Arenes on Metal Clusters

The Molecular Structure of $[Os_3Rh_4(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^1\text{-}C_6H_5CH_3)(CO)_{13}]$: A Face-Capping Bonding Mode for Arenes in Organometallic Clusters[**]

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The interactions of benzene (arenes) with transition-metal surfaces comprise an important area of research in surface science.[1] The determination of the adsorption geometry of arenes on metal surfaces can give insights into the elementary steps of the dissociation and catalytic reactions of these molecules.[2] A number of adsorption sites for benzene on atomically planar metal surfaces such as the (111) face of face centered cubic (fcc) packing and the (0001) face of hexagonal centered packing (hcp) have been identified,[3] (Figure 1). This type of compound also plays an important role in homogeneous catalytic processes, such as, the hydrogenation of benzene to cyclohexane. An established catalysis precursor for this process under biphasic condition is $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]Cl_2$.[4]

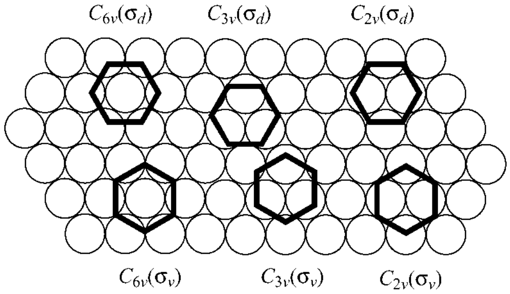

Figure 1. Schematic representation of adsorption sites and orientations of benzene on a planar close packed metal surface.

Soluble molecular metal clusters that mimic these bonding modes are known for $C_{6v}(\sigma_d)$, $C_{6v}(\sigma_v)$, $C_{3v}(\sigma_d)$, $C_{2v}(\sigma_d)$, and $C_{2v}(\sigma_v)$ and shown in Figure 1.[5] Transition-metal clusters with face-capping arene ligands which are coordinated to three metal atoms and show a weak trigonal distortion toward a Kekulé structure have been extensively investigated. Lewis, Johnson, and colleagues developed facile synthetic routes to a range of arene clusters with the general formula $[M_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5R)]$, where R = H, Me, and showed that the trigonal ring distortion is because of an internal mixing of the benzene π system that leads to increased overlap in the C−C bonds, thus eclipsing the metal atoms.[6] Another class of face-capping arene system, $[(CpCo)_3(\mu_3\text{-arene})]$ ($Cp = C_5H_5$) was developed by Wadepohl et al. from substituted styrene derivatives and Jonas reagent $[CpCo(C_2H_4)_2]$.[7] In all of the cluster compounds with bridging arene ligands that have been structurally characterized, the $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ bonding mode is most commonly observed in the solid state. Herein, we report the isolation and structural characterization of an Os–Rh mixed-metal cluster that bears a toluene ligand in an unusual $\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^1$ face-capping mode.

The treatment of $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ with toluene under reflux in the presence of excess 4-vinylphenol (as a hydride acceptor) leads to the formation of the brown cluster $[Os_3Rh_4(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^1\text{-}C_6H_5CH_3)(CO)_{13}]$ (**1**) in 10% yield after chromatographic separation. X-ray analysis[8] of **1** shows that the metal framework can be described as a tricapped tetrahedron in which four Rh atoms define a tetrahedral core with three triangular faces each capped by an $Os(CO)_3$ unit (Figure 2). The most salient structural feature is the remaining Rh_3, which is face-capped by a toluene ligand in the unprecedented $\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^1$ coordination mode. This coordination geometry of benzene has been observed on many metal surfaces, such as Rh (111),[9] Os (0001),[10] and Ru (0001).[11] A closely related molecular system with $C_{3v}(\sigma_v)$ is also known for the $[\{(C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}\eta^3{:}\eta^3\text{-}C_6H_6)]^{2+}$ ion, however, the interaction of the C_6 ring to the triangular metal framework is not symmetrical.[12] The average vertical distance between carbon atoms and the Rh_3 plane in **1** is 2.21(2) Å. This is almost 0.1 Å longer than that observed in the Ru/benzene system (2.11(4) Å) when studied with the LEED technique,[3] although the difference is not statistically significant because of the low accuracy of surface studies. There is a very small crownlike buckling distortion of the C_6 ring of about 0.1 Å in the capped toluene ligand. A similar buckling

