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Facile Changes in Bonding Modes of Azulene in Di- and Triruthenium Clusters upon Interaction with CO

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Summary: Carbonylation of the known cluster $[Ru_3(CO)_6(\mu\text{-}CO)(\mu_3\text{-}\eta^5{:}\eta^3{:}\eta^3\text{−}C_{10}H_8)]$ (***1***) *gives the metastable trinuclear derivative* $[Ru_3(CO)_8(\mu_3\text{-}\eta^5{:}\eta^2{:}\eta^1\text{-}C_{10}H_8)]$ (***2***)*. On further carbonylation of* ***1*** *the stable product* $[Ru_2(CO)_5(\mu_2\text{-}\eta^5{:}\eta^3\text{-}C_{10}H_8)]$ (***3***) *is obtained. X-ray diffraction studies and full spectroscopic assignment of* ***3*** *show that the azulene ligand is bonded through a π-Cp to one metal and via a π-allyl moiety to the other. Compound* ***3*** *reacts reversibly with CO to yield* $[Ru_2(CO)_6(\mu_2\text{-}\eta^5{:}\eta^1\text{-}C_{10}H_8)]$ (***4***)*, which maintains the π-Cp bond while the heptadienyl ring contributes to the bonding only through one σ-C−Ru interaction.*

Introduction

The interaction of arene ligands with clusters has been extensively studied over the last two decades[1,2] mainly with a view to obtain a deeper understanding of chemisorption processes of organic molecules onto metal surfaces.[3] Arene-containing clusters with metal nuclearities ranging from three to eight have been reported.[1] In general, arenes tend to coordinate to the metal centers via either terminal[4] or face capping[5] bonding modes which, in some systems, are known to undergo interconversion.[2] Other modes of interactions are also known, as in $[Ru_2(CO)_5(\mu\text{-}CO)\{\mu\text{-}\eta^2{:}\eta^4\text{-}(C_6H_4)_2\}]$.[6] However, the factors affecting the observed coordination scheme are still only partially elucidated.

The study of polycyclic aromatics, by virtue of their multiple ring sites and π-orbital electrons, enables new insights into the interactions between π-systems and metal centers to be gained. An early example of this is the azulene complex $[Ru_3(CO)_6(\mu\text{-}CO)(\mu_3\text{-}\eta^5{:}\eta^3{:}\eta^3\text{-}C_{10}H_8)]$[7] reported by Churchill and Wormald. However, until the recent studies into the related derivatives $Ru_2(CO)_5(\mu_2\text{-}\eta^5{:}\eta^3$-4,6,8-trimethylazulene), $Ru_3(CO)_6(\mu\text{-}CO)(\mu_3\text{-}\eta^5\text{-}\eta^3\text{-}\eta^3$-7-isopropyl-1,4-di-methylazulene), and $Ru_4(CO)_9(\mu_3\text{-}\eta^5{:}\eta^3{:}\eta^3$-4,6,8-trimethylazulene)[8] the reactivity of these types of clusters had received scant attention. These ligand-reinforced, azulene cluster frameworks have been described as promising models for the activation of molecular hydrogen on bulk metal surfaces due to the observed hydrogenation of the coordinated ligand.[9] In this work we explore the reactions of $Ru_3(CO)_6(\mu\text{-}CO)(\mu_3\text{-}\eta^5{:}\eta^3{:}\eta^3$-azulene) and $Ru_2(CO)_5(\mu_3\text{-}\eta^5{:}\eta^3$-azulene) with carbon monoxide.

