Reactivity of Arenes, Cycloheptatriene, and Dicyclopentadiene with a Basal Edge-Bridged Square Pyramidal Hexaruthenium Dihydride

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The reactions of 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) with arenes at high temperature (>110 °C) give [$Ru_6(\mu_3\text{-H})_2(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^6\text{-arene})(\mu\text{-CO})_2(CO)_{11}$] (arene = C_6H_6 **2a**, C_6H_5Me **2b**, 1,4-$C_6H_4Me_2$ **2c**). These complexes result from the substitution of the arene for the three CO ligands of the apical Ru atom of **1**. Cycloheptatriene reacts with complex **1** in chlorobenzene at reflux temperature to give a mixture of products from which the hexanuclear cluster complexes [$Ru_6(\mu_3\text{-H})(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^5\text{-}C_7H_9)(\mu_3\text{-CO})(\mu\text{-CO})_2(CO)_{11}$] (**3**), [$Ru_6(\mu_3\text{-H})(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_3\text{-}\eta^7\text{-}C_7H_7)(\mu\text{-CO})_2(CO)_{11}$] (**4**), [$Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_2\text{-}\eta^7\text{-}C_7H_7)_2(\mu\text{-CO})(CO)_9$] (**5**), and [$Ru_6(\mu_6\text{-C})(\mu_3\text{-}\eta^7\text{-}C_7H_7)_2(\mu\text{-CO})_2(CO)_8$] (**6**) have been isolated and characterized. While compound **3** has a terminal η^5-cycloheptadienyl ligand, **4** contains a face-capping η^5:η^2-cycloheptatrienyl ligand, and **5** has two edge-bridging η^4:η^3-cycloheptatrienyl ligands. Compound **6**, a minor product of this reaction, contains an octahedral metallic skeleton with a μ_6-carbide and two face-capping η^3:η^2:η^2-cycloheptatrienyl ligands. It has been established that the thermolysis of complex **3** gives **4** and that complex **5** arises from the reaction of **4** with cycloheptatriene. Treatment of dicyclopentadiene with complex **1** in chlorobenzene at reflux temperature has allowed the isolation of [$Ru_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-CO})_2(CO)_2$] and three cluster derivatives, [$Ru_6(\mu_3\text{-H})(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^5\text{-}C_5H_5)(\mu_3\text{-CO})(\mu\text{-CO})_2(CO)_{11}$] (**7**), [$Ru_6(\mu_3\text{-H})_2(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-CO})(\mu\text{-CO})(CO)_9$] (**8**), and [$Ru_5(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_4\text{-}\eta^4\text{-}C_{10}H_{10})(\mu\text{-CO})_2(CO)_{10}$] (**9**). Compounds **7** and **8** are hexanuclear and contain one and two terminal cyclopentadienyl ligands, respectively. The pentanuclear derivative **9** features an unprecedented η^2:η^2-enyne ligand that derives from the activation of two adjacent H−C(sp^2) bonds of dicyclopentadiene. With the exception of compounds **6** and **9**, the remaining clusters have the same $Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})$ framework as compound **1** and have the apical Ru atom attached to hydrocarbon ligands.

Introduction

During a study of the reactivity of carbonyl ruthenium clusters derived from 2-aminopyridines,[1] we recently observed that [$Ru_3(CO)_{12}$] can condense with triruthenium clusters of the type [$Ru_3(\mu\text{-H})(\mu_3\text{-}\kappa^2\text{-HapyR})(CO)_9$] ($H_2$apyR = 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.[2,3] 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 [$Ru_3(CO)_{12}$].[4−6] Their reactivity has not been studied, probably because of their low-yield preparations.

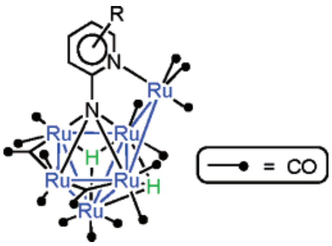

Figure 1. Schematic structure of compounds of the type [$Ru_6(\mu_3\text{-H})_2(\mu_5\text{-}\kappa^2\text{-apyR})(\mu\text{-CO})_2(CO)_{14}$].

Our efficient method of synthesizing this type of cluster complexes opened up the possibility of exploring their reactivity. We have recently reported the reactions of tertiary phosphines,[3] diphenylacetylene,[7] diphenylbutadiyne,[8] and [PPN][BH_4][9] with

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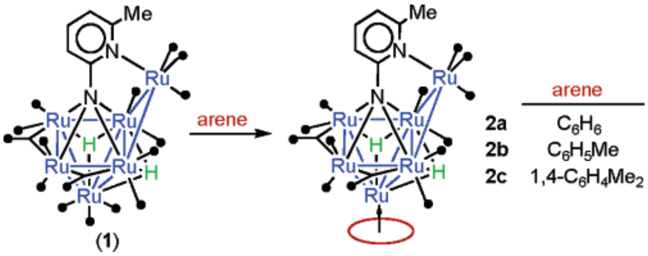
Scheme 1



$[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$ (**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.[3]

Studying the above-mentioned 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 cyclohydrocarbons. We now report the reactivity of compound **1** with benzene and methylated benzenes, cycloheptatriene, and cyclopentadiene dimer (dicyclopentadiene). These results include the synthesis 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.

Results and Discussion

Reactivity of Compound 1 with Arenes. No change was observed when compound **1** was stirred in benzene at reflux temperature for 16 h. However, the arene derivatives $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^6\text{-arene})(\mu\text{-}CO)_2(CO)_{11}]$ (arene = C_6H_5Me **2b**, $1,4\text{-}C_6H_4Me_2$ **2c**) were prepared when **1** was refluxed in toluene (12 h, 69%) and *p*-xylene (2 h, 66%), respectively (Scheme 1). It was then clear that the boiling temperature of benzene (80 °C) is too low to induce the activation of complex **1**. The synthesis of $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^6\text{-}C_6H_6)(\mu\text{-}CO)_2(CO)_{11}]$ (**2a**) was achieved performing the reaction of **1** with benzene in 3:1 decane−dioxane at reflux temperature (21 h, 27%). Such a solvent mixture dissolves complex **1** and has an appropriate boiling point (ca. 115 °C).

The structure of complex **2b** was determined by X-ray diffraction (Figure 2, Table 1). It can be described as resulting from the formal substitution of an η^6-toluene molecule for the three CO ligands of the apical $Ru(CO)_3$ unit of compound **1**. Excluding the atoms of the toluene ligand, the remaining atoms of **2b** maintain the same positions they have in compound **1**.[3]

The great similarity of the IR and ^1H NMR spectra of compounds **2a**−**c** confirms that these complexes have the same structure. Their ^1H NMR spectra also indicate that there is free rotation of the arene ligand around the axis defined by the apical Ru atom and the centroid of the arene ring. Barriers to arene rotation in terminal η^6-arene clusters are very small, being similar to those found in mononuclear systems.[10]

The regioselectivity of these reactions is high in the sense that they give only one η^6-arene product. This is remarkable because, due to the low symmetry of compound **1**, several different reaction sites are potentially available and arenes can also coordinate in face-capping positions.[10] The high temperature required by these reactions suggests that the products are thermodynamically controlled. In this context, studying the reactivity of **1** with phosphine ligands, we determined that the activation of compound **1** implies the initial loss of a CO ligand from the Ru atom that is attached to the pyridine fragment, but a subsequent thermally induced CO ligand rearrangement directs the substitution toward the apical Ru atom.[3] Experimental[11,12] and theoretical[12] studies have established that terminal η^6-arene clusters are thermodynamically more stable than face-capping η^6-arene clusters. This explains the observed regioselectivity.

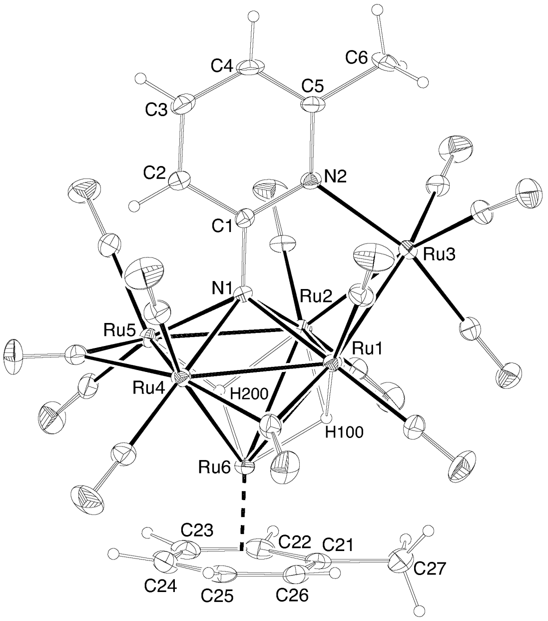


Figure 2. Molecular structure of compound **2b**.