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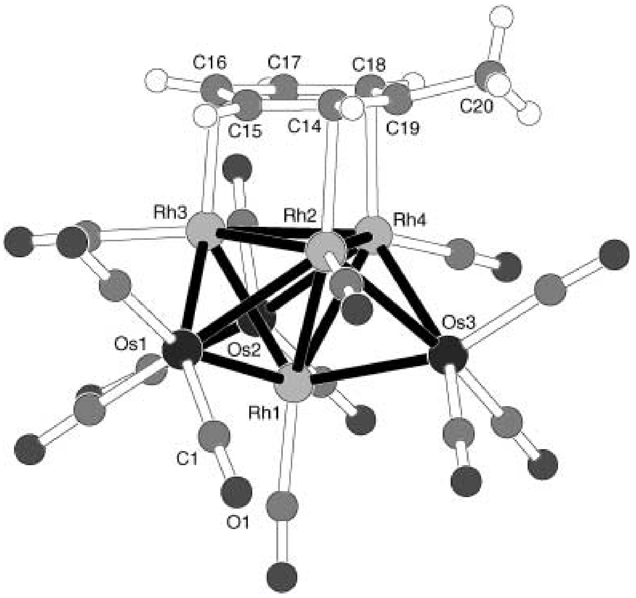

Figure 2. Molecular structure of **1**. Selected interatomic distances [Å] and angles [°]: Os1-Rh1 2.521(2), Os1-Rh2 2.667(2), Os1-Rh3 2.654(2), Os2-Rh1 2.537(2), Os2-Rh3 2.647(2), Os2-Rh4 2.665(2), Os3-Rh1 2.523(2), Os3-Rh2 2.661(2), Os3-Rh4 2.663(2), Rh1-Rh2 2.731(2), Rh1-Rh3 2.720(2), Rh1-Rh4 2.712(2), Rh2-Rh3 2.657(2), Rh2-Rh4 2.661(2), Rh3-Rh4 2.672(2), Rh2-C14 2.25(2), Rh3-C16 2.21(2), Rh4-C18 2.27(2), Rh2···C15 2.55(2), Rh2···C19 2.74(2), Rh3···C15 2.64(2), Rh3···C17 2.60(2), Rh4···C17 2.64(2), Rh4···C19 2.66(2), C14-C15 1.36(3) C14-C19 1.43(3), C15-C16 1.43(3), C16-C17 1.49(3), C17-C18 1.40(3), C18-C19 1.35(3), C19-C20 1.53(3); Rh3-Rh2-Rh4 60.33(6), Rh2-Rh3-Rh4 59.90(6), Rh2-Rh4-Rh3 59.77(6), C15-C14-C19 120(2), C14-C15-C16 122(2), C15-C16-C17 115(1), C16-C17-C18 117(2), C17-C18-C19 123(2) and C14-C19-C18 120(2), C14-C19-C20 117(2), C18-C19-C20 119(2).

distortion is observed for benzene that is adsorbed on the Ru (0001) surface.[3] The methyl substituent appears to tilt away from the Rh_3 plane, presumably a result of steric interactions (Figure 3).

Clearly, this is a reasonably good model to mimic the surface-bound benzene on the atomically flat closed pack structure in the $C_{3v}(\sigma_v)$ local symmetry. Although in most of the previously established face-capping arenes on M_3 triangular systems the μ_3-η^2:η^2:η^2 mode is the observed ground state structure, the arene ligand can undergo a 1,2 ring-hopping motion. The energy barrier for this process is around 50 kJ mol^{-1} in the case of $[Os_3(CO)_8(\eta^2\text{-}CH_2CHPh)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$.[13] ^{1}H NMR spectroscopy studies of **1** indicate that both isomers with μ_3-η^2:η^2:η^2 and μ_3-η^1:η^1:η^1-capping toluene are present in solution in the temperature range of 213 K to 298 K. The ratio of the two isomers at room temperature is approximately 2:3. Attempts to determine the activation parameters for this process have met with little success because of solubility problems.

