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Reaction of Triruthenium Dodecacarbonyl with Isopropenylbenzene: Synthesis of $Ru_3(\mu_2\text{-}H)(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C_3H_2Ph)$ and $Ru_5(\mu_3\text{-}H)(CO)_{14}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3\text{-}C_3H_2Ph)$

Alexander J. Blake,[†] Paul J. Dyson,[‡] Petra E. Gaede,[†]
Brian F. G. Johnson,*[,§] and Simon Parsons[†]

Departments of Chemistry, The University of Edinburgh, West Mains Road,
Edinburgh EH9 3JJ, U.K., Imperial College of Science, Technology and Medicine,
South Kensington, London SW7 2AY, U.K., and Cambridge University,
Lensfield Road, Cambridge CB2 1EW, U.K.

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*Summary: On reaction with $Ru_3(CO)_{12}$, the isopropenylbenzene ligand affords a number of products including two in which only the isopropenyl side arm interacts with the cluster, these being the new cluster-allyl compounds $Ru_3(\mu_2\text{-}H)(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C_3H_2Ph)$ (**1**) and $Ru_5(\mu_3\text{-}H)(CO)_{14}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3\text{-}C_3H_2Ph)$ (**2**). Further heating of **1** with $Ru_3(CO)_{12}$ does not result in the formation of **2**, but instead the known alkyne cluster $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C_2HPh)$ (**3**) is produced. These compounds have been characterized on the basis of full spectroscopic analysis, and clusters **1** and **2** have been analyzed by single-crystal X-ray diffraction. The metal atom geometry in **2** is highly unusual, comprising a Ru_4-butterfly arrangement with one of the wing tip-hinge edges bridged by an additional Ru atom.*

Introduction

The reactions which organic molecules undergo at metal surfaces are of great importance in metal−organic chemistry, and processes such as dehydrogenation, hydrogenation, and C−C bond activation are frequently encountered.[1] The study of transformations of this type which take place at metal centers in molecular clusters are fundamental to understanding those which occur at the surface since such transformations may be probed more readily by high-resolution analytical techniques.

The reactivity of clusters toward unsaturated organic rings (both *homo*- and *hetero*cycles) has been studied intensively over the last few years.[2,3] We have been particularly interested in the preparation of clusters with arene ligands (as well as other organic ligands) which display multicenter bonding modes, since the resulting structural and chemical properties of such ligands are often markedly different from those bonded to a single metal center. As part of this study, we have investigated the reaction between $Ru_3(CO)_{12}$ and arenes with α-methylstyrene substituents, *viz.* isopropenylbenzene and 1,3-diisopropenylbenzene. We have found that when isopropenylbenzene ($PhCMeCH_2$) is heated with $Ru_3(CO)_{12}$, several distinct reaction pathways take place, and the products obtained may be grouped into four categories: (i) coordination of the ring to a Ru_3 face through all unsaturated π-bonds; (ii) ring closure (metallacycle formation); (iii) cluster buildup; (iv) allyl formation.

The compounds isolated from reaction types i−iii have been reported elsewhere.[4,5] In this article we report two further compounds which have been identified from the reaction of $Ru_3(CO)_{12}$ with isopropenylbenzene, *viz.* $Ru_3(\mu_2\text{-}H)(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C_3H_2Ph)$ (**1**) and $Ru_5(\mu_3\text{-}H)(CO)_{14}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3\text{-}C_3H_2Ph)$ (**2**). These differ from the others in that the arene ring is not bonded directly to the cluster unit; instead the ligand bonds through the isopropenyl group *via* π-allyl interactions, and in **2** the metal core is highly unusual.

Results and Discussion

Thermolysis of $Ru_3(CO)_{12}$ with isopropenylbenzene in heptane for 5 h results in the formation of a number of products, as evidenced by IR spectroscopy and thin-layer chromatography. After this time, the solvent is removed from reaction mixture under reduced pressure and the residue redissolved in a minimum amount of dichloromethane and chromatographed on silica using 30% dichloromethane−hexane as eluent. The major products have been reported previously and are comprised of the π-bonded complexes in which the ligand formally donates eight π-electrons to the metal cluster.[4] In lower yield, metallacyclic derivatives in which both π- and σ-bonding from the isopropenyl group and phenyl ring are also observed.[5] The remaining two products previously unidentified have now been fully characterized by spectroscopy and also by single-crystal X-ray diffraction analysis. These compounds are the trinuclear and pentanuclear clusters $Ru_3(\mu_2\text{-}H)(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C_3H_2Ph)$ (**1**) and $Ru_5(\mu_3\text{-}H)(CO)_{14}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3\text{-}C_3H_2Ph)$ (**2**), which are closely related in terms of the allylic-type coordination of the ligand in which the arene ring plays no part.