Table 1. Selected Interatomic Distances (Å) in Compound 2b

Ru(1)−Ru(2)	2.754(1)	Ru(1)−Ru(3)	2.756(2)
Ru(1)−Ru(4)	2.7401(2)	Ru(1)−Ru(6)	2.885(2)
Ru(2)−Ru(3)	2.688(1)	Ru(2)−Ru(5)	2.786(2)
Ru(2)−Ru(6)	2.847(2)	Ru(4)−Ru(5)	2.716(2)
Ru(4)−Ru(6)	2.844(2)	Ru(5)−Ru(6)	2.887(2)
N(1)−Ru(1)	2.171(6)	N(1)−Ru(2)	2.169(6)
N(1)−Ru(4)	2.267(7)	N(1)−Ru(5)	2.221(6)
N(2)−Ru(3)	2.215(7)	C(21)−Ru(6)	2.233(9)
C(22)−Ru(6)	2.188(9)	C(23)−Ru(6)	2.19(1)
C(24)−Ru(6)	2.22(1)	C(25)−Ru(6)	2.23(1)
C(26)−Ru(6)	2.24(1)	C−C(arene)$_{av}$	1.40(1)

Most previously known arene ruthenium clusters have been prepared either by using cyclohexadienes as arene precursors or by treating cationic mononuclear arene complexes with anionic ruthenium clusters.[10] Some ruthenium clusters having terminal η^6-arene ligands are byproducts of reactions carried out in arene solvents at high temperatures.[7,8,13]

Reactivity of Compound 1 with Cycloheptatriene. Treatment of compound **1** with cycloheptatriene in chlorobenzene at reflux temperature (132 °C) afforded a mixture of compounds that was separated by chromatographic methods. Four cluster complexes were isolated: $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^5\text{-}C_7H_9)(\mu_3\text{-}CO)(\mu\text{-}CO)_2(CO)_{11}]$ (**3**), $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_3\text{-}\eta^7\text{-}$

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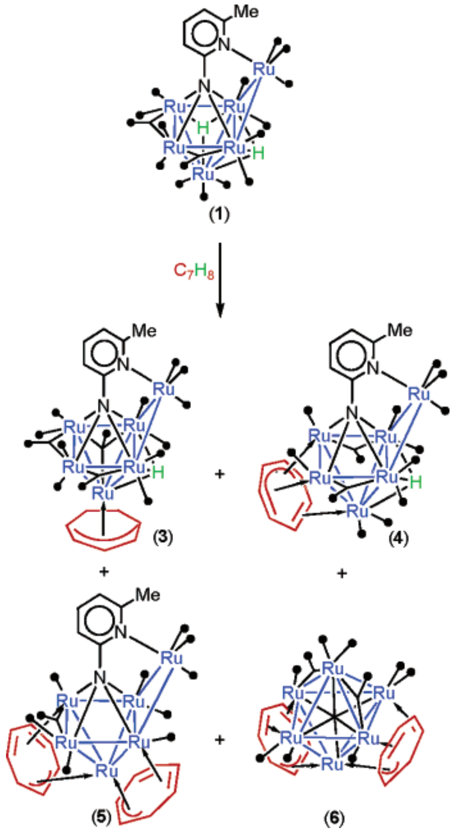
Scheme 2



$C_7H_7)(\mu\text{-}CO)_2(CO)_{11}]$ (**4**), $[Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_2\text{-}\eta^7\text{-}C_7H_7)_2(\mu\text{-}CO)(CO)_9]$ (**5**), and $[Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^7\text{-}C_7H_7)_2(\mu\text{-}CO)_2(CO)_8]$ (**6**) (Scheme 2). All these complexes were characterized by X-ray diffraction as well as by spectroscopic techniques. Only four reports have previously described reactions of ruthenium clusters with cycloheptatriene.[14−17]

In separate experiments, we determined that the thermolysis of complex **3** gives **4** and that complex **5** arises from the reaction of **4** with cycloheptatriene. However, this does not imply that all complex **4** arises from **3**, since its formation from **1**, without the intermediacy of complex **3**, cannot be ruled out.

The molecular structure of compound **3** is shown in Figure 3. A selection of interatomic distances is given in Table 2. Its $Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})$ fragment is similar to that of complex **1**. A cycloheptadienyl ligand is attached to the axial Ru(6) atom through the five C atoms of the dienyl fragment, which is planar. As expected, the two uncoordinated sp^3 atoms C(16) and C(17) are not coplanar with the dienyl fragment, the angle between the planes C(11)−C(12)−C(13)−C(14)−C(15) and C(15)−C(16)−C(17)−C(11) being 130.9(5)°. One hydride and one CO ligand cap two triangular faces of the metallic skeleton. The cluster shell is completed by two edge-bridging and 11 terminal CO ligands. Two ruthenium carbonyl clusters containing cycloheptadienyl ligands, namely, $[Ru_3(\mu\text{-}\eta^6\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)(\mu\text{-}CO)_2(CO)_4]$[14] and $[Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)(\mu\text{-}CO)(CO)_{10}]$,[17] have been previously characterized by X-ray diffraction.

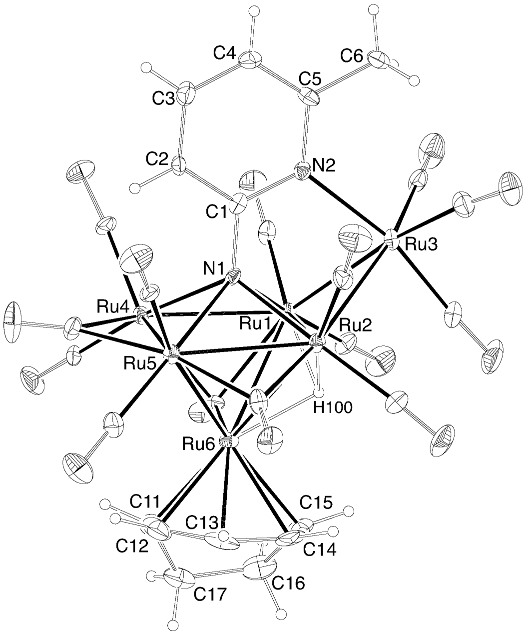


Figure 3. Molecular structure of compound **3**.

At room temperature, most of the ^{1}H NMR resonances of the cycloheptadienyl ligand of compound **3** are broad, indicating that the ligand is involved in a fluxional process. A variable-temperature ^{1}H NMR study (Figure 4) was carried out using $C_6D_5CD_3$ as solvent for high-temperature spectra and $CDCl_3$ for spectra at ambient temperature and below (**3** is sparingly soluble in toluene). The hydride and ampy ligand resonances are sharp at all temperatures. At high temperatures, a pseudomirror plane cuts the ligand into two halves. At low temperatures (the shape of the resonances of spectra measured at temperatures below 0 °C is comparable to those of the 0 °C spectrum), such a pseudomirror plane is not observed. These results are compatible with a fluxional process that involves the rotation of the cycloheptadienyl ligand about the axis defined by the apical Ru atom and the centroid of the pentadienyl moiety. An activation $\Delta G^{\ddagger}$ parameter of ca. 14.1 kcal mol^{-1} has been estimated from the coalescence temperature.[18]

The structure of compound **4** is shown in Figure 5. Table 2 contains a selection of bond distances. Its $Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})$ fragment is similar to that of complex **1**. A cycloheptatrienyl ligand caps the Ru(4)−Ru(5)−Ru(6) face of the cluster in such a way that the Ru(4)−Ru(5) edge is spanned by an η^5-pentadienyl fragment, while the two remaining C atoms are attached to Ru(6) as an η^2-alkene fragment. The cycloheptatrienyl ligand is not planar, the angle between the planes C(11)−C(12)−C(14)−C(15)−C(16)−C(17) and C(12)−C(13)−C(14) being 23.2(9)°. Such a coordination mode is unprecedented for cycloheptatrienyl ligands. The cluster shell is completed by a face-capping hydride and 13 CO ligands (two in edge-bridging and the remaining in terminal positions).

