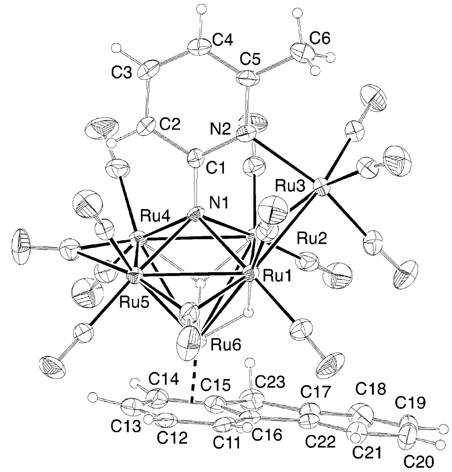


Figure 3. Molecular structure of compound **4**.

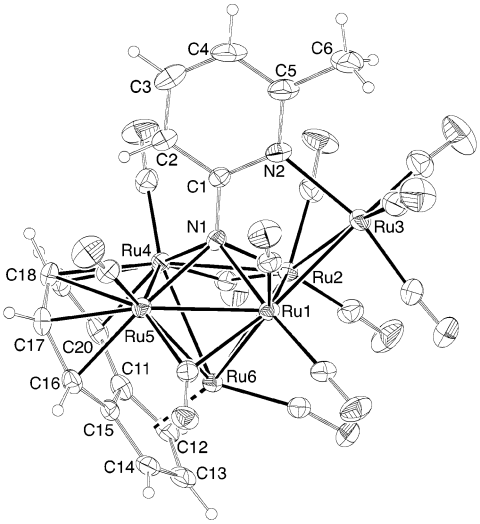


Figure 4. Molecular structure of compound **5**.

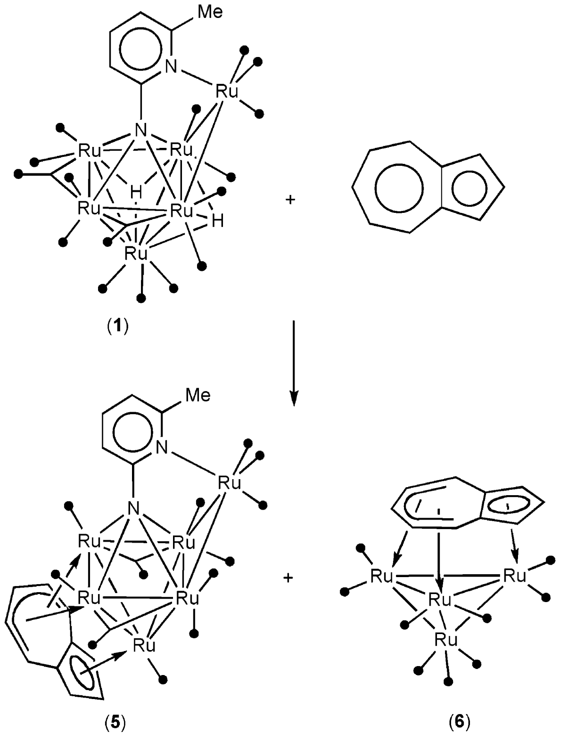
cap two triangular faces of the metallic skeleton. The cluster shell is completed by 2 edge-bridging and 11 terminal CO ligands. The structure resembles that of $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-}ampy)(\eta^6\text{-}PhMe)(\mu\text{-}CO)_2(CO)_{11}]$, which has also been characterized by X-ray diffraction.[9] Its spectroscopic data are fully consistent with this structure and are similar to those of monocyclic η^6-arene derivatives of complex **1**.[9]

The synthesis of some ruthenium carbonyl clusters derived from 9-ethynylfluoren-9-ol has been published.[16] However, no metal carbonyl clusters containing simple fluorene or fluorenyl ligands have been hitherto reported. This may be a consequence of the lower reactivity of fluorene toward ruthenium carbonyl clusters (confirmed in this work), as compared with that of indene (see above), simple arenes, or cyclopentadiene.[9]

Reactivity of Compound 1 with Azulene. Treatment of compound **1** with azulene in decane at reflux temperature for 50 min afforded a mixture of compounds from which two novel cluster derivatives, the hexanuclear $[Ru_6(\mu_5\text{-}\kappa^2\text{-}ampy)(\mu_3\text{-}\eta^{10}\text{-}C_{10}H_8)(\mu\text{-}CO)_2(CO)_{10}]$ (**5**) and the tetranuclear $[Ru_4(\mu_3\text{-}\eta^{10}\text{-}C_{10}H_8)(CO)_9]$ (**6**), were separated by chromatographic methods (Scheme 3).

The X-ray molecular structure of compound **5** is shown in Figure 4. A selection of interatomic distances is given in Table 1. The compound contains the same $Ru_6(\mu_5\text{-}\kappa^2\text{-}ampy)$ fragment as complex **1**. An azulene ligand caps the Ru(4)−Ru(5)−Ru(6) triangular face of the metallic pyramid in such a way that all the carbon atoms of the azulene ligand are bonded to metal atoms. The atoms of the five-membered ring are attached to the apical Ru(6) atom, while the remaining atoms, C(16)−C(20), form a dienyl fragment that symmetrically bridges the Ru(4)−Ru(5) cluster edge. As a consequence of the size of the azulene ligand, the distances of the central atom of the dienyl fragment, C(18), to the closest metal atoms, Ru(4) and Ru(5), are 0.3−0.4 Å longer than the remaining Ru−C distances. Two bridging and ten terminal CO ligands complete the cluster shell.

Scheme 3



The ^1H NMR spectrum of compound **5** confirms that the symmetric structure observed in solid state (C_S) is maintained in solution, since only five resonances attributable to the azulene ligand are observed. Their low chemical shifts (6.19 to 2.76 ppm) confirm the coordination of all the H-containing C atoms to the cluster.

Compound **6** was characterized by a combination of analytical methods. Its composition was clearly shown by its CHN microanalysis and FAB mass spectrum, which contained the corresponding cluster of molecular ion isotopomers. Its ^1H NMR spectrum contains only five resonances at low chemical shifts (5.91−2.00 ppm), indicating that a symmetry plane cuts the η^{10}-azulene ligand into halves. More definitively, the stretching ν_{CO} region of its IR spectrum is very similar to that of $[Ru_4(\mu_3\text{-}\eta^{10}\text{-}guaiazulene)(CO)_9]$, whose structure has been determined by X-ray diffraction.[17] All of these data strongly support the notion that the structure of compound **6** is as shown in Scheme 3.

The face-capping coordination mode displayed by the azulene ligand complexes **5** and **6** has been observed before in the ruthenium derivatives $[Ru_3(\mu_3\text{-}\eta^{10}\text{-}azu)(\mu\text{-}CO)(CO)_6]$[17,18] and $[Ru_4(\mu_3\text{-}\eta^{10}\text{-}azu)(CO)_9]$[17,18b,19] (azu = azulene or substituted azulene).