Results and Discussion

Churchill and Wormald reported[7] that the thermal reaction of $Ru_3(CO)_{12}$ with azulene yields the triruthenium cluster $Ru_3(CO)_6(\mu\text{-}CO)(\mu_3\text{-}\eta^5{:}\eta^3{:}\eta^3\text{-}C_{10}H_8)$ (**1**). Its X-ray structure showed that the azulene ligand is arched across the face of the cluster. The five-membered ring coordinates to one ruthenium atom in a conventional π-cyclopentadienyl mode, while the remaining five carbons in the seven-membered ring are bonded to the remaining two ruthenium atoms with a μ_2-pentadienyl interaction. This interaction may be classified as a "three-center−three-electron" bond, involving the two ruthenium atoms each bearing two terminal carbonyl ligands with one bridging carbonyl between them. Such a bonding scheme is extremely uncommon[10] and has been found only for azulene (and its derivatives) coordinated to metal clusters.[11] The ^{13}C NMR spectrum of the azulene ring in (**1**) (see Experimental Section) is

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Table 1. ^1H and ^{13}C NMR Data of $[Ru_2(CO)_5(\mu_2\text{-}\eta^5\text{:}\eta^3\text{-}C_{10}H_8)]$ (3)

H	δ (ppm)	^3J (Hz)	C (ligand)	δ (ppm)
		$^3J_{1,2} = 2.9$	1	87.2
1	5.9 ddd	$^3J_{1,3} = 1.8$	2	84.2
		$^3J_{1,8} = 0.6$	3	79.9
2	5.8 dd	$^3J_{2,3} = 2.8$	4	56.6
3	4.0 m	$^3J_{3,4} = 0.7$	5	78.7
4	5.11 m	$^3J_{4,6} = 1.5$	6	50.7
		$^3J_{4,7} = 0.7$	7	128.4
5	5.6 ddd	$^3J_{5,6} = 6.1$	8	117.1
		$^3J_{5,7} = 0.5$	9	88.5
6	3.7 ddd	$^3J_{6,8} = 0.8$	10	86.3
7	5.14 d	$^3J_{6,7} = 8.2$		
		$^3J_{7,8} = 10.5$		
8	5.2 ddd			

entirely consistent with the structure found in the solid state as it shows six resonances (four of intensity 2 and two of intensity 1). The shifts of C(5) and C(7) at δ 69.8 and C(6) at δ 32.1 respectively are in agreement with the proposed bonding scheme based on the two π-allylic moieties.[12] The Cp ring carbon resonances are unremarkable and fall in the expected region with values of δ 77.1 to 87.3. The carbonyl region is highly fluxional at ambient temperature: only a sharp singlet, centered at δ 196.2, is observed. The variable-temperature ^{13}CO spectrum of an enriched (~40%) sample of (**1**) at −90 °C, the low-temperature limit, shows four signals as expected at δ 267.9 (1), 203.6 (2), 192.4 (2), and 192.3 (2). Interestingly on increasing the temperature all of these resonances start broadening simultaneously, suggesting the presence of a single dynamic process involving all the carbonyl groups across all three metallic sites. The variable-temperature ^1H and the ^{13}C NMR solution spectra, in the ligand region, are identical through the entire temperature range explored (−90 °C to +25 °C).

The reaction of $Ru_3(CO)_6(\mu\text{-}CO)(\mu_3\text{-}\eta^3\text{:}\eta^3\text{:}\eta^3\text{-}C_{10}H_8)$ (**1**) with carbon monoxide at room temperature in CH_2Cl_2 leads to the formation of $[Ru_2(CO)_5(\mu_2\text{-}\eta^5\text{:}\eta^3\text{-}C_{10}H_8)]$ (**3**) and $Ru_3(CO)_{12}$. Cluster **3** can be isolated by preparative thin-layer chromatography. Cluster **3** was characterized by standard ^1H and $^{13}C\{^1H\}$ (see Table 1), ^1H COSY, one bond $^1H\{^{13}C\}$ shift correlation (gradient HMQC) and infrared spectroscopy. The IR spectrum of **3** in cyclohexane shows five terminal carbonyl bands (2058 s, 2004 vs, 1990 vs, 1947 m, 1939 w cm^{-1}).