The molecular structure of the bis(cycloheptatrienyl) derivative **5** is depicted in Figure 6. Selected bond distances are given in Table 2. In addition to the usual $Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})$ fragment, this compound contains two cycloheptatrienyl ligands spanning two nonbasal edges of the square pyramid part of the metallic skeleton. Both ligands are equivalent, being attached to the apical Ru(6) atom through the three C atoms of an η^3-allyl fragment and to one of the Ru atoms of the pyramid base through the remaining four C atoms, which behave as a chelating η^4-diene. In agreement with their coordination mode, the

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Table 2. Selected Interatomic Distances (Å) in Compounds 3−5

	3	4	5
Ru(1)−Ru(2)	2.785(1)	2.7648(9)	2.721(1)
Ru(1)−Ru(3)	2.679(1)	2.7147(9)	2.690(1)
Ru(1)−Ru(4)	2.794(1)	2.7085(9)	2.770(1)
Ru(1)−Ru(6)	2.800(2)	2.920(1)	2.912(1)
Ru(2)−Ru(3)	2.749(2)	2.714(1)	2.752(1)
Ru(2)−Ru(5)	2.752(1)	2.6983(9)	2.740(1)
Ru(2)−Ru(6)	3.001(1)	2.9388(9)	2.887(1)
Ru(4)−Ru(5)	2.710(1)	2.7831(9)	2.698(1)
Ru(4)−Ru(6)	2.875(1)	2.8247(8)	2.898(1)
Ru(5)−Ru(6)	2.924(2)	2.8248(9)	2.952(1)
N(1)−Ru(1)	2.179(7)	2.176(5)	2.161(7)
N(1)−Ru(2)	2.165(7)	2.176(5)	2.149(7)
N(1)−Ru(4)	2.221(8)	2.201(5)	2.250(7)
N(1)−Ru(5)	2.262(7)	2.231(5)	2.174(7)
N(2)−Ru(3)	2.194(8)	2.222(5)	2.192(7)
C(11)−Ru(4)		2.242(7)	2.12(1)
C(11)−Ru(6)	2.26(1)		
C(12)−Ru(4)		2.143(8)	2.58(1)
C(12)−Ru(6)	2.19(1)		
C(13)−Ru(4)		2.52(1)	
C(13)−Ru(5)		2.54(1)	
C(13)−Ru(6)	2.21(1)		2.251(1)
C(14)−Ru(5)		2.148(8)	
C(14)−Ru(6)	2.19(1)		2.101(1)
C(15)−Ru(5)		2.237(8)	
C(15)−Ru(6)	2.31(1)		2.16(1)
C(16)−Ru(4)			2.55(2)
C(16)−Ru(6)		2.254(7)	
C(17)−Ru(4)			2.13(1)
C(17)−Ru(6)		2.259(7)	
C(21)−Ru(2)			2.18(1)
C(22)−Ru(2)			2.42(1)
C(23)−Ru(6)			2.30(1)
C(24)−Ru(6)			2.12(1)
C(25)−Ru(6)			2.17(1)
C(26)−Ru(2)			2.51(1)
C(27)−Ru(2)			2.17(1)
C(11)−C(12)	1.33(2)	1.37(1)	1.55(3)
C(11)−C(17)	1.46(2)	1.43(1)	1.34(3)
C(12)−C(13)	1.34(2)	1.43(1)	1.32(2)
C(13)−C(14)	1.46(2)	1.44(1)	1.39(2)
C(14)−C(15)	1.48(2)	1.38(1)	1.43(2)
C(15)−C(16)	1.50(2)	1.44(1)	1.39(2)
C(16)−C(17)	1.54(2)	1.41(1)	1.54(3)
C(21)−C(22)			1.44(2)
C(21)−C(27)			1.36(2)
C(22)−C(23)			1.42(2)
C(23)−C(24)			1.33(2)
C(24)−C(25)			1.48(2)
C(25)−C(26)			1.47(2)
C(26)−C(27)			1.46(2)

cycloheptatrienyl ligands of **5** are not planar, but have a pseudoboat conformation. In one cycloheptatrienyl ligand, the angles of the plane C(12)−C(13)−C(15)−C(16) with the C(13)−C(14)−C(15) and C(11)−C(12)−C(16)−C(17) planes are 18.96(2)° and 25.15(1)°, respectively. In the other cycloheptatrienyl ligand, the angles of the plane C(22)−C(23)−C(25)−C(26) with the C(23)−C(24)−C(25) and C(21)−C(22)−C(26)−C(27) planes are 25.95(1)° and 20.52(2)°, respectively. One bridging and nine terminal CO ligands complete the cluster shell. Ruthenium carbonyl clusters containing edge-bridging cycloheptatrienyl ligands are very rare, the tetranuclear cluster $[Ru_4(\mu\text{-}\eta^7\text{-}C_7H_7)_2(\mu\text{-}CO)(CO)_6]$ being the only precedent of such compounds.[16]

Compound **6** is a minor product (1%) of the reaction of **1** with cycloheptatriene. Its X-ray structure (Figure 7, Table 3) shows that it is a hexanuclear cluster with an octahedral skeleton. It contains two face-capping cycloheptatrienyl ligands, a μ_6-carbide, two edge-bridging CO ligands, and eight terminal CO ligands. The molecule has a noncrystallographic 2-fold axis that relates both cycloheptatrienyl ligands. The face-capping coordination mode of the cycloheptatrienyl ligands of complex **6** is different from that shown by this ligand in complex **4**. In **6**, two η^2-alkene moieties of each cycloheptatrienyl ligand are attached to two metal atoms, while the remaining three C atoms of each ligand are attached to Ru(1) in an η^3-allyl fashion. Six C atoms of these ligands are roughly coplanar, the central C atom of their allyl moiety being the only atom that deviates from that plane. The angle between the planes C(21)−C(22)−C(23)−C(24)−C(25)−C(26) and C(21)−C(27)−C(26) is 21.9-

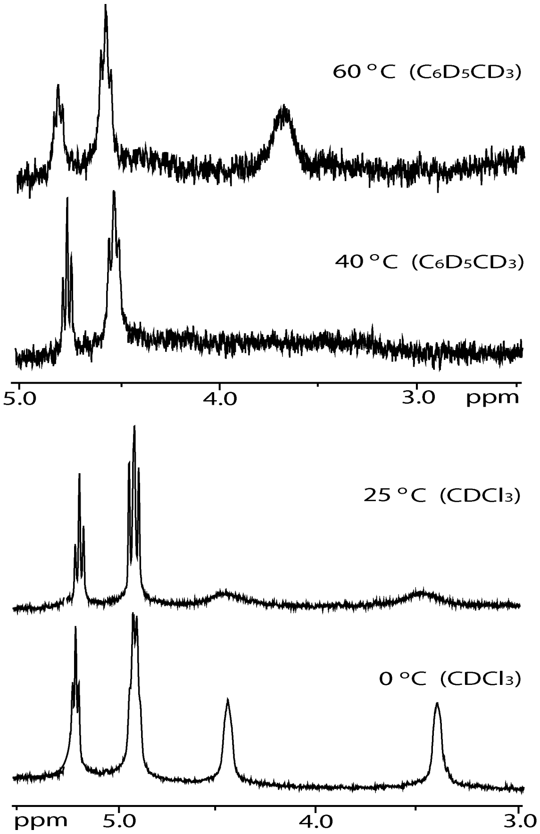


Figure 4. Variable-temperature ^1H NMR spectra (400 MHz) of compound **3** in the region of the pentadienyl proton resonances.

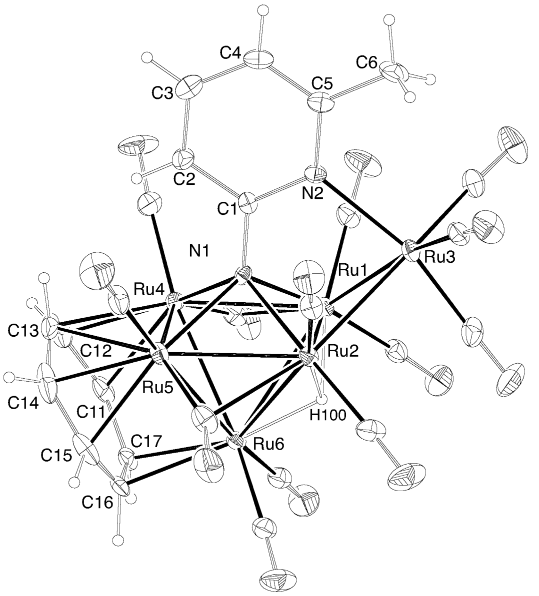


Figure 5. Molecular structure of compound **4**.