One mononuclear η^5-azulene derivative of ruthenium, $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_{10}H_8)]^+$,[20] and quite a few binuclear derivatives

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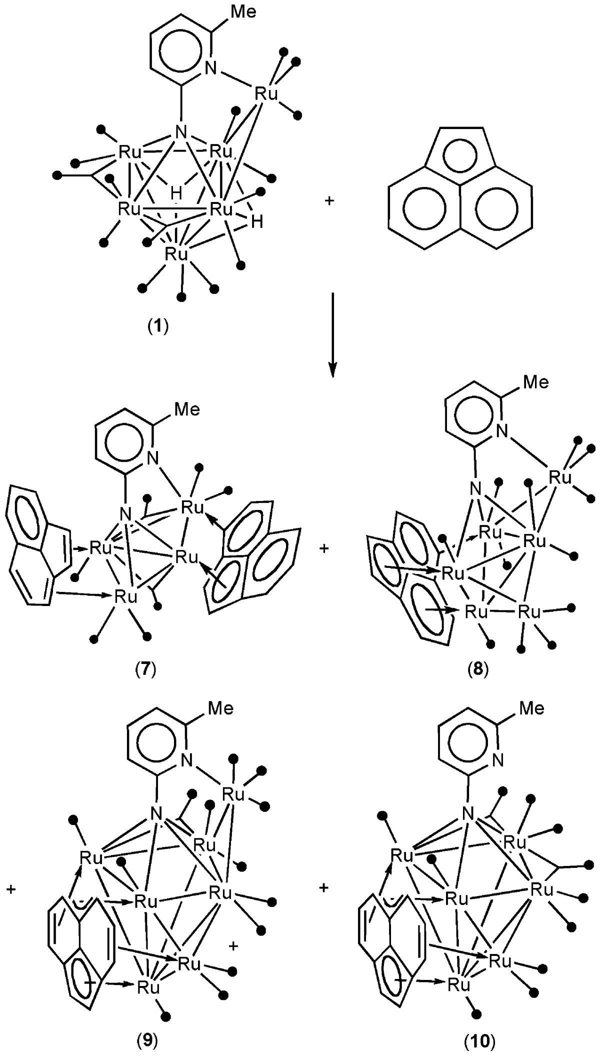
[16] Lau, C. S. W.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1999**, 607.

[17] Johnson, B. F. G.; Shephard, D. S.; Edwards, A. J.; Braga, D.; Parisini, E.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1995**, 3307.

Scheme 4



of the type $[\mathrm{Ru}_2(\mu\text{-}\eta^5\text{-}\eta^3\text{-azu})(\mathrm{CO})_5]$[18b−d,21] are known. However, although complexes having terminal and edge-bridging azulene ligands have to be intermediates in the synthesis of the face-capped clusters **5** and **6**, such species have not been detected. Therefore, under energetic reaction conditions, azulene is prone to coordinate to ruthenium carbonyl clusters in a face-capping coordination mode.

Reactivity of Compound 1 with Acenaphthtylene. Treatment of compound **1** with an excess of acenaphthtylene in decane at reflux temperature for 1.5 h led to a mixture of products that was separated by chromatographic methods. The following compounds were separated and characterized: $[\mathrm{Ru}_4(\mu_4\text{-}\kappa^2\text{-ampy})(\mu\text{-}\eta^6\text{-C}_{12}\mathrm{H}_8)(\mu\text{-}\eta^4\text{-C}_{12}\mathrm{H}_8)(\mu\text{-CO})_2(\mathrm{CO})_5]$ (**7**), $[\mathrm{Ru}_6(\mu_4\text{-}\kappa^2\text{-ampy})(\mu_3\text{-}\eta^{10}\text{-C}_{12}\mathrm{H}_8)(\mathrm{CO})_{12}]$ (**8**), $[\mathrm{Ru}_7(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_4\text{-}\eta^{12}\text{-C}_{12}\mathrm{H}_8)(\mu\text{-CO})(\mathrm{CO})_{12}]$ (**9**), and $[\mathrm{Ru}_6(\mu_4\text{-}\kappa^1\text{-ampy})(\mu_4\text{-}\eta^{12}\text{-C}_{12}\mathrm{H}_8)(\mu\text{-CO})_2(\mathrm{CO})_9]$ (**10**) (Scheme 4). As noted below, the metallic framework of the starting material is not maintained in any of these products and only one, the heptanuclear derivative **9**, has the ampy ligand coordinated in the same way (μ_5-κ^2N,N) as in compound **1**.

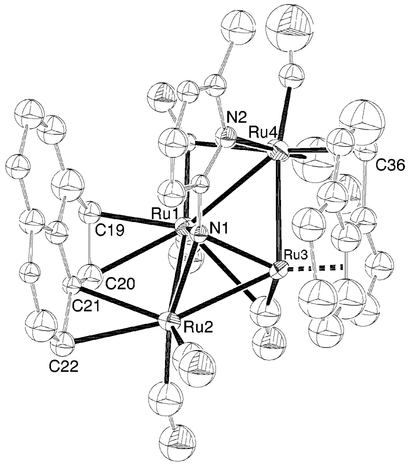


Figure 5. Molecular structure of compound **7** (after isotropic refinement of one of the two crystallographically independent molecules found in the unit cell). Hydrogen atoms have not been included.

As far as we know, there are only five previous publications dealing with reactivity of acenaphthylene with transition-metal carbonyl clusters. They report triruthenium[22] and triosmium[23] derivatives, but not clusters of higher nuclearity.

A crystal of compound **7** was analyzed by X-ray diffraction.[24] The unit cell contains two independent molecules. One of them was severely disordered, and it could not be fit to a suitable model. The other molecule was appropriately modeled and was refined isotropically. Therefore, the atom connectivity could be established (Figure 5), but no accurate structural parameters could be obtained. The metallic skeleton of **7** comprises four ruthenium atoms in a butterfly arrangement. An ampy ligand is attached to the four metallic atoms in such a way that the imido N atom caps the Ru(1)-Ru(2)−Ru(3) wing while the pyridine N atom is attached to Ru(4). Two cluster edges are spanned by acenaphthylene ligands. One of these ligands bridges the Ru(1)−Ru(2) edge as a four-electron donor through the diene fragment defined by C(19), C(20), C(21), and C(22), and the other one bridges the Ru(3)−Ru(4) edge as a six-electron donor, being attached to Ru(3) through the atoms of the five-membered ring and to Ru(4) through the C(36) carbon atom. This latter interaction implies an unusual side-on coordination of a single carbon atom of an aromatic ring to a metal atom. The cluster shell is completed by seven CO ligands. With 64 electrons and 5 Ru−Ru bonds, the cluster obeys the EAN rule. The coordina-

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(18) (a) Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1973**, *21*, 191. (b) Nagashima, H.; Suzuki, A.; Nobata, M.; Aoki, K.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2441. (c) Matsubara, K.; Ryu, K.; Maki, T.; Iura, T.; Nagashima, H. *Organometallics* **2002**, *21*, 3023. (d) Arce, A. J.; De Sanctis, Y.; Galarza, E.; Garland, M. T.; Gobetto, R.; Machado, R.; Manzur, J.; Russo, A.; Spodine, E.; Stchedroff, M. J. *Organometallics* **2001**, *20*, 359.

(19) (a) Churchill, M. R.; Gold, K.; Bird, P. H. *Inorg. Chem.* **1969**, *8*, 1956. (b) Wang, F.; Lai, Y. H.; Han, M. Y. *Org. Lett.* **2003**, *5*, 4791.