Crystals of **3** suitable for single-crystal X-ray analysis were obtained by slow evaporation of concentrated pentane solution. Crystal data and structure refinement are summarized in Table 2; selected bond lengths and angles are given in Table 3. An ORTEP projection of the structure is shown in the Figure 1. The azulene ligand arches over the two ruthenium atoms with metal−metal distances of 2.867(3) Å. Within the molecule the two ruthenium atoms are bonded directly to the azulene ligand. Ru(2) interacts with the prevalent π-cyclopentadienylmetal linkage in the azulene complexes of transition metals. Ru(2) also bears two CO ligands and is η^5 coordinated to the five-membered ring with the Ru(2)−C(π-cyclopentadienyl) distances ranging from 2.237(4) to 2.255(3) Å with an average metal carbon distance of 2.247(2) Å. From this it may be concluded that the azulene Ru(2) bonding may be described as an essentially symmetrical (π-cyclopentadienyl) metal linkage. Individual carbon−carbon distances within the five-membered ring range from 1.407(6) Å, C(1)−C(2), to 1.451(5) Å, C(9)−C(10). However,

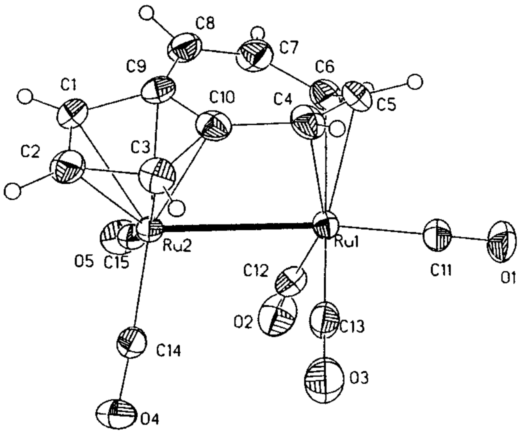

Figure 1. ORTEP plot of $[Ru_2(CO)_5(\mu_2\text{-}\eta^5\text{:}\eta^3\text{-}C_{10}H_8)]$, with the thermal ellipsoids at 30%.

Table 2. Crystal Data and Structure Refinement for $[Ru_2(CO)_5(\mu_2\text{-}\eta^5\text{:}\eta^3\text{-}C_{10}H_8)]$ (3)

emp form	$C_{15}H_8O_5Ru_2$
form wt	470.35
T (K)	293(2)
wavelength (Å)	0.71073
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimensions	
$A = 7.897(2)$	$\alpha = 80.04(2)$
$b = 8.115(2)$	$\beta = 74.95(2)$
$c = 13.434(3)$	$\gamma = 61.56(2)$
volume (Å^3)	729.7(3)
Z	2
d_{calcd} (Mg/m^3)	2.141
absorption coeff (mm^{-1})	2.088
F(000)	452
cryst size (mm)	0.24 × 0.10 × 0.07
θ range for data collection	1.57 to 25.05
limiting indices	h −9 to 9 k −9 to 9 l 0 to 15
reflns collected	2706
independent reflns	2586 ($R_{int} = 0.0143$)
abs corr	ψ-scan
max and min transmission	0.784 and 0.747
refinement method	Full-matrix least-squares on F2
data/restraints /parameters	2571/1/231
GOF on F^2	1.064
final R indices [$I > 2\sigma(I)$]	R1 = 0.0230, wR2 = 0.0446
R indices (all data)	R1 = 0.0351, wR2 = 0.0582
largest diff. peak and hole	0.303 and −0.357 e Å^{-3}

Table 3. Selected Bond Distances (Å) and Angles (degrees) for $[Ru_2(CO)_5(\mu_2\text{-}\eta^5\text{:}\eta^3\text{-}C_{10}H_8)]$ (3)

Ru(1)−C(11)	1.898(4)	C(8)−C(9)	1.445(5)
Ru(1)−C(13)	1.917(4)	C(7)−C(8)	1.333(6)
Ru(1)−C(12)	1.920(4)	C(6)−C(7)	1.456(6)
Ru(1)−C(5)	2.196(4)	C(5)−C(6)	1.432(6)
Ru(1)−C(4)	2.285(4)	C(4)−C(5)	1.397(6)
Ru(1)−C(6)	2.317(4)	C(4)−C(10)	1.452(5)
Ru(1)−Ru(2)	2.8673(6)	C(3)−C(10)	1.433(5)
Ru(2)−C(14)	1.862(4)	C(2)−C(3)	1.410(6)
Ru(2)−C(15)	1.873(4)	C(1)−C(2)	1.407(6)
Ru(2)−C(3)	2.237(4)		
Ru(2)−C(9)	2.243(3)		
Ru(2)−C(1)	2.249(4)	C(11)−Ru(1)−Ru(2)	172.98(12)
Ru(2)−C(2)	2.250(4)	C(5)−C(6)−C(7)	124.5(4)
Ru(2)−C(10)	2.255(3)	C(4)−C(5)−C(6)	123.0(4)
C(1)−C(9)	1.424(5)	C(9)−C(10)−C(4)	129.2(3)
C(9)−C(10)	1.451(5)	C(5)−C(4)−C(10)	124.7(4)