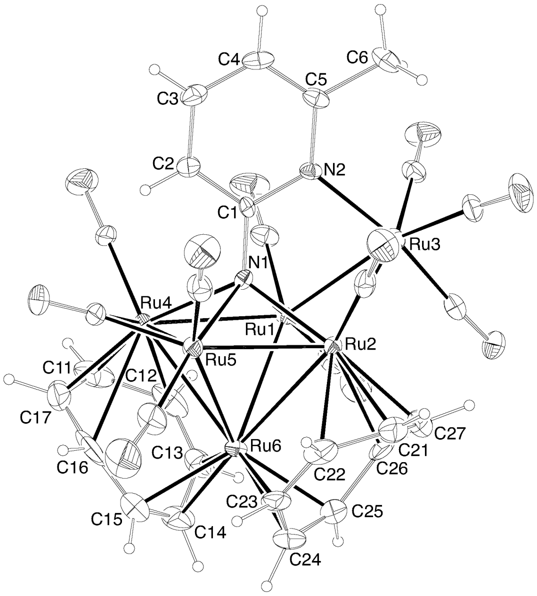


Figure 6. Molecular structure of compound **5**.

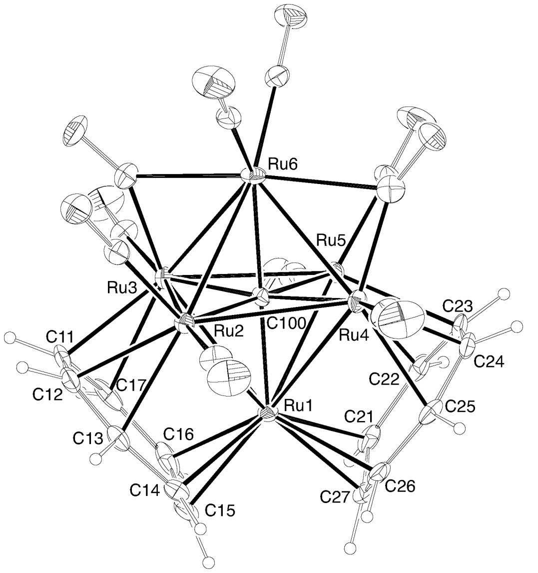


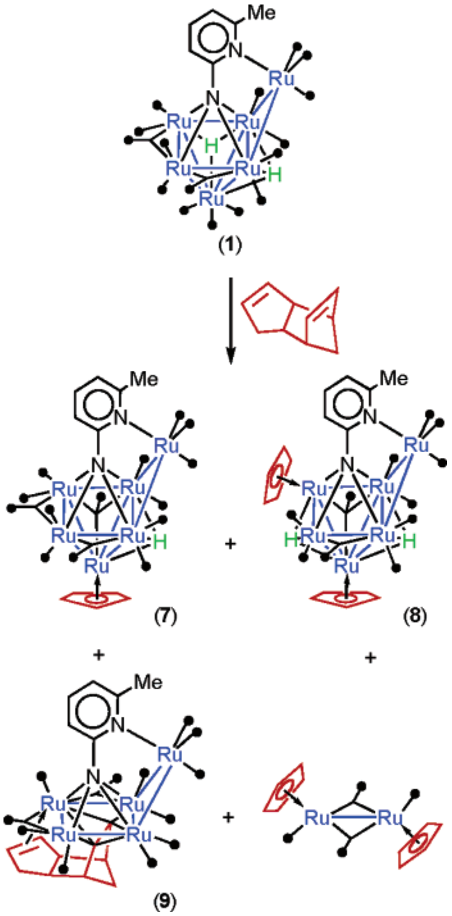
Figure 7. Molecular structure of compound **6**.

Table 3. Selected Interatomic Distances (Å) in Compound 6

Ru(1)−Ru(2)	2.8606(7)	Ru(1)−Ru(3)	2.954(1)
Ru(1)−Ru(4)	2.9274(7)	Ru(1)−Ru(5)	2.8470(9)
Ru(2)−Ru(3)	2.910(1)	Ru(2)−Ru(4)	2.9338(7)
Ru(2)−Ru(6)	2.9374(9)	Ru(3)−Ru(5)	2.8826(7)
Ru(3)−Ru(6)	2.8317(7)	Ru(4)−Ru(5)	2.936(1)
Ru(4)−Ru(6)	2.845(1)	C(11)−Ru(3)	2.221(5)
C(12)−Ru(2)	2.311(6)	C(13)−Ru(2)	2.237(6)
C(14)−Ru(1)	2.316(6)	C(15)−Ru(1)	2.140(5)
C(16)−Ru(1)	2.263(6)	C(17)−Ru(3)	2.246(6)
C(21)−Ru(1)	2.334(5)	C(22)−Ru(5)	2.198(5)
C(23)−Ru(5)	2.336(5)	C(24)−Ru(4)	2.207(5)
C(25)−Ru(4)	2.241(5)	C(26)−Ru(1)	2.295(6)
C(27)−Ru(1)	2.146(5)	C(100)−Ru(1)	1.986(5)
C(100)−Ru(2)	2.079(5)	C(100)−Ru(3)	2.050(5)
C(100)−Ru(4)	2.059(5)	C(100)−Ru(5)	2.056(5)
C(100)−Ru(6)	2.084(5)		

(5)°. Such a face-capping coordination mode has been previously found in the solid-state structures of $[Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)(\mu\text{-}CO)(CO)_{10}]$[15] and $[Ru_3(\mu_3\text{-}SBu^t)(\mu_3\text{-}\eta^7\text{-}C_7H_7)(CO)_6]$.[17]

Scheme 3



It has been reported that the reaction of $[Ru_6(\mu_6\text{-}C)(CO)_{17}]$ with an excess of cycloheptatriene in refluxing octane gives a mixture of $[Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)(\mu\text{-}CO)(CO)_{10}]$, $[Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^2\text{-}enbd)(CO)_{15}]$ (enbd = ethylenenorbornadiene), $[Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^6\text{-}C_7H_8)(\mu\text{-}CO)(CO)_{13}]$, and $[Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^6\text{-}C_5H_5Me)(\mu\text{-}CO)(CO)_{13}]$.[15] As compound **6**, which has two cycloheptatrienyl ligands, is not a product of this reaction, its formation in the reaction of **1** with cycloheptatriene seems to imply the condensation of two trinuclear cycloheptatrienyl species.

In solution, the cycloheptatrienyl ligands of compounds **4**−**6** rotate freely, since the ^1H NMR spectra of these compounds display singlet resonances for the protons of their cycloheptatrienyl ligands even at −80 °C. Therefore, the barriers to rotation of these ligands are very low, regardless of their edge-bridging or face-capping coordination mode.

Reactivity of Compound 1 with Dicyclopentadiene. The results stated above on reactions of compound **1** with arenes and cycloheptatriene led us to attempt the preparation of cyclopentadienyl derivatives of complex **1**. As the high temperatures (>110 °C) required for the activation of compound **1** are incompatible with the use of cyclopentadiene as reagent (bp = 42 °C), we decided to use dicyclopentadiene (bp = 170 °C) because this dimeric molecule gives the monomer at temperatures close to its boiling point.[19]

Treatment of compound **1** with dicyclopentadiene in chlorobenzene at reflux temperature afforded a mixture of compounds that were separated by chromatographic methods. Three novel cluster derivatives, $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-}ampy)(\eta^5\text{-}C_5H_5)(\mu_3\text{-}CO)(\mu\text{-}CO)_2(CO)_{11}]$ (**7**), $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-}ampy)(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)(\mu\text{-}CO)(CO)_9]$ (**8**), and $[Ru_5(\mu_5\text{-}\kappa^2\text{-}ampy)(\mu_4\text{-}\eta^4\text{-}C_{10}H_{10})(\mu\text{-}$

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[19] (a) Magnusson, G. *J. Org. Chem.* **1985**, *50*, 1998. (b) Moffet, R. B. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 238.

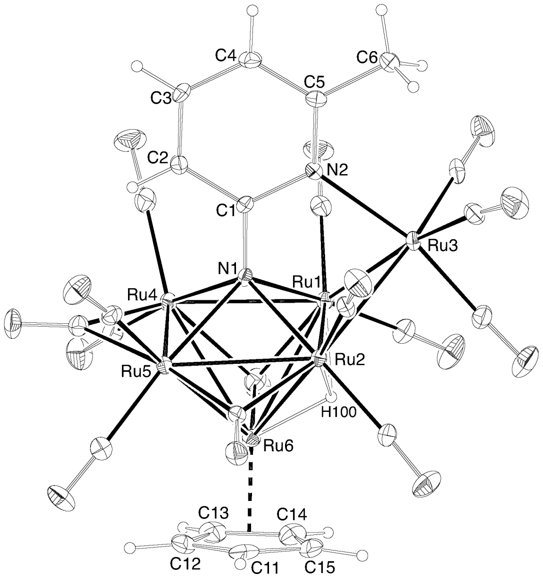

Figure 8. Molecular structure of compound **7**.