(20) McNair, A. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 2519.

(21) For additional examples of diruthenium complexes having azulene ligands, see: (a) Cabeza, J. A.; del Río, I.; García-Granda, S.; Martínez-Méndez, L.; Moreno, M.; Riera, V. *Organometallics* **2003**, *22*, 1164. (b) Matsubara, K.; Oda, T.; Nagashima, H. *Organometallics* **2001**, *20*, 881. (c) Matsubara, K.; Mima, S.; Oda, T.; Nagashima, H. *J. Organomet. Chem.* **2002**, *650*, 96. (d) Cotton, F. A.; Hanson, B. E.; Kolb, J. R.; Lahuerta, P.; Stanley, G. G.; Stults, B. R.; White, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 3673. (e) Knox, S. A. R.; Sosinsky, B. A.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1647.

(22) (a) Nagashima, H.; Fukahori, T.; Aoki, K.; Itoh, K. *J. Am. Chem. Soc.* **1993**, *115*, 10430. (b) Nagashima, H.; Suzuki, A.; Iura, T.; Ryu, K.; Matsubara, K. *Organometallics* **2000**, *19*, 3579. (c) Nagashima, H.; Suzuki, A.; Kondo, H.; Nobata, M.; Aoki, K.; Itoh, K. *J. Organomet. Chem.* **1999**, *580*, 239. (d) Nagashima, H.; Suzuki, A.; Nobata, M.; Aoki, K.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2231.

(23) Adams, R. D.; Captain, B.; Smith, J. L., Jr. *J. Organomet. Chem.* **2003**, *683*, 421.

(24) Selected crystal data for **7**: monoclinic, $C2/c$, $a = 30.817(5)$ Å, $b = 16.268(3)$ Å, $c = 19.752(3)$ Å, $\beta = 99.312(3)°$, R1 $= 0.1664$, wR2 $= 0.5038$.

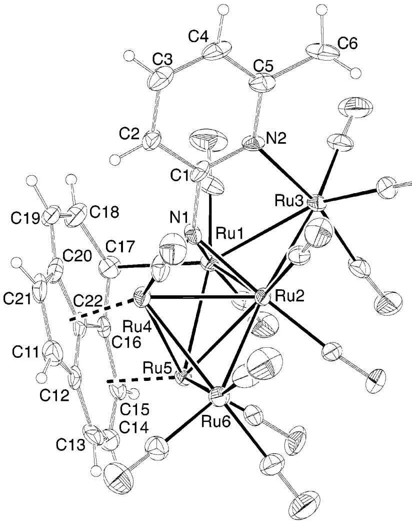

Figure 6. Molecular structure of compound **8**.

Table 2. Selected Interatomic Distances (Å) in Compound 8

Ru(1)−Ru(2)	2.709(2)	Ru(1)−Ru(3)	2.787(2)
Ru(1)−Ru(5)	2.765(2)	Ru(2)−Ru(3)	2.758(2)
Ru(2)−Ru(4)	2.735(2)	Ru(2)−Ru(5)	2.759(2)
Ru(2)−Ru(6)	2.703(2)	Ru(4)−Ru(5)	2.845(2)
Ru(4)−Ru(6)	2.776(2)	Ru(5)−Ru(6)	2.752(2)
N(1)−Ru(1)	2.158(8)	N(1)−Ru(2)	2.055(9)
N(1)−Ru(4)	2.068(9)	N(2)−Ru(3)	2.208(9)
C(11)−Ru(4)	2.299(13)	C(12)−Ru(4)	2.498(11)
C(12)−Ru(5)	2.571(11)	C(13)−Ru(5)	2.375(12)
C(14)−Ru(5)	2.280(12)	C(15)−Ru(5)	2.211(10)
C(16)−Ru(5)	2.362(11)	C(17)−Ru(1)	2.317(12)
C(20)−Ru(4)	2.345(11)	C(21)−Ru(4)	2.229(12)
C(22)−Ru(4)	2.414(10)	C(22)−Ru(5)	2.509(11)

tion modes displayed by the acenaphthylene ligands of this complex are unprecedented.

The ^1H NMR of **7** contains 16 resonances that correspond to the protons of two acenaphthylene ligands, thus confirming that the asymmetry found in the solid state is maintained in solution. The composition of **7** was also supported by its FAB MS, which shows the most abundant molecular ion isotopomer at *m/z* 1012.

The structure of compound **8** was established by X-ray diffraction (Figure 6, Table 2). The metallic skeleton comprises six ruthenium atoms, arranged in such a way that Ru(2), Ru(4), Ru(5), and Ru(6) form a tetrahedron that shares a vertex, Ru(2), with a triangle defined by Ru(1), Ru(2), and Ru(3). An additional Ru−Ru bond connects Ru(1) with Ru(5). A μ_4-ampy ligand caps the open Ru(1)-Ru(2)−Ru(4) triangle through the imido N atom and is attached to Ru(3) through the pyridine N atom. The acenaphthylene ligand bridges three metal atoms, having the five-membered ring attached in an η^5 fashion to Ru(4), one of the six-membered rings attached in an η^6 manner to Ru(5), and the C(17) carbon atom attached side-on to Ru(1). Apart from the C(18)−C(19) distance, 1.35(2) Å, which involves the only uncoordinated C atoms of the ligand, the remaining C−C distances of the acenaphthylene ligand are longer than 1.40 Å, confirming the coordination of the corresponding C atoms. The particular geometry of the acenaphthylene ligand dictates that the distances from the C(12) and C(22) carbon atoms to the ruthenium atoms Ru(4) and Ru(5) are ca. 0.2 Å longer than the remaining Ru−C bonding distances. The cluster shell is completed by 12 CO ligands. Considering the acenaphthylene ligand as a 10-electron donor, the cluster electron count is 88. Therefore, with 10 metal−metal bonds, this cluster obeys the EAN rule. The coordination mode displayed by the acenaphthylene ligand of this complex has not been reported before.

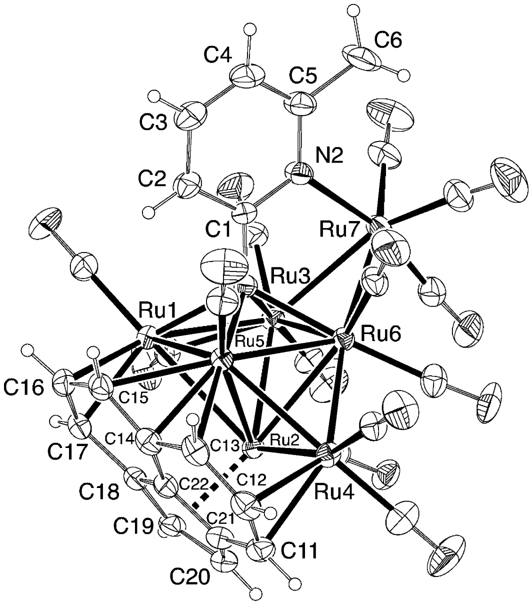

Figure 7. Molecular structure of compound **9**.