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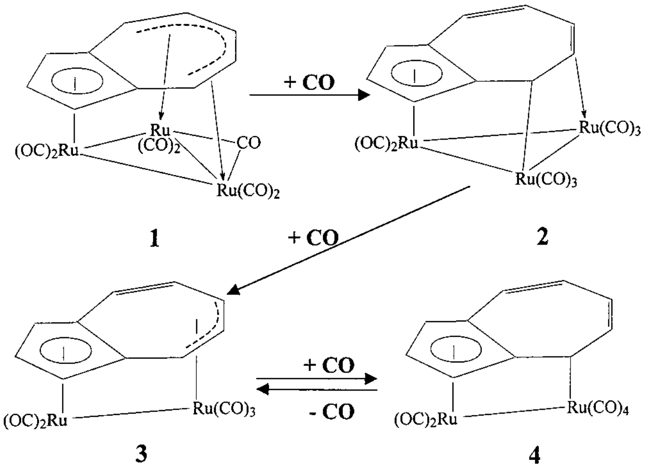
Table 4. ^{1}H NMR Data of [Ru$_3$(CO)$_8$(μ_3-η^5:η^2:η^1-C$_{10}$H$_8$)] (intermediate derivative) (2)

H	δ (ppm)	^3J (Hz)
1	5.4	$^3J_{1,2} = 2.7$
2	5.32 dd	$^3J_{1,3} = 0.9$
3	4.38 s	$^3J_{2,3} = 2.7$
4	3.46 d	$^3J_{4,5} = 7.6$
5	5.18 dd	$^3J_{5,6} = 7.3$
6	4.68 dd	$^3J_{6,7} = 7.1$
7	6.14 dd	$^3J_{7,8} = 8.2$
8	5.06 d	

the mean C−C distances are 1.425(5) Å, while the accepted C−C (π-cyclopentadienyl) distances are of the order of ~1.43 Å.

In the seven-membered ring, two carbon atoms, C(9) and C(10), are already incorporated in the π-cyclopentadienyl Ru(CO)$_2$ bonding, two C(7) and C(8) are linked by simple uncoordinated ethylene bonds length 1.333(6) Å, and the remaining three, C(4), C(5), and C(6), are within bonding distance to Ru(1). This group of three atoms forms a pyramidal substructure, with the carbon atoms of the Ru(1)(CO)$_3$ group and participates in the π-allyl−ruthenium linkage. The value of 123.0(4)° obtained for the apical angle between C(6), C(5), and C(4) and the carbon−carbon bond lengths, 1.397(6), 1.432(6) Å, are all in the range observed from organic crystallographic studies of π-allyl palladium species.[13] The values of the Ru(1) carbon−carbon distances in the π-allyl system (2.285(4), 2.196(4), and 2.317(4) Å) are very similar to those found in related structures.[14] However, we believe that the variation in the Ru−C (allyl) bond lengths in this cluster is best explained as part of a general pattern of strain in the molecule in order to accommodate the simultaneous π-allyl−metal, π-cyclopentadienyl−metal, and metal−metal interactions in the molecule. This distortion leads to two main features: first, the azulene is not planar as shown by the dihedral angles in the five- and the seven-membered rings; second, the ruthenium−π-allyl linkage is not strictly symmetrical. The ^{13}C{^{1}H} NMR spectrum, in the ligand region, shows 10 resonances for the 10 nonequivalent carbons of the azulene ligand. As in (**1**) the Cp-carbons fall in the range of δ 79.9−88.5 whereas the carbons C(7) and C(8) are observed at δ 128.4 and 117.1, respectively, thus supporting the view that no interaction is taking place between them and the metallic moiety. The carbonyl region consists of five resonances at δ 214.0, 210.0, 203.9, 192.8, and 191.4. The shift of the lowest field resonances (δ 214.0 and 210.0) reflects some semibridging character, which would be expected for the necessary balancing of the electric charge within the structure.[15]