The ^1H NMR spectra of **1** and **2** in $CDCl_3$ are closely related. Both contain signals at relatively high fre-

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[†] The University of Edinburgh.

[‡] Imperial College of Science, Technology and Medicine.

[§] Cambridge University.

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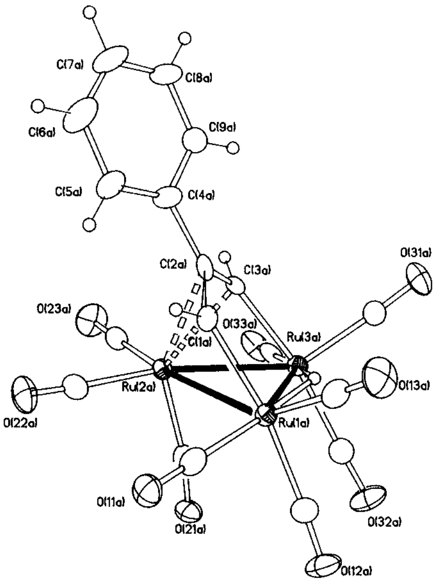

Figure 1. Molecular structure of one of the two crystallographically independent molecules of **1** in the solid state. C atoms of CO ligands bear the same numbering as the O atoms.

Table 1. Relevant Bond Lengths (Å) for 1 (A and B)

Ru(1)−Ru(2)	2.7840(9)	2.8028(10)
Ru(1)−Ru(3)	2.9297(11)	2.9377(10)
Ru(2)−Ru(3)	2.8054(11)	2.7840(11)
Ru(1)−C(1)	2.077(5)	2.069(5)
Ru(3)−C(3)	2.054(5)	2.069(5)
Ru(2)−C(1)	2.234(5)	2.243(5)
Ru(2)−C(2)	2.291(5)	2.280(5)
Ru(2)−C(3)	2.214(5)	2.222(5)
C(1)−C(2)	1.393(8)	1.423(7)
C(2)−C(3)	1.430(7)	1.421(7)
C(2)−C(4)	1.509(7)	1.501(7)
mean C−C$_{\text{(phenyl ring)}}$	1.406(11)	1.407(9)
mean Ru−C$_{\text{(CO)}}$	1.924(6)	1.920(6)
mean C−O$_{\text{(CO)}}$	1.132(7)	1.136(7)

quency [δ 8.70 (s) for **1** and two doublets at δ 8.02 (2.4 Hz, 1H) and 6.33 (2.4 Hz, 1H) for **2**] which may be assigned to the allylic protons. Multiplet resonances are also present [δ range 7.20−7.39 and 7.43−7.44 for **1** and **2**, respectively] which correspond to the phenyl ring protons. Singlet resonances indicative of hydride ligands are also present [δ −20.65 and −19.42 for **1** and **2**, respectively].

The molecular structure of **1** is depicted in Figure 1 with relevant bond parameters listed in Table 1. Two different but closely related molecules are found in the asymmetric unit. Analogues of **1** involving a range of substituted allyl ligands have been reported before, and the bonding of the ligand to the underlying metal triangle is similar to that observed here.[6] The Ru_3 core is defined by a triangle which is bridged along one edge by a hydride; this edge, Ru(1)−Ru(3), is significantly longer than the other two. A tricarbonyl unit is coordinated to each Ru atom, with two carbonyl ligands essentially equatorial and the third axial. On each of the metals which form Ru−C σ-bonds with the ligand one of the equatorial carbonyls is markedly bent away from the plane of the Ru triangle such that approximate octahedral geometry is maintained at the Ru centers. The most noteworthy feature of this structure is the face-bridging coordination mode adopted by the C_3H_2-Ph allyl ligand with respect to the ruthenium triangle. This ligand formally donates five electrons to the metal triangle, bonding to Ru(1) and Ru(3) *via* two σ-interactions and to Ru(2) through a η^3 π-allylic bond. The angles between the Ru_3 and C_3 allyl planes are 61 and 59° for molecules A and B, respectively. Similarly, angles of 31 and 32° are observed between the allyl and phenyl-ring planes.