Table 4. Selected Interatomic Distances (Å) in Compounds 7−9

	7	8	9
Ru(1)−Ru(2)	2.7426(7)	2.770(1)	2.7052(8)
Ru(1)−Ru(3)	2.7002(7)	2.686(1)	2.6687(8)
Ru(1)−Ru(4)	2.7792(8)	2.722(1)	2.7288(7)
Ru(1)−Ru(6)	2.7834(9)	2.840(1)	
Ru(2)−Ru(3)	2.7374(8)	2.721(1)	2.7659(9)
Ru(2)−Ru(5)	2.7454(7)	2.725(1)	2.7112(8)
Ru(2)−Ru(6)	2.8910(7)	2.959(1)	
Ru(4)−Ru(5)	2.7083(7)	2.785(1)	2.7609(8)
Ru(4)−Ru(6)	2.8570(8)	2.796(1)	
Ru(5)−Ru(6)	2.8543(9)	2.872(1)	
N(1)−Ru(1)	2.176(4)	2.149(8)	2.176(5)
N(1)−Ru(2)	2.157(4)	2.182(7)	2.166(4)
N(1)−Ru(4)	2.233(4)	2.217(7)	2.226(4)
N(1)−Ru(5)	2.244(4)	2.267(8)	2.259(5)
N(2)−Ru(3)	2.195(4)	2.233(7)	2.237(5)
C(11)−Ru(6)	2.210(6)	2.20(1)	
C(12)−Ru(6)	2.226(6)	2.19(1)	
C(13)−Ru(6)	2.202(5)	2.18(1)	
C(14)−Ru(6)	2.207(6)	2.22(1)	
C(15)−Ru(6)	2.217(6)	2.21(1)	
C(21)−Ru(4)		2.17(1)	
C(22)−Ru(4)		2.20(1)	
C(23)−Ru(4)		2.20(1)	
C(24)−Ru(4)		2.20(1)	
C(25)−Ru(4)		2.17(1)	
C(11)−Ru(1)			2.249(6)
C(11)−Ru(2)			2.134(6)
C(11)−Ru(5)			2.342(6)
C(12)−Ru(1)			2.338(6)
C(12)−Ru(4)			2.094(6)
C(12)−Ru(5)			2.294(6)
C(18)−Ru(5)			2.224(6)
C(19)−Ru(5)			2.204(6)
$C-C(Cp)_{av}$	1.398(9)	1.41(2)	
C(11)−C(12)			1.445(9)
C(17)−C(18)			1.50(1)

$CO)_2(CO)_{10}]$ (**9**), and the known binuclear complex $[Ru_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_2(CO)_2]$ (Scheme 3) were isolated and were characterized by X-ray diffraction (**7**−**9**) as well as by spectroscopic techniques.

The X-ray molecular structure of compound **7** is shown in Figure 8. A selection of interatomic distances is given in Table 4. The structure is entirely analogous to that of complex **3**, but having a terminal cyclopentadienyl ligand attached to the axial Ru(6) atom (instead of the pentadienyl fragment of the cycloheptadienyl ligand of complex **3**).

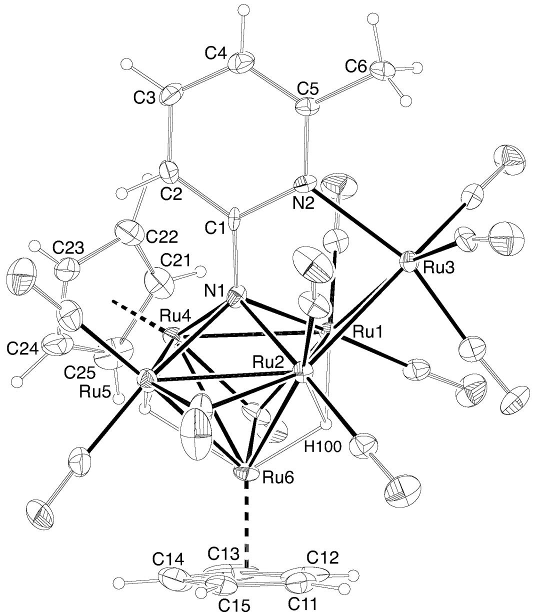

Figure 9. Molecular structure of one of the two crystallographically independent molecules of compound **8**.

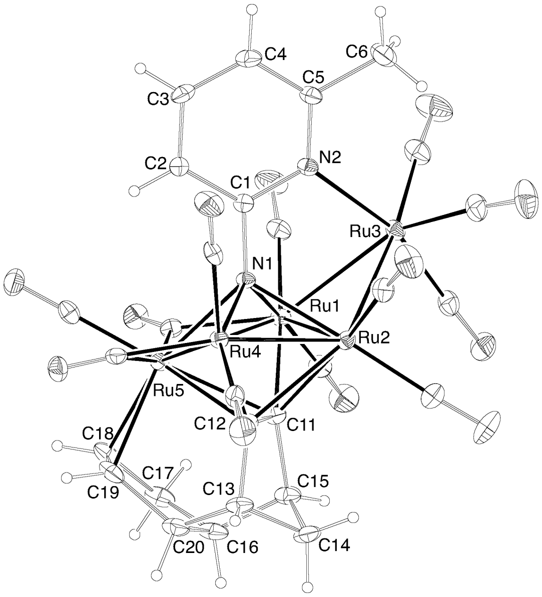

Figure 10. Molecular structure of compound **9**.

The structure of compound **8** (Figure 9, Table 4) can be described as resulting from the substitution of a hydride and a cyclopentadienyl ligand for one edge-bridging and two terminal CO ligands of **7**. The new cyclopentadienyl ligand is attached to Ru(4), while the new hydride caps the Ru(4)−Ru(5)−Ru(6) face.

The structure of compound **9** is shown in Figure 10. A selection of interatomic distances is given in Table 4. The compound is pentanuclear and has its five metal atoms attached to the ampy ligand in a way analogous with that found for the $Ru_5(\mu_5\text{-}\kappa^2\text{-ampy})$ moiety of all the complexes described in this paper. A hydrocarbon ligand, which formally derives from the activation of both C−H bonds of one of the alkene moieties of dicyclopentadiene, is attached through the C(11) and C(12) atoms to the Ru(1), Ru(2), Ru(4), and Ru(5) atoms in the same way as a μ_4-alkyne,[20−22] while the C atoms of its alkene fragment, C(18) and C(19), are also bound to Ru(5). Now, the Ru(1), Ru(2), Ru(4), and Ru(5) atoms are not coplanar but distorted toward an incipient butterfly arrangement. This structure is reminiscent of those of $[Ru_5(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_4\text{-}\eta^2\text{-PhCCPh})(\mu\text{-CO})(CO)_{12}]$,[7] $[Ru_5(\mu_4\text{-S})(\mu_4\text{-}\eta^2\text{-PhCCH})(\mu\text{-CO})(CO)_{13}]$,[21] and $[Ru_5(\mu_4\text{-NH})(\mu_4\text{-}\eta^2\text{-PhCCH})(\mu\text{-CO})(CO)_{13}]$,[22] since these complexes and compound **9** have in common their metallic skeletons and the way the alkyne coordinates to the metals. The enyne ligand of compound **9** is unprecedented.

The formation of the pentanuclear cluster **9** from **1** and dicyclopentadiene should be accompanied by the release of mononuclear species. This accounts for the observation of a small amount of $[Ru_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-CO})_2(CO)_2]$[24] among the reaction products.

To our knowledge, dicyclopentadiene has never been used to directly introduce cyclopentadienyl ligands into carbonyl metal clusters. Mono- and bis(cyclopentadienyl) ruthenium clusters have previously been prepared via the reaction of $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ with anionic precursors, such as $[Ru_5(\mu_5\text{-C})(CO)_{14}]^{2-}$ and $[Ru_6(\mu_6\text{-C})(CO)_{16}]^{2-}$.[23]

Concluding Remarks

The present work is the first reactivity study involving hexaruthenium cluster complexes of basal edge-bridged square pyramidal metallic skeleton and unsaturated carbocycles. Compound **1** reacts with benzene and substituted benzenes to give, selectively, hexanuclear derivatives containing an η^6-arene ligand in an apical position (**2a**−**c**). The high selectivity of this reaction contrasts with those of **1** with cycloheptatriene and dicyclopentadiene, from which four (**3**−**6**) and three (**7**−**9**) novel cluster complexes have been isolated, respectively. While compounds **3**−**6** are rare examples of cluster complexes containing η^5-cycloheptadienyl (**3**) and μ_2- (**5**) and μ_3-η^7-cycloheptatrienyl (**4**, **6**) ligands, **7** and **8** are the first examples of cyclopentadienyl cluster complexes made directly from dicyclopentadiene. Compound **9** contains an unprecedented enyne ligand that arises from the activation of two adjacent H−C(sp^2) bonds of dicyclopentadiene.