Scheme 1. The Proposed Stepwise Reaction of [Ru$_3$(CO)$_6$(μ-Co)(μ_3-η^5:η^3:η^3-C$_{10}$H$_8$)] (1) with CO



When the reaction of [Ru$_3$(CO)$_6$(μ-CO)(μ_3-η^5:η^3:η^3-C$_{10}$H$_8$)] (**1**) with carbon monoxide is monitored in situ at ambient temperature in the NMR tube by ^{1}H NMR spectroscopy, a relatively rapid build-up of eight signals is observed (Table 4) which are slowly replaced, yielding a simple spectrum consisting of the eight resonances associated with compound **3**. This demonstrates that the initial observed resonances are due to an intermediate **2**, which is gradually converted to the final product **3**. To stabilize this intermediate, the reactants were mixed and rapidly cooled to −60 °C. On repeating this reaction, using ^{13}CO (99%) as the reactant, we found that **2** possesses eight carbonyl resonances at δ 210.3, 203.9, 201.6, 197.0, 195.1, 192.2, 191.0, and 185.7. The ^{1}H and ^{13}C{^{1}H} data suggested that **2** may be formulated as Ru$_3$(CO)$_8$(C$_{10}$H$_8$), with the azulene ligand in a different coordination scheme with respect to **1**. The bonding scheme adopted by the azulene to the cluster unit has been clarified by the ^{1}H NMR spectrum. By analogy with the ^{1}H spectra of **1** and **3**, which have been fully assigned by 2D methods, it seems reasonable to assume that the resonances in the range δ 4.38 to 5.40 (H (1−3) in Table 4) belong to the Cp-moiety. Similarly, the resonances at δ 6.14 and 5.06 ($^3J_{H,H} = 8.2$ Hz) are typical of a free olephinic linkage as found in **3**. The remaining three resonances (δ 3.46, 5.18, and 4.68) are not typical of a π-allyl system. The highest field resonance (δ 3.46) is representative of a methine moiety bound to a metallic center, whereas the olefinic resonances at δ 5.18 and 4.68 ($^3J_{H,H} = 7.3$ Hz) are consistent with localized coordination to a single metallic center. On this basis a structure containing the azulene ligand bound η^5:η^1:η^2 to the cluster triangle is proposed for **2** (Scheme 1).

The treatment of **3** with CO (5 atm of pressure, room temperature) leads to the formation of compound **4**, which displays six resonances in the carbonyl region at δ 209.3, 207.3, 201.9, 192.4, 191.2, and 189.0. The structural details of the bonding of the azulene to the bimetallic moiety can be deduced from the ^{1}H and ^{13}C{^{1}H} spectra of the ligand (see Table 5). However, for an unambiguous assignment the ^{1}H COSY and ^{1}H{^{13}C} shift correlation have also been performed. From these data it is straightforward to assign the stoichiometry Ru$_2$(CO)$_6$(C$_{10}$H$_8$) to this new compound. The presence of a π-Cp ring coordination is supported by the shifts of the three carbon resonances at δ 86.9, 86.3, and 74.7 and their corresponding ^{1}H signals (δ 5.72, 5.56, and 3.70, respectively). For the heptadienyl ring the presence of ^{13}C{^{1}H} resonances at δ 142.0, 124.6, 129.4, and 116.5 is in agreement with free olefinic linkages whereas the high-field resonance at δ 12.2 can be associated to a methine carbon bound to a Ru atom. We also propose that the interaction of the azulene ligand with the two

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Table 5. ^{1}H and ^{13}C NMR Data $[Ru_2(CO)_6(\mu_3\text{-}\eta^5{:}\eta^1\text{-}C_{10}H_8)]$ (4)