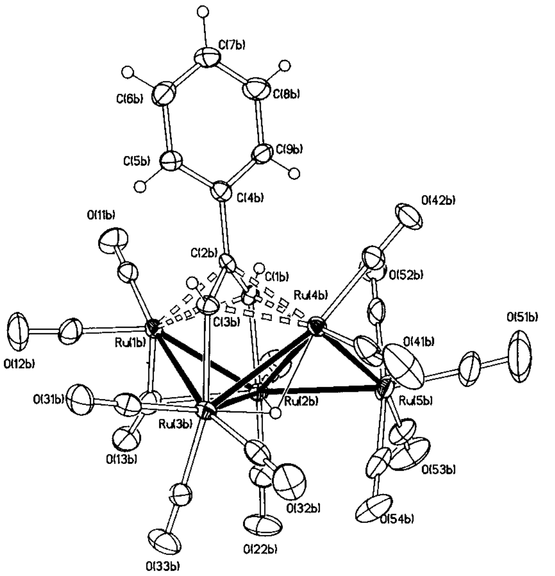

Figure 2. Molecular structure of one of the two crystallographically independent molecules of **2** in the solid state. C atoms of CO ligands bear the same numbering as the O atoms.

Table 2. Relevant Bond Lengths (Å) for 2 (A and B)

Ru(1)−Ru(2)	2.7457(10)	2.7646(9)
Ru(1)−Ru(3)	2.8050(9)	2.7982(10)
Ru(2)−Ru(3)	2.9574(8)	2.9428(9)
Ru(2)−Ru(4)	2.7967(8)	2.8087(9)
Ru(3)−Ru(4)	2.9233(9)	2.9240(8)
Ru(2)−Ru(5)	2.7848(9)	2.7693(9)
Ru(4)−Ru(5)	2.7585(9)	2.7495(9)
Ru(1)−C(1)	2.229(5)	2.224(5)
Ru(1)−C(2)	2.314(5)	2.278(5)
Ru(1)−C(3)	2.323(5)	2.331(5)
Ru(2)−C(1)	2.146(5)	2.152(5)
Ru(3)−C(3)	2.107(5)	2.127(5)
Ru(4)−C(1)	2.266(5)	2.263(5)
Ru(4)−C(2)	2.314(5)	2.321(5)
Ru(4)−C(3)	2.424(5)	2.382(5)
C(1)−C(2)	1.454(8)	1.458(7)
C(2)−C(3)	1.432(7)	1.428(7)
C(2)−C(4)	1.502(8)	1.507(7)
Ru(1)−C(13)	1.952(6)	1.940(7)
Ru(2)−C(13)	2.331(5)	2.441(6)
C(13)−O(13)	1.165(6)	1.159(7)
mean C−C$_{\text{(phenyl ring)}}$	1.375(9)	1.382(9)
mean Ru−C$_{\text{(CO)}}$	1.911(7)	1.907(8)
mean C−O$_{\text{(CO)}}$	1.134(7)	1.137(8)

The solid-state structure of **2** is illustrated in Figure 2, and principal bond distances are found in Table 2. Two slightly different conformers are present in the cell. The Ru core is highly unusual, being comprised of a Ru_4 butterfly bridged along a wing tip-hinge edge by an