From this work, it is evident that the ampy ligand behaves as a reliable anchor that is able not only to maintain the pentanuclear edge-bridged square metal framework in reactions performed at high temperatures (>110 °C) but also to direct the reactivity toward the apical metal atom. In fact, with the exception of compounds **6** (which is a very minor product) and **9** (which is an alkyne derivative and it is known the great tendency of alkynes to coordinate to square faces[7,8]), the remaining clusters have the same $Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})$ framework as compound **1** and have the apical Ru atom attached to hydrocarbon ligands.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (hydrocarbons, THF) or CaH_2 (dichloromethane) 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.[3] IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. ^1H NMR spectra were run on Bruker DPX-300 or AV-400 instruments, using the dichloromethane solvent resonance as internal standard ($\delta = 5.30$). 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.

$[Ru_6(\mu_3\text{-H})_2(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^6\text{-}C_6H_6)(\mu\text{-CO})_2(CO)_{11}]$ (2a). A mixture of compound **1** (30 mg, 0.026 mmol) and benzene (1 mL) in 3:1 decane−dioxane (15 mL) was stirred at reflux temperature for 21 h. A considerable amount of intractable black solid precipitated. The solvent was removed under vacuum. The residue was extracted with dichloromethane, the solution was filtered, the solvent was removed, and the residue was recrystallized by sequentially adding THF (1 mL) and hexane (50 mL) to give compound **2a** as a reddish-brown solid (8 mg, 27%). Anal. Calcd for $C_{25}H_{14}N_2O_{13}Ru_6$ (1156.80): C, 25.96; H, 1.22; N, 2.42. Found: C, 26.05; H, 1.24; N, 2.45. FAB-MS: 1158 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2069 (m), 2034 (s), 2014 (vs), 2001 (m, sh), 1992 (m, sh), 1976 (m, br), 1955 (m, br), 1940 (w, sh), 1839 (w, br), 1807 (w, br). ^1H NMR ($CDCl_3$, 293 K): δ 7.00 (t, $J = 7.9$ Hz, 1 H, ampy), 6.42 (d, $J = 7.9$ Hz, 1 H, ampy), 5.76 (d, $J = 7.9$ Hz, 1 H, ampy), 5.13 (s, 6 H, benzene), 2.43 (s, 3 H, Me, ampy), −13.54 (d, $J = 1.7$ Hz, 1 H), −16.55 (d, $J = 1.7$ Hz, 1 H).

$[Ru_6(\mu_3\text{-H})_2(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^6\text{-}C_6H_5Me)(\mu\text{-CO})_2(CO)_{11}]$ (2b). A solution of compound **1** (33 mg, 0.028 mmol) in toluene was stirred at reflux temperature for 12 h. The solvent was removed under vacuum. The residue was extracted with dichloromethane, the solution was filtered, the solvent was removed, and the residue was recrystallized by sequentially adding THF (1 mL) and hexane (50 mL) to give compound **2b** as a reddish-brown solid (23 mg, 69%). Anal. Calcd for $C_{26}H_{16}N_2O_{13}Ru_6$ (1170.83): C, 26.67; H, 1.38; N 2.39. Found: C, 26.71; H, 1.35; N, 2.38. FAB-MS: 1172 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2067 (m), 2033 (s), 2013 (vs), 1998 (m, sh), 1990 (m, sh), 1976 (m, br), 1953 (m, br), 1935 (w, sh), 1837 (w, br), 1806 (w, br). ^1H NMR ($CDCl_3$, 293 K): δ 6.99 (t, $J = 7.8$ Hz, 1 H, ampy), 6.42 (d, $J = 7.8$ Hz, 1 H, ampy), 5.76 (d, $J = 7.8$ Hz, 1 H, ampy), 5.17 (d, $J = 5.5$ Hz, 2 H, toluene), 5.03 (t, $J = 5.5$ Hz, 2 H, toluene), 4.86 (t, $J = 5.5$ Hz, 1 H, toluene), 2.44 (s, 3 H, ampy), 2.13 (s, 3 H, toluene), −13.65 (d, $J = 2.0$ Hz, 1 H), −16.68 (d, $J = 2.0$ Hz, 1 H).

$[Ru_6(\mu_3\text{-H})_2(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^6\text{-1,4-}C_6H_4Me_2)(\mu\text{-CO})_2(CO)_{11}]$ (2c). A solution of compound **1** (31 mg, 0.027 mmol) in *p*-xylene was stirred at reflux temperature for 2 h. The solvent was removed under vacuum. The residue was extracted with dichloromethane, the solution was filtered, the solvent was removed, and the residue was recrystallized by sequentially adding THF (1 mL) and hexane (50 mL) to give compound **2c** as a reddish-brown solid (21 mg, 66%). Anal. Calcd for $C_{27}H_{18}N_2O_{13}Ru_6$ (1184.86): C, 27.37; H, 1.53; N, 2.36. Found: C, 27.22; H, 1.47; N, 2.29. FAB-MS: 1186 $[M]^+$.

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(20) See, for example: (a) Blohm, M. L.; Gladfelter, W. L. *Organometallics* **1986**, *5*, 1049. (b) Ho, E. N. M.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1998**, 513. (c) Ho, E. N. M.; Lin, Z.; Wong, W. T. *Eur. J. Inorg. Chem.* **2001**, 1321. (d) Cabeza, J. A.; del Río, I.; García-Granda, S.; Moreno, M.; Riera, V.; Rosales-Hoz, M. J.; Suárez, M. *Eur. J. Inorg. Chem.* **2001**, 2899. (e) Corrigan, J. F.; Doherty, S.; Taylor, N. J.; Carty, A. J. *Organometallics* **1985**, *4*, 2066. (f) Corrigan, J. F.; Doherty, S.; Taylor, N. J.; Carty, A. J. *Organometallics* **1993**, *12*, 1365. (g) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. *J. Chem. Soc., Chem. Commun.* **1980**, 1190. (h) Braga, D.; Grepioni, F.; Brown, D. B.; Johnson, B. F. G.; Calhorda, M. J. *Organometallics* **1996**, *15*, 5723. (i) Deeming, A. J.; Speel, D. M. *Organometallics* **1997**, *16*, 289. (j) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2002**, 3879. (k) Bruce, M. I.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *Aust. J. Chem.* **1999**, *52*, 681.

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IR (CH_2Cl_2): ν_{CO} 2067 (m), 2033 (s), 2012 (vs), 1997 (m, sh), 1989 (m, sh), 1976 (m, br), 1951 (m, br), 1934 (w, sh), 1836 (w, br), 1802 (w, br). ^1H NMR ($CDCl_3$, 293 K): δ 6.98 (t, $J = 7.7$ Hz, 1 H, ampy), 6.41 (d, $J = 7.7$ Hz, 1 H, ampy), 5.76 (d, $J = 7.7$ Hz, 1 H, ampy), 5.07 (s, 4 H, *p*-xylene), 2.44 (s, 3 H, ampy), 2.07 (s, 6 H, *p*-xylene), −13.73 (d, $J = 1.0$ Hz, 1 H), −17.14 (d, $J = 1.0$ Hz, 1 H).

Reaction of Compound 1 with Cycloheptatriene. A solution of compound **1** (150 mg, 0.129 mmol) and cycloheptatriene (1 mL) in chlorobenzene was stirred at reflux temperature for 1.5 h. The dark brown initial color changed to dark green. The solvent was removed under vacuum, and the residue was dissolved into dichloromethane (4 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 two minor unidentified bands. Hexane−dichloromethane (2:1) eluted a brown band that afforded compound **3** (10 mg, 6%). Hexane−dichloromethane (1:1) eluted a dark green band that afforded compound **4** (38 mg, 25%). Subsequent elution with hexane−dichloromethane (1:4) eluted a brown solution that contained a mixture of compounds. This solution was supported on silica gel (4 g), and the resulting solid was transferred onto a silica gel column (2 × 10 cm) packed in hexane. The elution of this column with hexane−diethyl ether (1:1) afforded a minor unidentified brown band. Subsequent elution with hexane−diethyl ether (1:2) separated two brown bands that, in order of elution, afforded compounds **5** (4 mg, 3%) and **6** (2 mg, 1%).