H	δ (ppm)	^3J (Hz)	C (ligand)	δ (ppm)
1	5.56 ddd	$^3J_{1,2} = 2.6$	1	86.9
		$^3J_{1,3} = 1.8$	2	86.3
		$^3J_{1,8} = 0.5$	3	74.7
2	5.72 dd	$^3J_{2,3} = 2.7$	4	12.2
3	3.70 m	$^3J_{3,4} = 0.3$	5	142.0
		$^3J_{3,8} = 0.8$	6	124.6
4	3.55 dd	$^3J_{4,5} = 7.9$	7	129.4
5	6.14 ddd	$^3J_{5,6} = 11.7$	8	116.5
		$^3J_{5,7} = 0.8$	9	92.2
6	5.02 ddd	$^3J_{6,7} = 7.4$	10	94.8
7	5.48 ddd	$^3J_{6,8} = 0.9$		
8	5.75 m	$^3J_{7,8} = 11.5$		

ruthenium atoms involves a π-Cp bond, while the heptadienyl ring contributes to the bonding only through one σ-C−Ru bond (structure 4 in Scheme 1).

In the progressive stepwise coordination of CO on the parent $[Ru_3(CO)_6(\mu\text{-}CO)(\mu_3\text{-}\eta^5{:}\eta^3{:}\eta^3\text{-}C_{10}H_8)]$ cluster (Scheme 1), we have demonstrated that the azulene ligand is able to coordinate the polymetallic framework in a high variety of bonding modes with the azulene behaving as a ten-, eight-, or six-electron donor to fulfill the electronic requirements of the metallic cluster moiety.

Experimental Section

$Ru_3(CO)_{12}$, azulene, and $Me_3NO{\cdot}2H_2O$ were used as supplied by Aldrich Chemical Company. All solvents were purified by standard techniques.[16] All reactions were carried out under an atmosphere of nitrogen by using standard Schlenk techniques. NMR spectra were recorded using Bruker Avance DRX600 and JEOL EX400 spectrometers at 14.1 and 9.4 T, respectively. ^{1}H COSY spectra resulted from 512 × 1024 data matrix, 16 scans per t_1 increment, recycle time 1 s. One-bond $^1H\{^{13}C\}$ correlation (gradient-selected HMQC) spectra resulted from 128 × 1024 data matrix, 4 scans per t_1 increment, evolution delay 3.5 ms, and a recycle time of 1 s. All 2D spectra were zero filled to a 1024 × 1024, real points, matrix and a $\pi/2$ shifted sine-bell filter was applied prior to Fourier transformation in both dimensions.

Crystallography. All measurements were carried out on a Siemens R3m diffractometer. Two standard reflections, checked in every 98 acquired, showed less than 2% decay. The structure was solved by direct methods, the final solution was obtained (including H atoms) using differential Fourier synthesis. The data collection from 23 selected reflections was carried out by using Siemens P3/P4 V4.27(1991). Lorentz and polarization corrections were carried out with XDISK in SHELXTL/PCV4.2.[17] The final structural solution using least-squares refinements was carried out with SHELXTL/PC V5.9, Siemens.[18]

Synthesis of $[Ru_3(CO)_6(\mu\text{-}CO)(\mu_3\text{-}\eta^5{:}\eta^3{:}\eta^3\text{-}C_{10}H_8)]$ (1). $Ru_3(CO)_{12}$ 0.250 g (0.39 mmol) and azulene (0.39 mmol) were dissolved in *n*-octane (100 mL) and refluxed under nitrogen for 1.5 h. On monitoring the reaction by IR spectroscopy, essentially complete conversion to $[Ru_3(CO)_6(\mu\text{-}CO)(\mu_3\text{-}\eta^5{:}\eta^3{:}\eta^3\text{-}C_{10}H_8)]$ was observed. On cooling the solution a red solid precipitate was obtained, which was then purified by TLC (SiO_2, eluent methylene chloride:pentane 2:8) to give a red band (yield 0.208 g, 85%) and a trace of $Ru_3(CO)_{12}$. The IR and ^{1}H NMR spectra were identical to those previously reported.[7]

Spectroscopic data of **1**: ^{13}C NMR (100.25 MHz, CD_2Cl_2, RT) δ 87.3 (C(1) and C(3)), 83.0 (C(2)), 77.1 (C(9) and C(10)), 69.8 (C(5) and C(7)), 64.8 (C(4) and C(8)), and 32.1 (C(6)).