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Scheme 1

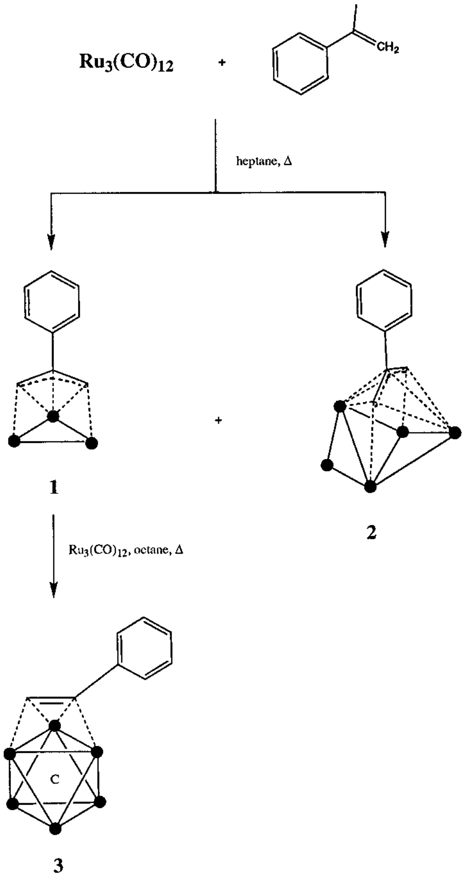

Table 3. Crystal Data and Structure Refinement for 1 and 2

	1	2
formula	$C_{18}H_8O_9Ru_3$	$C_{23}H_8O_{14}Ru_5$
MW	671.45	1013.65
temp (K)	150.0(2)	150.0(2)
cryst system	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.802(3)	11.099(3)
b (Å)	14.871(5)	16.085(4)
c (Å)	17.421(6)	17.501(4)
α (deg)	114.59(2)	81.763(12)
β (deg)	92.51(2)	72.346(13)
γ (deg)	98.45(2)	72.93(2)
V (Å^3)	2037.0(12)	2841.1(12)
Z	4	4
D_{calc} (g cm^{-3})	2.189	2.370
μ (mm^{-1})	2.243	2.664
max and min transmission factors	0.654, 0.488	0.698, 0.578
cryst size (mm)	0.47 × 0.31 × 0.14	0.22 × 0.17 × 0.12
cryst color	yellow	dark green
θ range (deg)	2.55−27.52	2.61−25.03
no. reflcns collcd	9773	10005
no. indepdt reflcns	8114	10005
R(int)	0.028	
R_1 [$I > 2\sigma(I)$]	0.0404	0.0323
wR_2 (all data)	0.1110	0.0667
S	0.984	1.084
params refined	548	765
$\Delta\rho_{\max}$ (e Å^{-3})	1.21	0.90
$\Delta\rho_{\min}$ (e Å^{-3})	−2.66	−0.68

additional Ru atom. The C_3H_2Ph ligand lies between the wings of one of the butterflies, while the alternative butterfly cavity is *not* bridged by a ligand. This difference is reflected in the angle between the butterfly wings, the angle for the unbridged unit being larger [135.7 and 134.9° *versus* 100.6 and 101.9°, for molecules A and B, respectively]. For the purpose of this discussion the central butterfly is defined by Ru(1)−Ru(2)−Ru(3)−Ru(4), with Ru(5) considered to be an additional bridge. This metal geometry is unique. While other clusters with the metal−metal connectivities are known for other transition metals, they form planar raft structures[7] or, alternatively, the metal atoms with the metal−metal connectivity of two are folded in the same direction relative to each other,[8] the opposite situation to that observed in **2**. A hydride bridges the triangular face defined by Ru(2)−Ru(3)−Ru(4) on the underside of the wing. The carbonyl distribution is quite varied; four terminal COs are coordinated to Ru(5), three to Ru(3), and two to of each Ru(4), Ru(2), and Ru(1). In addition, Ru(1) and Ru(2) share one asymmetric bridging CO. The organoligand is similar to that found in **1**, comprising an allylic fragment with a phenyl ring attached to the central carbon atom. The difference between the ligand in **2** and in **1** is the manner in which it bonds to the metal cluster. Instead of interacting with a trimetal face, it lies between the wings of the butterfly forming two η^3 π-interactions with the wing tip atoms, Ru(1) and Ru(4), and two σ-bonds with the hinge atoms, Ru(2) and Ru(3). This bonding mode has been observed in the butterfly-cluster $[Fe_4(CO)_{11}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3\text{-}C_3H_2Me)]^-$.[9] The torsion angle between the allyl and phenyl-ring planes is 39 and 32° for molecules A and B, respectively, this being the main difference between the two molecules in the asymmetric unit.