Data for [$Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^5\text{-}C_7H_9)(\mu_3\text{-}CO)(\mu\text{-}CO)_2(CO)_{11}$] (3). Anal. Calcd for $C_{27}H_{16}N_2O_{14}Ru_6$ (1198.84): C, 27.05; H, 1.35; N, 2.34. Found: C, 27.20; H, 1.42; N, 2.31. FAB-MS: 1200 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2076 (m), 2042 (s), 2023 (vs), 2009 (m), 1986 (m, br), 1965 (m, br), 1949 (vw, sh), 1838 (w, br), 1803 (m, br). ^1H NMR ($CDCl_3$, 293 K): δ 7.10 (t, $J = 7.8$ Hz, 1 H, ampy), 6.52 (d, $J = 7.8$ Hz, 1 H, ampy), 6.02 (d, $J = 7.8$ Hz, 1 H, ampy), 5.23 (t, $J = 6.9$ Hz, 1 H, cycloheptadienyl), 4.95 (t, $J = 6.9$ Hz, 2 H, cycloheptadienyl), 4.5 (s, br, 1 H, cycloheptadienyl), 3.5 (s, br, 1 H, cycloheptadienyl), 2.45 (s, 3 H, ampy), 2.1−2.0 (m, 2 H, cycloheptadienyl), 1.4−0.8 (s, br, 2 H, cycloheptadienyl), −17.72 (s, 1 H).

Data for [$Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_3\text{-}\eta^7\text{-}C_7H_7)(\mu\text{-}CO)_2(CO)_{11}$] (4). Anal. Calcd for $C_{26}H_{14}N_2O_{13}Ru_6$ (1168.82): C, 26.72, H, 1.21; N, 2.40. Found: C, 27.00; H, 1.26; N, 2.36. FAB-MS: 1170 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2069 (s), 2025 (m), 2011 (vs), 2001 (s, sh), 1974 (m, br), 1856 (w, br). ^1H NMR ($CDCl_3$, 293 K): δ 6.99 (t, $J = 7.8$ Hz, 1 H, ampy), 6.47 (d, $J = 7.8$ Hz, 1 H, ampy), 5.12 (d, $J = 7.8$ Hz, 1 H, ampy), 3.85 (s, 7 H, cycloheptatrienyl), 2.61 (s, 3 H, ampy), −16.07 (s, 1 H). ^1H NMR (CD_2Cl_2, 193 K): δ 7.05 (t, $J = 7.7$ Hz, 1 H, ampy), 6.50 (d, $J = 7.7$ Hz, 1 H, ampy), 5.03 (d, $J = 7.7$ Hz, 1 H, ampy), 3.86 (s, 7 H, cycloheptatrienyl), 2.51 (s, 3 H, ampy), −16.10 (s, 1 H).

Data for [$Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_2\text{-}\eta^7\text{-}C_7H_7)_2(\mu\text{-}CO)(CO)_9$] (5). Anal. Calcd for $C_{30}H_{20}N_2O_{10}Ru_6$ (1174.91): C, 30.67; H, 1.72; N, 2.38. Found: C, 30.72; H, 1.76; N, 2.31. FAB-MS: 1176 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2050 (s), 1991 (vs, br), 1981 (vs, br), 1966 (s, sh), 1940 (m, sh), 1929 (m, sh), 1894 (w, br), 1768 (w, br). ^1H NMR ($CDCl_3$, 293 K): δ 7.50−7.35 (m, 2 H, ampy), 6.64 (d, $J = 7.5$ Hz, 1 H, ampy), 3.87 (s, 7 H, cycloheptatrienyl), 3.71 (s, 7 H, cycloheptatrienyl), 2.51 (s, 3 H, ampy). ^1H NMR (CD_2Cl_2, 233 K): δ 7.48 (t, $J = 7.8$ Hz, 1 H, ampy), 7.42 (d, $J = 7.8$ Hz, 1 H, ampy), 6.71 (d, $J = 7.8$ Hz, 1 H, ampy), 3.89 (s, 7 H, cycloheptatrienyl), 3.76 (s, 7 H, cycloheptatrienyl), 2.49 (s, 3 H, ampy).

Data for [$Ru_6(\mu_6\text{-}C)(\mu_3\text{-}\eta^7\text{-}C_7H_7)_2(\mu\text{-}CO)_2(CO)_8$] (6). Anal. Calcd for $C_{25}H_{14}O_{10}Ru_6$ (1080.78): C, 27.78; H, 1.31. Found: C, 28.03; H, 1.35. FAB-MS: 1082 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2037 (s), 2006 (vs), 1988 (m, br), 1947 (w, sh), 1803 (w, br). ^1H NMR ($CDCl_3$, 293 K): δ 3.44 (s, cycloheptatrienyls).

Thermolysis of Compound 3. A solution of **3** (10 mg, 0.008 mmol) in chlorobenzene (10 mL) was heated at reflux temperature for 20 min. The color changed from dark brown to dark green. The solution was supported on silica gel (2 g), and the resulting solid was transferred onto a silica gel column (2 × 10 cm) packed in hexane. Hexane−dichloromethane (3:1) eluted compound **1** (2 mg, 23%). Hexane−dichloromethane (1:1) eluted compound **4** (6 mg, 62%).

Reaction of Compound 4 with Cycloheptatriene. A solution of compound **4** (25 mg, 0.021 mmol) and cycloheptatriene (0.5 mL) in decane (5 mL) was stirred at reflux temperature for 1 h. The dark green color of the initial solution changed to dark brown. A considerable amount of black solid precipitated. The solvent was removed under vacuum, and the residue was extracted into dichloromethane (4 mL). The black solid was insoluble. The 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 a minor brown unidentified band. Hexane−dichloromethane (1:2) eluted a green band containing unreacted starting material (2 mg, 8%). Hexane−dichloromethane (1:3) separated a brown band that afforded compound **5** (5 mg, 20%).

Reaction of Compound 1 with Dicyclopentadiene. A solution of compound **1** (100 mg, 0.086) and dicyclopentadiene (0.5 mL) in chlorobenzene (15 mL) was stirred at reflux temperature for 2.5 h. The initial dark brown color changed to greenish brown. The solvent was removed under vacuum, the solid residue was dissolved in dichloromethane (3 mL), and the resulting solution was supported onto silica gel TLC plates. Elution of the plates with hexane−dichloromethane (2:3) separated several bands, some of which contained trace amounts of compounds that were not identified. Only the major bands were worked up to give (in order of elution) **9** (brown, 7 mg, 8%), an mixture of two compounds (^1H NMR) that could not be subsequently separated (green, 8 mg), **7** (dark greenish-brown, contaminated with a colorless organic compound), [$Ru_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_2(CO)_2$] (yellow, 6 mg), and **8** (brown, 2 mg, 2%). The fraction that contained compound **7** was purified by column chromatography (2 × 15 cm), eluting with hexane−dichloromethane (3:1), to give pure **7** (24 mg, 24%).

Data for [$Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^5\text{-}C_5H_5)(\mu_3\text{-}CO)(\mu\text{-}CO)_2(CO)_{11}$] (7). Anal. Calcd for $C_{25}H_{12}N_2O_{14}Ru_6$ (1170.79): C, 25.65; H, 1.03; N, 2.39. Found: C, 25,69; H, 1.13; N, 2.35. FAB-MS: 1172 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2079 (m), 2044 (s), 2024 (vs), 2004 (m, sh), 1989 (m, br), 1969 (m, br), 1953 (m, br), 1936 (vw, sh), 1844 (w, br), 1810 (w, br), 1768 (w, br). ^1H NMR ($CDCl_3$, 293 K): δ 7.14 (t, $J = 8.1$ Hz, 1 H, ampy), 6.55 (d, $J = 8.1$ Hz, 1 H, ampy), 5.98 (d, $J = 8.1$ Hz, 1 H, ampy), 4.55 (s, 5 H, cyclopentadienyl), 2.48 (s, 3 H, ampy), −15.38 (s, 1 H).