Table 3. Selected Interatomic Distances (Å) in Compounds 9 and 11

	9	**11**		**9**	**11**
Ru(1)−Ru(2)	2.916(1)	2.934(2)	N(1)−Ru(6)	2.132(4)	2.184(8)
Ru(1)−Ru(3)	2.5815(9)	2.706(2)	N(2)−Ru(7)	2.212(5)	
Ru(1)−Ru(5)	2.772(1)	2.748(2)	S(1)−Ru(3)		2.311(3)
Ru(2)−Ru(3)	2.863(1)	2.912(2)	C(11)−Ru(4)	2.219(6)	2.224(10)
Ru(2)−Ru(4)	2.775(1)	2.769(2)	C(12)−Ru(4)	2.226(6)	2.215(9)
Ru(2)−Ru(5)	2.760(1)	2.777(2)	C(13)−Ru(5)	2.235(6)	2.351(8)
Ru(2)−Ru(6)	2.824(1)	2.856(2)	C(14)−Ru(5)	2.122(6)	2.127(9)
Ru(3)−Ru(6)	2.688(1)	2.720(2)	C(15)−Ru(5)	2.362(6)	2.361(9)
Ru(3)−Ru(7)	2.758(1)		C(16)−Ru(1)	2.189(6)	2.206(9)
Ru(4)−Ru(5)	2.730(1)	2.734(2)	C(17)−Ru(1)	2.132(6)	2.177(9)
Ru(4)−Ru(6)	2.680(1)	2.688(2)	C(18)−Ru(2)	2.315(5)	2.326(9)
Ru(5)−Ru(6)	2.6493(9)	2.668(2)	C(19)−Ru(2)	2.287(5)	2.293(10)
Ru(6)−Ru(7)	2.746(1)		C(20)−Ru(2)	2.220(6)	2.227(9)
N(1)−Ru(1)	2.268(5)	2.204(8)	C(21)−Ru(2)	2.243(5)	2.236(8)
N(1)−Ru(3)	2.192(4)	2.292(7)	C(22)−Ru(2)	2.242(5)	2.234(8)
N(1)−Ru(5)	2.097(4)	2.070(7)			

Cluster **9** is heptanuclear (Figure 7, Table 3). It maintains the $Ru_6(\mu_5-\kappa^2\text{-ampy})$ fragment of the starting complex **1** but has an additional Ru atom, Ru(4), capping the Ru(2)−Ru(5)−Ru(6) face. This metallic skeleton is thus comparable to that of the indenyl derivative **2**. The acenaphthylene ligand spans four metal atoms using its 12 carbon atoms, being η^5 coordinated to Ru(2) through the atoms of the five-membered ring, η^3 coordinated to Ru(5) through the C(13), C(14), and C(15) carbon atoms, η^2 coordinated to Ru(1) through C(16) and C(17), and η^2 coordinated to Ru(4) through C(11) and C(12). The Ru(1), Ru(2), Ru(4), and Ru(5) atoms are roughly coplanar. The plane they define is approximately parallel to the acenaphthylene ligand (dihedral angle 176.77(5)°). The cluster shell is completed by 1 edge-bridging and 12 terminal CO ligands. Assuming that the acenaphthylene ligand contributes 12 electrons, the cluster, with 12 Ru−Ru bonds and 100 electrons, obeys the EAN rule.

In the chemical literature, there are no precedents for quadruply bridging acenaphthylene ligands. The coordination of all carbon atoms of an acenaphthylene molecule is also unprecedented. The coordination mode observed for acenaphthylene in the trinuclear complexes $[Ru_3(\mu_3\text{-}\eta^{10}\text{-}C_{12}H_8)(\mu\text{-CO})(CO)_6]$[22a] and $[Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^{10}\text{-}C_{12}H_8)(SiMe_2CH_2Ph)(CO)_6]$[22b]

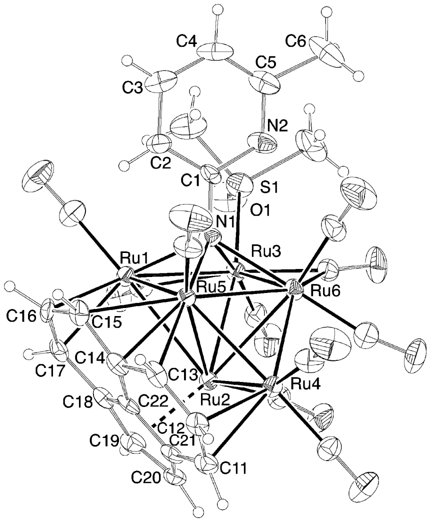

Figure 8. Molecular structure of compound **11**.

is related to that observed in **1**, but the ligands of these trinuclear complexes have an uncoordinated HC═CH fragment.

Compound **10** was sparingly soluble in common organic solvents, moderately soluble in THF, and soluble in dimethyl sulfoxide. A crystal taken from a batch obtained by allowing a hexane layer to diffuse into a solution of complex **10** in dimethyl sulfoxide−dichloromethane (1:3), over a period of 2 months, was studied by X-ray diffraction. It corresponded to the dimethyl sulfoxide derivative $[Ru_6(\mu_4\text{-}\kappa^1\text{-ampy})(\mu_4\text{-}\eta^{12}\text{-}C_{12}H_8)(Me_2SO)(\mu\text{-}CO)_2(CO)_8]$ (**11**) (Figure 8, Table 3). Its structure can be described starting from that of compound **9**, as the result of the formal substitution of one edge-bridging carbonyl ligand for the $Ru(7)(CO)_3$ fragment and a sulfur-coordinated dimethyl sulfoxide ligand for a terminal carbonyl ligand on Ru(3). Therefore, the complex is hexanuclear and, for the first time in cluster chemistry, the pyridine N atom of the ampy ligand is not coordinated. The cluster, with 86 electrons and 11 Ru−Ru bonds, obeys the EAN rule.

The above results led us to think that, if **11** arises from a fast reaction of **10** with dimethyl sulfoxide, the NMR spectra obtained from solutions of complex **10** in $Me_2SO\text{-}d_6$ might not correspond to **10** but to **11**-d_6. To check this, complex **10** was treated with a 10-fold excess of dimethyl sulfoxide in THF. No reaction was observed at room temperature after 2 h. At reflux temperature, compound **11** was obtained, but it took 14 h to observe the complete consumption of complex **10**. The slow rate of this reaction indicates that the species present in solution after dissolving **10** in $Me_2SO\text{-}d_6$ is **10** and not **11**-d_6. However, as stated above, some **11** is formed at room temperature from **10** and dimethyl sulfoxide after long reaction times (months).

The fact that compound **11** has its pyridyl fragment uncoordinated does not necessarily imply that this also happens in complex **10**. However, the chemical shifts of their ampy methyl groups, 2.12 ppm (**10**, in $Me_2SO\text{-}d_6$) and 2.08 ppm (**11**, in $Me_2SO\text{-}d_6$), differ by 0.3−0.5 ppm from those of **8** (2.40 ppm, in CD_2Cl_2) and **9** (2.63 ppm, in $Me_2SO\text{-}d_6$). This supports the notion that the ampy ligands of **10** and **11** are similar (their pyridyl fragment is uncoordinated) and confirms that they are different from those of **8** and **9** (their pyridyl fragment is coordinated).