Synthesis and Characterization of $[Ru_3(CO)_8(\mu_3\text{-}\eta^5{:}\eta^2{:}\eta^1\text{-}C_{10}H_8)]$ (2). A solution of $[Ru_3(CO)_7(\mu_3\text{-}\eta^5{:}\eta^3{:}\eta^3\text{-}C_{10}H_8)]$ (**1**) in CD_2Cl_2 was kept in a Younge's tap NMR tube under 1 atm of ^{13}CO at −60 °C. Partial conversion of the $[Ru_3(CO)_7(\mu_3\text{-}\eta^5{:}\eta^3{:}\eta^3\text{-}C_{10}H_8)]$ (**1**) to $[Ru_3(CO)_8(\mu_3\text{-}\eta^5{:}\eta^2{:}\eta^1\text{-}C_{10}H_8)]$ (**2**) was achieved, as determined by ^{1}H and $^{13}CO\{^1H\}$ NMR spectroscopy (see Table 4). On increasing the temperature of the NMR probe from −60 to 25 °C a complete conversion to $[Ru_2(CO)_5(\mu_2\text{-}\eta^5{:}\eta^3\text{-}C_{10}H_8)]$ (**3**) and $Ru_3(CO)_{12}$ was achieved. Both clusters were isolated by TLC and characterized by IR and NMR spectroscopy.

Synthesis of $[Ru_2(CO)_5(\mu_2\text{-}\eta^5{:}\eta^3\text{-}C_{10}H_8)]$ (3). $Ru_3(CO)_{12}$ (0.250 g, 0.39 mmol) was dissolved in 100 cm^3 of THF, and azulene (0.39 mmol) was added to the solution while refluxing under nitrogen. $Me_3NO{\cdot}2H_2O$ (0.08 g, 0.78 mmol) was then added dropwise to the refluxing solution. When all of the $Me_3NO{\cdot}2H_2O$ has been added, the solution was refluxed for an additional 1 h, after which time (by IR) all of the $Ru_3(CO)_{12}$ had reacted. The solvent was removed under reduced pressure, and the solid residue was separated by TLC (SiO_2, eluent pentane) affording only one compound that was characterized as $[Ru_2(CO)_5(\mu_2\text{-}\eta^5{:}\eta^3\text{-}C_{10}H_8)]$ (**3**).

Synthesis and characterization of $[Ru_2(CO)_6(\mu_2\text{-}\eta^5{:}\eta^1\text{-}C_{10}H_8)]$ (4). A solution of $[Ru_2(CO)_5(\mu_2\text{-}\eta^5{:}\eta^3\text{-}C_{10}H_8)]$ (**3**) in acetone-d_6 was kept under 5 atm of ^{13}CO for 30 min in a Young's tap NMR tube. A complete conversion of $[Ru_2(CO)_5(\mu_2\text{-}\eta^5{:}\eta^3\text{-}C_{10}H_8)]$ (**3**) to $[Ru_2(CO)_6(\mu_2\text{-}\eta^5{:}\eta^1\text{-}C_{10}H_8)]$ (**4**) was achieved, as determined by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy (see Table 5). On releasing the pressure of CO in the NMR tube a complete conversion back to $[Ru_2(CO)_5(\mu_2\text{-}\eta^5{:}\eta^3\text{-}C_{10}H_8)]$ (**3**), the starting cluster, was achieved.

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Supporting Information Available: A listing of tables giving the positional parameters of the non-hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, the positional parameters of the hydrogen atoms and lists of bond lengths, angles and torsion angles for $[Ru_2(CO)_5(\mu_2\text{-}\eta^5\text{-}\eta^3\text{-}C_{10}H_8)]$ (**3**). A CIF file is also available via the Internet only. This material is available free of charge via the Internet at http://pubs.acs.org.

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