The isolation of compounds **1** and **2** shows that, apart from coordination of the ring, a further reaction type may take place in which only the substituent group plays a role in the reaction between isopropenylbenzene and $Ru_3(CO)_{12}$. One can envisage that **2** is derived from **1** and that a tetraruthenium intermediate links the two clusters. Surprisingly, compound **1** does not appear to be an intermediate on route to **2**. Heating **1** with $Ru_3(CO)_{12}$ results in elimination of a CH fragment from the allyl ligand to give phenylacetylene with the simultaneous cluster buildup affording $Ru_6C(CO)_{15}(C_2HPh)$ (**3**) (Scheme 1). This cluster has been reported previously, obtained from the oxidative addition reaction between $[Ru_6C(CO)_{16}]^{2-}$ and phenylacetylene using iron(III) chloride as the oxidant.[10]

Experimental Section

Reactions were carried out under an atmosphere of nitrogen gas, while purification of products was carried out using standard laboratory grade solvents without precautions to exclude air. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier-transform instrument. Mass spectra were obtained by fast atom bombardment in positive mode on a Kratos MS50TC calibrated with CsI. ^{1}H NMR spectra were recorded using a Bruker AM360 spectrometer referenced to internal TMS. The cluster $Ru_3(CO)_{12}$ was prepared according to the

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literature method.[11] Isopropenylbenzene (PhCMeCH$_2$) was purchased from Aldrich and used without additional purification.

Reaction of Ru$_3$(CO)$_{12}$ with PhCMeCH$_2$. Ru$_3$(CO)$_{12}$ (250 mg) in heptane (20 mL) containing PhCMeCH$_2$ (1 mL) was heated under reflux for 5 h, after which time the reaction mixture became dark red-brown and the IR spectrum indicated nearly complete consumption of the Ru$_3$(CO)$_{12}$. The solvent was removed under reduced pressure, and the products were extracted by thin-layer chromatography using dichloromethane−hexane (1:4) as eluent. A number of bands are observed including four characterized spectroscopically as the following.

Ru$_3$(μ_2-H)(CO)$_9$(C$_9$H$_7$) (1) (Yellow, <5%). IR ν_{CO} (CH$_2$Cl$_2$): 2100 m, 2074 vs, 2046 vs, 2028 s, 2016 s, 1996 s (sh), 1955 w cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.70 (s, 2H), 7.39−7.20 (m, Ph), −20.65 (s, 1H) ppm. Positive FAB mass spectrum: 673 (calc 671) amu.

Ru$_5$(μ_3-H)(CO)$_{14}$(C$_9$H$_7$) (2) (Dark Green, <5%). IR ν_{CO} (CH$_2$Cl$_2$): 2108 m, 2084 s, 2037 vs (br), 1995 m, 1952 w, 1879 w cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.02 (d, 1H, 2.4 Hz), 7.74 (m, 2H), 7.43 (m, 3H) 6.33 (d, 1H, 2.4 Hz), −19.42 (s, 1H) ppm. Positive FAB mass spectrum: 958, M − 2COs (calc 957). Anal. Found (calc): C, 27.15 (27.25); H, 0.80 (0.59).

Reaction of Ru$_3$(μ_2-H)(CO)$_9$(C$_9$H$_7$) (1) with Ru$_3$(CO)$_{12}$. Ru$_3$(μ_2-H)(CO)$_9$(C$_9$H$_7$) (23 mg) and Ru$_3$(CO)$_{12}$ (20 mg) in octane (20 mL) were heated under reflux for 2 h. At this time IR spectroscopy indicated nearly complete consumption of the starting materials. The solvent was removed *in vacuo* and the product extracted by thin-layer chromatography using dichloromethane−hexane (1:4) as eluent. One major band was obtained and characterized spectrocopically as Ru$_6$C(CO)$_{15}$-(C$_2$HPh) (**3**) (brown, 20%).

IR ν_{CO} (CH$_2$Cl$_2$): 2088 w, 2044 vs, 2038 s (sh), 2018 m (sh), 2014 m, 1986 w, 1962 w (sh) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 10.17 (s, 1H), 7.41 (m, Ph) ppm. Positive FAB mass spectrum: 1145 (calc 1146) amu. These values are in excellent agreement with those previously reported.[10]

Crystallographic Determinations of Compounds 1 and 2. Diffraction data for species **1** and **2** were collected on a Stoë Stadi-4 four-circle diffractometer equipped with a low-temperature device.[12] Crystal data and details of measurement are summarized in Table 3. The metal atoms were located using automatic direct methods,[13] and SHELXL93 was used thereafter.[14]

Additional material available from the Cambridge Crystallographic Data Center comprises H atom coordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (P.E.G.) and The Royal Society for a University Research Fellowship (P.J.D.).

Supporting Information Available: Tables of crystallographic data, atom parameters, thermal parameters, and bond distances and angles (23 pages). Ordering information is given on any current masthead page.

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