Concluding Remarks

Polynuclear ruthenium carbonyl cluster complexes containing η^5- and μ-η^9-indenyl, η^6-fluorene, μ_3-η^{10}-azulene, and μ_2-η^4-, μ_2-η^6-, μ_3-η^{12}-, and μ_4-η^{12}-acenaphthylene ligands have been prepared from reactions of compound **1** with the appropriate ligands. The high temperatures required by these reactions (132−174 °C) promote fragmentation processes that give clusters of lower nuclearity and $Ru(CO)_n$ fragments. Both may undergo decomposition (a black insoluble solid is formed in all reactions) or aggregation to other cluster species present in solution to give products of higher nuclearity. This explains the various metallic frameworks observed in the isolated products and the low yields of some of them.

High reaction temperatures also promote cluster decarbonylation processes. This accounts for the observation that, with few exceptions (**3**, **4**, **7**), most of the reaction products contain the polycyclic hydrocarbon ligands attached through many carbon atoms to various metal atoms. In fact, the μ_2-indenyl ligand of **2**, the μ_3-azulenes of **5** and **6**, and the μ_4-acenaphthylenes of **9**−**11** are attached to the corresponding metal atoms through all of their carbon atoms. The four different coordination modes displayed by the acenaphthylene ligands in compounds **7**−**9** are unprecedented.

The coordination modes displayed by the ampy ligands in compounds **7** (μ_4-κ^2N,N), **8** (μ_4-κ^2N,N), and **10** (μ_4-κ^1N), in addition to the formation of the black insoluble solid in all reactions, indicate that, in contrast with previous observations in reactions of **1** performed at lower temperatures,[1,6,7,9] the ampy ligand is no longer efficient at maintaining its original coordination mode (μ_5-κ^2N,N in **1**) at temperatures as high as 174 °C.[25] It is noteworthy that the coordination mode of the ampy ligand in **10** and **11** (quadruply bridging, using only its imido N atom) has not been observed before.

Experimental Section

General Data. Solvents were used as received (chlorobenzene 99%, decane 99%) or were dried over sodium diphenyl ketyl (hydrocarbons, THF) or CaH_2 (dichloromethane, 1,2-dichloroethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk−vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and spot TLC. Compound **1** was prepared as previously reported.[1] IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. ^{1}H NMR spectra were run on Bruker DPX-300 and AV-400 instruments, using the dichloromethane solvent resonance as internal standard (δ 5.30). Microanalyses were obtained from the University of Oviedo Analytical Service. FAB-MS were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

Reactions of Compound 1 with Indene. A mixture of compound **1** (100 mg, 0.086 mmol) and indene (50 μL, 0.43 mmol) in chlorobenzene (10 mL) was stirred at reflux temperature for 6 h. The color changed from dark brown to dark red-brown. The solvent was removed under vacuum, and the residue was extracted into dichloromethane (15 mL). This solution was supported on silica gel (4 g), and the resulting solid was transferred onto a silica gel column (2 × 20 cm) packed in hexane. Hexane−dichloromethane (3:1) eluted a trace amount of a brown unidentified compound. Hexane−dichloromethane (2:1) eluted a yellow band that afforded $[Ru_2(\eta^5\text{-}C_9H_7)_2(\mu\text{-}CO)_2(CO)_2]$ (8 mg, 7%). Hexane−dichloromethane (1:1) eluted a red-brown band that afforded compound **2** (62 mg, 63%). In an alternative reaction, a mixture of compound **1** (50 mg, 0.043 mmol) and indene (1 mL) in chlorobenzene (10 mL) was stirred at 110 °C for 4 h. The color changed from dark brown to yellowish brown. The solvent was removed under vacuum, and the

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[25] Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D. *Organometallics* **2006**, *25*, 5672.

residue was extracted into dichloromethane (8 mL). This solution was supported on silica gel (4 g), and the resulting solid was transferred onto a silica gel column (2 × 20 cm) packed in hexane. Hexane−dichloromethane (5:1) eluted a minor unidentified yellow band. Hexane−dichloromethane (3:1) eluted a brown band that contained the starting material **1** (7 mg, 14%). Hexane−dichloromethane (2:1) eluted three bands. The first (green) contained a trace amount of an unidentified product. The second band (brown) afforded compound **3** (6 mg, 12%). The third band (yellow) gave [$Ru_2(\eta^5\text{-}C_9H_7)_2(\mu\text{-}CO)_2(CO)_2$] (20 mg, 29%).

Data for [$Ru_7(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-}$ampy$)(\mu\text{-}\eta^9\text{-}C_9H_7)(\mu\text{-}CO)_3(CO)_{11}$] (2). Anal. Calcd for $C_{29}H_{14}N_2O_{14}Ru_7$ (1321.93): C, 26.35; H, 1.07; N, 2.12. Found: C, 26.30; H, 1.11; N, 2.18. FAB MS: *m/z* 1322 [*M*]$^+$. IR (CH_2Cl_2): ν_{CO} 2067 (s), 2028 (s), 2010 (vs), 1972 (m, br), 1936 (m, br), 1875 (w, br), 1823 cm^{-1} (w, br). ^{1}H NMR (CD_2Cl_2, 293 K): δ 7.11 (t, J = 8.0 Hz, 1 H, ampy), 6.58 (d, J = 8.0 Hz, 1 H, ampy), 5.96 (d, J = 8.0 Hz, 1 H, ampy), 5.77 (t, J = 2.5 Hz, 1 H), 4.96 (t, J = 5.6 Hz, 1 H), 4.85 (t, J = 5.6 Hz, 1 H), 4.39 (m, 1 H), 4.20 (d, J = 5.6 Hz, 1 H), 4.06 (d, J = 5.6 Hz, 1 H), 3.77 (m, 1 H), 2.55 (s, 3 H, ampy), −15.47 (s, 1 H, μ_3-H).

Data for [$Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-}$ampy$)(\eta^5\text{-}C_9H_7)(\mu_3\text{-}CO)(\mu\text{-}CO)_2(CO)_{11}$] (3). Anal. Calcd for $C_{29}H_{14}N_2O_{14}Ru_6$ (1220.86): C, 28.53; H, 1.16; N, 2.29. Found: C, 28.59; H, 1.21; N, 2.23. FAB MS: *m/z* 1222 [*M*]$^+$. IR (CH_2Cl_2): ν_{CO} 2077 (m), 2043 (s), 2026 (vs), 2013 (m, sh), 1986 (m, br), 1971 (m, br), 1953 (m, br), 1843 (w, br), 1806 (w, br), 1765 cm^{-1} (w, br). ^{1}H NMR (CD_2Cl_2, 293 K): δ 7.33 (m, 2 H), 7.21 (m, 2 H), 7.10 (t, J = 8.0 Hz, 1 H, ampy), 6.50 (d, J = 8.0 Hz, 1 H, ampy), 5.92 (d, J = 8.0 Hz, 1 H, ampy), 5.18 (t, J = 2.5 Hz, 1 H), 4.73 (d, J = 2.5 Hz, 2 H), 2.42 (s, 3 H, ampy), −17.18 (s, 1 H, μ_3-H).