Data for [$Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)(\mu\text{-}CO)(CO)_9$] (8). Anal. Calcd for $C_{27}H_{18}N_2O_{11}Ru_6$ (1152.85): C, 28.13; H, 1.57; N, 2.43. Found: C, 27.91; H, 1.65; N, 2.54. FAB-MS: 1154 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2060 (s), 2004 (vs), 1994 (s, sh), 1944 (m, br), 1809 (w, br). ^1H NMR ($CDCl_3$, 293 K): δ 7.16 (t, $J = 7.8$ Hz, 1 H, ampy), 6.55 (d, $J = 7.8$ Hz, 1 H, ampy), 6.48 (d, $J = 7.8$ Hz, 1 H, ampy), 5.37 (s, 5 H, cyclopentadienyl), 4.56 (s, 5 H, cyclopentadienyl), 2.52 (s, 3 H, ampy), −12.52 (s, 1 H), −16.26 (s, 1 H).

Data for [$Ru_5(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_4\text{-}\eta^4\text{-}C_{10}H_{10})(\mu\text{-}CO)_2(CO)_{10}$] (9). Anal. Calcd for $C_{28}H_{16}N_2O_{12}Ru_5$ (1077.78): C, 31.20; H, 1.50; N, 2.60. Found: C, 31.22; H, 1.53; N, 2.57. FAB-MS: 1079 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2074 (m), 2054 (vs), 2011 (vs), 1999 (s, sh), 1986 (s, sh), 1960 (m, br), 1935 (w, sh), 1825 (w, br). ^1H NMR ($CDCl_3$, 293 K): δ 6.99 (t, $J = 7.6$ Hz, 1 H, ampy), 6.43 (d, $J = 7.6$ Hz, 1 H, ampy), 5.39 (d, $J = 7.6$ Hz, 1 H, ampy), 4.79 (m, 1 H), 3.96 (m, 1 H), 3.28 (m, 1 H), 2.78 (s, br, 1 H), 2.53 (m, 1 H), 2.52 (s, 3 H, ampy), 2.14 (m, 1 H), 2.06 (m, 1 H), 1.25 (m, 1H), 0.96 (m, 1 H), 0.82 (m, 1 H).

Table 5. Crystal, Measurement, and Refinement Data for Compounds 2b·0.5(CH$_2$Cl$_2$), 3, 4·1.5(C$_2$H$_4$Cl$_2$), and 5·(C$_4$H$_8$O)

	2b·0.5(CH$_2$Cl$_2$)	**3**	**4**·1.5(C$_2$H$_4$Cl$_2$)	**5**·(C$_4$H$_8$O)
formula	$C_{26}H_{16}N_2O_{13}Ru_6\cdot0.5(CH_2Cl_2)$	$C_{27}H_{16}N_2O_{14}Ru_6$	$C_{26}H_{14}N_2O_{13}Ru_6\cdot1.5(C_2H_4Cl_2)$	$C_{30}H_{20}N_2O_{10}Ru_6\cdot(C_4H_8O)$
fw	1213.29	1198.84	1317.24	1247.00
cryst syst	triclinic	orthorhombic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$
a, Å	10.417(6)	11.039(5)	9.809(3)	10.320(3)
b, Å	10.506(6)	15.971(8)	15.275(4)	10.367(3)
c, Å	16.286(10)	18.772(9)	25.395(7)	17.432(5)
α, deg	86.468(12)	90	90	98.535(6)
β, deg	89.220(10)	90	95.136(5)	101.697(6)
γ, deg	83.204(11)	90	90	97.669(6)
vol, Å^3	1766(2)	3310(3)	3790(2)	1780(1)
Z	2	4	4	2
F(000)	1150	2272	2508	1196
D_{calcd}, g cm^{-3}	2.281	2.406	2.309	2.326
μ(Mo Kα), mm^{-1}	2.638	2.738	2.605	2.544
cryst size, mm	0.24 × 0.13 × 0.10	0.46 × 0.32 × 0.21	0.33 × 0.07 × 0.06	0.38 × 0.21 × 0.12
temp, K	299(2)	296(2)	296(2)	293(2)
θ limits, deg	1.25 to 23.29	1.67 to 23.25	1.56 to 23.29	1.21 to 23.29
min./max. h, k, l	−11/11, −9/11, −17/16	−12/10, −17/17, −20/18	−10/10, −16/16, −19/28	−11/9, −10/11, −18/19
no. of collected reflns	7822	14 516	16 610	7928
no. of unique reflns	4965	4744	5430	5027
no. of reflns with $I > 2\sigma(I)$	4169	4487	4298	4474
no. of params/restraints	443/0	446/0	496/0	479/0
GOF on F^2	1.060	1.004	1.019	1.149
R_1 (on F, $I > 2\sigma(I)$)	0.0498	0.0320	0.0320	0.0459
wR_2 (on F^2, all data)	0.1422	0.0828	0.0795	0.1102
max./min. $\Delta\rho$, e Å^{-3}	2.905/−1.130	0.551/−0.997	1.070/−0.619	1.547/−0.799

Table 6. Crystal, Measurement, and Refinement Data for Compounds 6−9

	6	**7**	**8**	**9**
formula	$C_{25}H_{14}O_{10}Ru_6$	$C_{25}H_{12}N_2O_{14}Ru_6$	$C_{27}H_{18}N_2O_{11}Ru_6$	$C_{28}H_{16}N_2O_{12}Ru_5$
fw	1080.78	1170.79	1152.85	1077.78
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$C2/c$	$P2_1/c$	$Pca2_1$	$P2_1/n$
a, Å	32.288(5)	10.377(3)	21.283(7)	8.858(2)
b, Å	9.925(5)	30.051(8)	16.692(5)	14.857(3)
c, Å	17.2283(14)	10.964(3)	17.630(6)	23.261(5)
β, deg	99.214(13)	115.848(4)	90	93.376(4)
vol, Å^3	5450(3)	3077.2(14)	6263(3)	3055.9(12)
Z	8	4	8	4
F(000)	4064	2208	4368	2056
D_{calcd}, g cm^{-3}	2.634	2.527	2.445	2.343
μ(Mo Kα), mm^{-1}	3.297	2.942	2.881	2.482
cryst size, mm	0.15 × 0.10 × 0.04	0.21 × 0.09 × 0.07	0.25 × 0.18 × 0.15	0.22 × 0.15 × 0.14
temp, K	296(2)	299(2)	296(2)	296(2)
θ limits, deg	1.28 to 23.31	1.36 to 23.28	1.22 to 23.27	1.63 to 23.27
min./max. h, k, l	−35/33, −10/10, −18/19	−8/11, −33/30, −11/12	−23/23, −13/18, −19/19	−9/6, −16/16, −25/25
no. of collected reflns	11 710	13 685	26 787	13 301
no. of unique reflns	3884	4411	8741	4388
no. of reflns with $I > 2\sigma(I)$	2989	3821	8103	4059
no. of params/restraints	370/0	429/0	842/1	426/0
GOF on F^2	1.040	1.078	1.141	1.138
R_1 (on F, $I > 2\sigma(I)$)	0.0248	0.0251	0.0309	0.0319
wR_2 (on F^2, all data)	0.0544	0.0551	0.0687	0.0726
max./min. $\Delta\rho$, e Å^{-3}	0.454/−0.519	0.510/−0.616	0.738/−0.603	1.472/−0.658

X-ray Diffraction Analyses. A selection of crystal, measurement, and refinement data is given in Tables 5 and 6. Diffraction data were measured at room temperature on a Bruker AXS SMART 1000 diffractometer, using graphite-monochromatized Mo Kα radiation. Raw frame data were integrated with SAINT.[25] Absorption corrections were applied with SADABS.[26] Structures were solved by direct methods and refined by full matrix least-squares against F^2 with SHELXTL.[27] All hydride ligands were located in the corresponding Fourier maps, except H100 and H200 of one of the two crystallographically independent molecules found in the asymmetric unit of compound **8**, which were calculated with HYDEX.[28] The remaining hydrogen atoms were set in calculated positions and refined as riding atoms. The refined Flack parameter for compound **3** (space group $P2_12_12_1$) was 0.08(7). Racemic twining was found in the crystal of **8** (space group $Pca2_1$), for which a refined Flack parameter of 0.41(5) was obtained. The molecular

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

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plots were made with the PLATON program package.[29] WINGX program system[30] was used throughout the structure determinations. CCDC deposition numbers 298587 (**2b**·0.5(CH_2Cl_2)), 298588 (**3**), 298589 (**4**·1.5($C_2H_4Cl_2$)), 298590 (**5**·(C_4H_8O)), 298591 (**6**), 298592 (**7**), 298593 (**8**), and 298594 (**9**).

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

OM060153G

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(29) Spek, A. L. *PLATON: A Multipurpose Crystallographic Tool*; University of Utrecht: Utrecht, The Netherlands, 2003.
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