Reaction of Compound 1 with Fluorene. A mixture of compound **1** (150 mg, 0.129 mmol) and fluorene (64 mg, 0.387) in decane (15 mL) was stirred at reflux temperature for 8 h. The original dark brown color was maintained. A considerable amount of black solid precipitated. The solvent was removed under vacuum, and the residue was extracted with dichloromethane (15 mL). A considerable amount of black solid remained undissolved. The solution was supported on silica gel (4 g), and the resulting solid was transferred onto a silica gel column (2 × 20 cm) packed in hexane. Hexane−diethyl ether (20:1) eluted a red-brown band that afforded compound **4** (16 mg, 10%). More polar solvents eluted several bands containing trace amounts of unidentified compounds. A dark residue remained uneluted at the top of the column.

Data for [$Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-}$ampy$)(\eta^6\text{-}C_{13}H_{10})(\mu\text{-}CO)_2(CO)_{11}$] (4). Anal. Calcd for $C_{32}H_{18}N_2O_{13}Ru_6$ (1244.92): C, 30.87; H, 1.46; N, 2.25. Found: C, 31.00; H, 1.52; N, 2.23. FAB MS: *m/z* 1246 [*M*]$^+$. IR (CH_2Cl_2): ν_{CO} 2067 (m), 2033 (s), 2013 (vs), 2000 (m, sh), 1991 (m, sh), 1976 (m, br), 1953 (m, br), 1936 (w, sh), 1836 (w, br), 1802 cm^{-1} (w, br). ^{1}H NMR ($CDCl_3$, 293 K): δ 7.63 (m, 1 H), 7.50−7.30 (m, 3 H), 6.97 (t, J = 7.8 Hz, 1 H, ampy), 6.38 (d, J = 7.8 Hz, 1 H, ampy), 5.83 (m, 1 H), 5.75 (d, J = 7.8 Hz, 1 H, ampy), 5.62 (m, 1 H), 5.10−4.95 (m, 2 H), 3.67 (d, J = 22.8 Hz, 1 H, CH_2), 3.63 (d, J = 22.8 Hz, 1 H, CH_2), 2.38 (s, 3 H, ampy), −13.87 (d, J = 2.0 Hz, 1 H), −16.80 (d, J = 2.0 Hz, 1 H).

Reaction of Compound 1 with Azulene. A mixture of compound **1** (100 mg, 0.086 mmol) and azulene (13 mg, 0.103) in decane (8 mL) was stirred at reflux temperature for 50 min. The original dark brown color turned dark greenish brown. A considerable amount of black solid precipitated. The solvent was removed under vacuum, and the residue was extracted with dichloromethane (6 mL). The black solid remained undissolved. The solution was supported on silica gel (6 g), and the resulting solid was transferred onto a silica gel column (2 × 20 cm) packed in hexane. Hexane−dichloromethane (3:1) eluted one yellow and two brown bands that contained trace amounts of compounds and were not identified. Hexane−dichloromethane (1:1) eluted a yellow band with a long tail, which contained complex **6** (6 mg, 7%). Hexane−dichloromethane (1:2) started to elute a dark green band, having a very long tail, which was finally eluted and extracted with THF. This dark green solution was evaporated to dryness. The solid residue was dissolved in THF (4 mL), the resulting solution was supported on silica gel (6 g), and the resulting solid was transferred onto a silica gel column (2 × 20 cm) packed in hexane. Hexane−dichloromethane (1:1) eluted a yellow band that contained some compound **6** (2 mg). Hexane−dichloromethane (1:2) started to elute a dark green band, which was finally eluted with THF to give compound **5** (10 mg, 10%).

Data for [$Ru_6(\mu_5\text{-}\kappa^2\text{-}$ampy$)(\mu_3\text{-}\eta^{10}\text{-}C_{10}H_8)(\mu\text{-}CO)_2(CO)_{10}$] (5). Anal. Calcd for $C_{28}H_{14}N_2O_{12}Ru_6$ (1176.85): C, 28.58; H, 1.20; N, 2.38. Found: C, 28.65; H, 1.22; N, 2.45. FAB MS: *m/z* 1178 [*M*]$^+$. IR (CH_2Cl_2): ν_{CO} 2064 (s), 2004 (vs), 1967 (s), 1958 (m, sh), 1894 (w, br), 1819 cm^{-1} (w, br). ^{1}H NMR ($CDCl_3$, 293 K): δ 6.90 (t, J = 7.7 Hz, 1 H, ampy), 6.40 (d, J = 7.7 Hz, 1 H, ampy), 6.19 (dd, J = 7.6, 5.8 Hz, 2 H), 5.30 (m, 1 H), 5.24 (d, J = 7.7 Hz, 1 H, ampy), 4.39 (t, J = 2.8 Hz, 1 H), 3.22 (t, J = 5.8 Hz, 2 H), 2.76 (d, J = 2.8 Hz, 2 H), 2.45 (s, 3 H, ampy).

Data for [$Ru_4(\mu_3\text{-}\eta^{10}\text{-}C_{10}H_8)(CO)_9$] (6). Anal. Calcd for $C_{19}H_8O_9Ru_4$ (784.55): C, 29.09; H, 1.03. Found: C, 29.16; H, 0.99. FAB MS: *m/z* 786 [*M*]$^+$. IR (CH_2Cl_2): ν_{CO} 2058 (m), 2001 (s), 1963 (w), 1930 (w, br). ^{1}H NMR (CD_2Cl_2, 293 K): δ 5.91 (t, J = 3.1 Hz, 1 H), 5.11 (dd, J = 7.7, 5.8 Hz, 2 H), 4.27 (dd, J = 5.8, 1.2 Hz, 2 H), 4.04 (d, J = 3.1 Hz, 2 H), 2.00 (t, br, J = 7.7 Hz, 1 H).

Reaction of Compound 1 with Acenaphthylene. A mixture of compound **1** (100 mg, 0.086 mmol) and acenaphthylene (131 mg, 0.860 mmol) in decane (10 mL) was stirred at reflux temperature for 1.5 h. No color change was observed. A considerable amount of black solid precipitated. The solvent was removed under vacuum, and the residue was extracted with dichloromethane (6 mL). The black solid remained undissolved. The solution was supported on silica gel TLC plates. Repeated elution with hexane−dichloromethane (1:1) eluted nine bands, most of which contained only trace amounts of compounds. Band 1 (yellow) contained the excess of acenaphthylene. Bands 5 and 6 (both dark brown) afforded compounds **7** (2 mg, 3%) and **8** (4 mg, 4%), respectively. Band 9 (brownish green) was very broad and did not separate well from the baseline. This band and the baseline were extracted into THF (30 mL). The solution was supported on silica gel TLC plates. Diethyl ether eluted a green band that contained compound **9** (8 mg, 8%). The baseline was extracted into THF (30 mL) to give a red-brown solution that, upon evaporation to dryness, afforded compound **10** (19 mg, 19%)

Data for [$Ru_4(\mu_4\text{-}\kappa^2\text{-}$ampy$)(\mu\text{-}\eta^6\text{-}C_{12}H_8)(\mu\text{-}\eta^4\text{-}C_{12}H_8)(\mu\text{-}CO)_2(CO)_5$] (7). Anal. Calcd for $C_{37}H_{22}N_2O_7Ru_4$ (1010.86): C, 43.96; H, 2.19; N, 2.77. Found: C, 44.07; H, 2.26; N, 2.67. FAB MS: *m/z* 1012 [*M*]$^+$. IR (CH_2Cl_2): ν_{CO} 2020 (s), 2000 (s), 1965 (m, br), 1949 (m, br), 1846 cm^{-1} (w, br). ^{1}H NMR (CD_2Cl_2, 293 K): δ 7.60−7.45 (m, 2 H), 7.18 (m, 1 H), 7.15 (d, J = 7.7 Hz, 1 H, ampy), 7.01 (d, J = 7.7 Hz, 1 H, ampy), 6.86 (t, J = 7.7 Hz, 1 H, ampy), 6.58 (d, J = 6.0 Hz, 1 H), 6.53 (t, J = 7.6 Hz, 1 H), 6.40 (t, J = 7.5 Hz, 1 H), 6.15 (d, J = 7.5 Hz, 1 H), 6.07 (dd, J = 9.5, 5.4 Hz, 1 H), 5.94 (m, 1 H), 5.16 (d, J = 2.4 Hz, 1 H), 4.98 (d, br, J = 9.5 Hz, 1 H), 4.82 (d, J = 4.2 Hz, 1 H), 4.50 (d, J = 5.4 Hz, 1 H), 3.79 (d, J = 4.2 Hz, 1 H), 3.73 (d, J = 2.4 Hz, 1 H), 3.31 (d, J = 7.5 Hz, 1 H), 2.46 (s, 3 H, ampy).

Data for [$Ru_6(\mu_4\text{-}\kappa^2\text{-}$ampy$)(\mu_3\text{-}\eta^{10}\text{-}C_{12}H_8)(CO)_{12}$] (8). Anal. Calcd for $C_{30}H_{14}N_2O_{12}Ru_6$ (1200.87): C, 30.01; H, 1.18; N, 2.33. Found: C, 30.10; H, 1.24; N, 2.39. FAB MS: *m/z* 1202 [*M*]$^+$. IR (CH_2Cl_2): ν_{CO} 2068 (vs), 2042 (vs), 2004 (s, sh), 1996 (vs, br), 1980 (s, br), 1969 (m, sh), 1950 (w, sh), 1937 (m, br), 1911 cm^{-1} (w, sh). ^{1}H NMR (CD_2Cl_2, 293 K): δ 7.35 (t, J = 8.0 Hz, 1 H, ampy), 7.22 (d, J = 2.8 Hz, 1 H), 6.70−6.64 (m, 2 H), 6.60 (d, J = 8.0 Hz, 1 H, ampy), 6.28 (d, J = 8.0 Hz, 1 H, ampy), 6.18 (dd, J = 4.0, 2.4 Hz, 1 H), 4.88 (t, J = 6.2 Hz, 1 H), 3.97−3.90 (m, 2 H), 3.53 (d, J = 6.2 Hz, 1 H), 2.40 (s, 3 H, ampy).

Table 4. Crystal, Measurement, and Refinement Data for the Compounds Studied by X-ray Diffraction

	$\mathbf{2}\cdot C_4H_8O$	$\mathbf{4}\cdot 0.25_2H_4Cl_2$	$\mathbf{5}\cdot C_4H_8O$	$\mathbf{8}\cdot CH_2Cl_2$	$\mathbf{9}\cdot 0.5C_4H_8O$	$\mathbf{11}\cdot 0.1C_6H_{14}$
formula	$C_{29}H_{14}N_2O_{14}$-$Ru_7\cdot C_4H_8O$	$C_{32}H_{18}N_2O_{13}$-$Ru_6\cdot 0.25C_2H_4Cl_2$	$C_{28}H_{14}N_2O_{12}$-$Ru_6\cdot C_4H_8O$	$C_{30}H_{14}N_2O_{12}$-$Ru_6\cdot CH_2Cl_2$	$C_{31}H_{14}N_2O_{13}$-$Ru_7\cdot 0.5C_4H_8O$	$C_{30}H_{20}N_2O_{11}$-$Ru_6S\cdot 0.1C_6H_{14}$
formula wt	1394.02	1269.64	1248.94	1285.78	1366.00	1231.58
cryst syst	triclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	10.367(3)	10.443(2)	37.447(6)	10.945(8)	9.978(3)	9.521(6)
b, Å	12.976(3)	20.009(5)	10.154(2)	11.011(8)	10.522(4)	11.376(8)
c, Å	14.700(4)	18.511(4)	18.379(3)	15.261(11)	19.871(7)	18.859(13)
α, deg	100.509(4)	90	90	88.991(14)	81.90(3)	73.461(11)
β, deg	95.774(5)	98.114(4)	96.543(3)	78.875(12)	79.46(3)	77.744(12)
γ, deg	92.632(4)	90	90	86.026(14)	71.66(3)	69.587(12)
V, Å^3	1930.2(8)	3829(4)	6943(2)	1800(2)	1939(1)	1821(2)
Z	2	4	8	2	2	2
F(000)	1324	2418	4800	1220	1292	1174
D_{calcd}, g cm^{-3}	2.399	2.202	2.409	2.372	2.139	2.247
μ, mm^{-1} (radiation)	2.735 (Mo Kα)	2.405 (Mo Kα)	2.614 (Mo Kα)	2.665 (Mo Kα)	19.011 (Cu Kα)	2.541 (Mo Kα)
cryst size, mm	0.28 × 0.15 × 0.07	0.21 × 0.20 × 0.18	0.20 × 0.15 × 0.05	0.38 × 0.24 × 0.17	0.10 × 0.06 × 0.03	0.37 × 0.14 × 0.07
temp, K	293(2)	293(2)	296(2)	293(2)	293(2)	293(2)
θ limits, deg	1.60−23.28	1.51−23.27	1.09−23.27	1.36−23.35	4.44−74.55	1.96−23.45
min/max *h*, *k*, *l*	−11/+11, −13/+14, −16/+11	−11/+11, −18/+22, −20/+20	−30/+41, −11/+11, −20/+20	−12/+11, −7/+12, −16/+16	−11/+12, −12/+13, −24/+23	−10/+10, −10/+12, −20/+20
no. of collected rflns	8503	16 882	14 913	7070	24145	8162
no. of unique rflns	5432	5500	4985	4728	7684	5205
no. of rflns with $I > 2\sigma(I)$	4696	4845	4027	4356	6470	4399
no. of params/restraints	519/0	505/0	480/0	480/0	523/0	470/0
GOF on F^2	1.054	1.090	1.003	1.097	1.095	1.131
R1 (on *F*, $I > 2\sigma(I)$)	0.0303	0.0364	0.0271	0.0627	0.0342	0.0461
wR2 (on F^2, all data)	0.0773	0.0791	0.0717	0.1699	0.1119	0.1235
max/min $\Delta\rho$, e Å^{-3}	+0.744/−0.788	+0.825/−0.473	+0.625/−0.573	+1.596/−1.742	+0.789/−2.469	+1.716/−0.840

Data for [$Ru_7(\mu_5$-κ^2-ampy)(μ_4-η^{12}-$C_{12}H_8$)(μ-CO)(CO)$_{12}$] (9). Anal. Calcd for $C_{31}H_{14}N_2O_{13}Ru_7$ (1329.94): C, 28.00; H, 1.06; N, 2.11. Found: C, 28.06; H, 1.03; N, 2.16. FAB MS: *m/z* 1130 [*M*]$^+$. IR (THF): ν_{CO} 2062 (s), 2016 (vs), 2004 (vs), 1964 (m), 1954 (m), 1921 (w, br), 1825 cm^{-1} (w, br). ^{1}H NMR (Me$_2$SO-d_6, 293 K): δ 7.23 (t, J = 7.7 Hz, 1 H, ampy), 6.83 (d, J = 7.7 Hz, 1 H, ampy), 5.73 (t, J = 5.7 Hz, 1 H), 5.54−5.47 (m, 2 H, ampy + $C_{12}H_8$), 5.42 (d, J = 5.7 Hz, 1 H), 5.35 (t, J = 5.7 Hz, 1 H), 4.96 (d, J = 5.7 Hz, 1 H), 4.47 (d, J = 5.7 Hz, 1 H), 3.86 (d, J = 2.8 Hz, 1 H), 3.05 (d, J = 2.8 Hz, 1 H), 2.63 (s, 3 H, ampy).

Data for [$Ru_6(\mu_4$-κ^1-ampy)(μ_4-η^{12}-$C_{12}H_8$)(μ-CO)$_2$(CO)$_9$] (10). Anal. Calcd for $C_{29}H_{14}N_2O_{11}Ru_6$ (1172.86): C, 29.70; H, 1.20; N, 2.39. Found: C, 29.81; H, 1.16; N, 2.44. FAB MS: *m/z* 1146 [*M* − CO]$^+$. IR (THF): ν_{CO} 2030 (vs), 1991 (vs), 1976 (s, sh), 1966 (vs, br), 1954 (m, sh), 1917 (w, br), 1893 (w, br), 1837 (w, br), 1798 cm^{-1} (m, br). ^{1}H NMR (Me$_2$SO-d_6, 293 K): δ 6.60 (t, J = 7.7 Hz, 1 H, ampy), 6.30 (d, J = 7.7 Hz, 1 H, ampy), 6.16 (t, J = 5.8 Hz, 1 H), 5.93 (d, J = 5.8 Hz, 1 H), 5.60 (t, J = 5.8 Hz, 1 H), 5.47 (d, J = 5.8 Hz, 1 H), 5.16 (d, J = 5.8 Hz, 1 H), 4.38 (d, J = 5.8 Hz, 1 H), 4.27 (d, J = 7.7 Hz, 1 H), 3.95 (d, J = 2.8 Hz, 1 H), 3.14 (d, J = 2.8 Hz, 1 H), 2.12 (s, 3 H, ampy).

Reaction of Compound 10 with Dimethyl Sulfoxide. A solution of compound **10** (11 mg, 0.009 mmol) and dimethyl sulfoxide (0.1 mL) in THF (15 mL) was stirred at reflux temperature until the consumption of the starting complex was observed by IR spectroscopy (14 h). The color changed from red-brown to orange-brown. The solvent was removed under vacuum, the solid residue was dissolved in THF (10 mL), the resulting solution was supported on silica gel (4 g), and the resulting solid was transferred onto a silica gel column (2 × 15 cm) packed in hexane. Hexane−dichloromethane (1:1) eluted two bands (brown and red-brown) that contained trace amounts of unidentified compounds. Hexane−dichloromethane (1:3) eluted an orange-brown band that afforded [$Ru_6(\mu_4$-κ^1-ampy)(μ_4-η^{12}-$C_{12}H_8$)(Me$_2$SO)(μ-CO)$_2$(CO)$_8$] (**11**; 7 mg, 64%). Anal. Calcd for $C_{30}H_{20}N_2O_{11}Ru_6S$ (1222.97): C, 29.46; H, 1.65; N, 2.29. Found: C, 29.52; H, 1.60; N, 2.32. FAB MS: *m/z* 1224 [*M*]$^+$. IR (CH$_2$Cl$_2$): ν_{CO} 2041 (s), 1981 (vs, br), 1958 (vs, br), 1924 (m, br), 1901 (w, sh), 1855 (w, br), 1832 cm^{-1} (w, br). ^{1}H NMR (Me$_2$SO-d_6, 293 K): δ 6.70 (t, J = 7.8 Hz, 1 H, ampy), 6.38−6.25 (m, 2 H, ampy + $C_{12}H_8$), 5.80 (d, J = 5.8 Hz, 1 H), 5.48 (d, J = 5.8 Hz, 2 H), 5.08 (t, J = 5.8 Hz, 1 H), 4.32 (d, J = 7.8 Hz, 1 H, ampy), 4.27 (d, J = 5.8 Hz, 1 H), 3.93 (d, J = 2.8 Hz, 1 H), 3.56 (s, 3 H, Me$_2$SO), 3.51 (s, 3 H, Me$_2$SO), 3.04 (d, J = 2.8 Hz, 1 H), 2.08 (s, 3 H, ampy).

X-ray Diffraction Analyses. Diffraction data for $\mathbf{2}\cdot C_4H_8O$, $\mathbf{4}\cdot 0.25C_2H_4Cl_2$, $\mathbf{5}\cdot C_4H_8O$, $\mathbf{8}\cdot CH_2Cl_2$, and $\mathbf{11}\cdot 0.1C_6H_{14}$ were measured at room temperature on a Bruker AXS SMART 1000 diffractometer, using graphite-monochromated Mo Kα radiation. Raw frame data were integrated with SAINT.[26] Absorption corrections were applied with SADABS.[27] Diffraction data for $\mathbf{9}\cdot 0.5C_4H_8O$ were measured on an Oxford Xcalibur diffractometer, using graphite-monochromated Cu Kα radiation. Raw frame data were integrated and corrected for absorption with CRYSALIS-RED.[28] All structures were solved by direct methods and refined by full-matrix least squares against F^2 with SHELXTL.[29] The position of the hydrides of **2** and **4** were calculated with XHYDEX.[30] The remaining hydrogen atoms were set in calculated positions and refined as riding atoms. The molecular plots were made with the PLATON program package.[31] The WINGX program system[32] was used throughout the structure determinations. A selection of crystal, measurement, and refinement data is given in Table 4. CCDC deposition numbers: 609262 ($\mathbf{2}\cdot C_4H_8O$), 609263 ($\mathbf{4}\cdot 0.25C_2H_4Cl_2$), 609265 ($\mathbf{5}\cdot C_4H_8O$), 609266 ($\mathbf{8}\cdot CH_2Cl_2$), 626722 ($\mathbf{9}\cdot 0.5C_4H_8O$), and 609267 ($\mathbf{11}\cdot 0.1C_6H_{14}$).

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(26) SAINT+: SAX Area Detector Integration Program, Version 6.02; Bruker AXS, Inc., Madison, WI, 1999.

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(28) CRYSALIS-RED, Version 1.171.31.5; Oxford Diffraction Ltd., Oxford, U.K., 2006.

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Supporting Information Available: CIF files giving crystallographic data for the compounds studied by X-ray diffraction. This material is available free of charge via the Internet at http://pubs.acs.org.

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