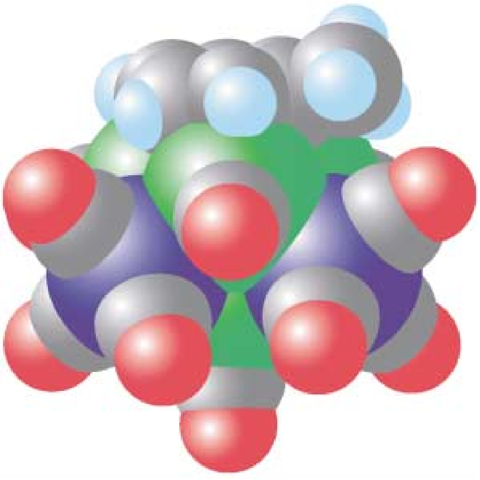

Figure 3. Space-filling diagram of the structure **1** with Os dark blue, Rh green, O red, H light blue, C gray.

The metal–metal bonds observed in **1** are relatively short. There are two distinct types of Rh−Rh bonds in **1**. The bond lengths (av. 2.663(3) Å) between the Rh atoms that are capped by toluene ligand are significantly shorter than other Rh−Rh bonds (av. 2.721(3) Å) within the structure. All the Os−Rh bonds are much shorter than those observed in the other Rh–Os mixed-metal clusters that have been reported recently.[14] In terms of the capping principle that was developed by Mingos,[15] one expects that a tricapped tetrahedral cluster should have an electron count of 96. However, the cluster only has an electron count of 92, which is four electrons less than expected. This unusual electron count could arise because many rhodium complexes may conform to the 16-electron rule instead of the 18-electron rule. In fact, a tetrahedral transition-metal cluster that has an electron count of 60 possesses six skeletal bonding pairs. However, a tetrahedral cluster may also adopt an electron-deficient configuration by having only four skeletal bonding pairs instead of six. The electron count of 92 for the tricapped tetrahedron in **1** may be a result of the electron deficiency in the tetrarhodium metal core. This type of metal skeleton with such an electron count is not commonly observed, but an established example is a closely related tetrarhodium cluster, $[Rh_4(\mu_2\text{-}H)_4(cod)_4]$ (cod = cyclooctadiene)[16] which has an electron count of 56. In addition, a density functional theory calculation[17] on our osmium–rhodium cluster gives weaker Rh−Rh bonds than Os−Rh bonds. The average bond index[18] is 0.18 Å for the Rh−Rh bonds and 0.31 Å for the Os−Rh bonds.

Experimental Section

All work was carried out under nitrogen using Schlenk techniques. The solvents used were freshly prepared distilled, dried, and saturated with N_2.

1: $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ (100 mg, 0.10 mmol) and an excess of 4-vinylphenol were stirred in refluxing toluene (40 cm^3) for 2 h. The solution gradually turned from yellow to brown. After filtration the volume of the solution was reduced to 5 cm^3 in vacuo. Purification by TLC on silica using hexane: CH_2Cl_2 (2:1 v/v) as eluent yielded complex **1** as a brown solid in 10% yield (14.4 mg, 0.01 mmol). The major product isolated from the reaction was $[Os_5Rh_2(\mu\text{-}CO)(\eta^6\text{-}C_6H_5CH_3)(CO)_{16}]$[19] (50% yield, 87.3 mg, 0.05 mmol), and two other uncharacterized cluster compounds in very low yields were detected. Elemental analysis calcd (%) for $C_{20}H_8O_{13}Os_3Rh_4$: C 16.70, H 0.56; found: C 16.70, H 0.60; IR(CH_2Cl_2): $\tilde{\nu}$ = 2075w, 2046vs, 2020w, 1996s, 1971 cm^{-1} w. Positive FAB mass spectrometry (calcd *m/z*: 1438; found: 1438). ^{1}H NMR spectroscopy study at 298 K showed the presence of isomers **1a** (μ_3-η^2:η^2:η^2) and **1b** (μ_3-η^1:η^1:η^1) in a ratio of approximately 2:3. **1a**: ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 7.71$ (m, 1H), 7.55 (m, 1H), 7.48 (d, 1H), 7.42 (t, 1H), 7.16 ppm (dd, 1H), 2.12 (s, 3H); **1b**: ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 6.99$ (t, 2H), 6.70 (t, 1H), 6.58 (m, 2H), 2.22 ppm (s, 3H). Variable temperature ^{1}H NMR studies in 213–298 K did not reveal any hydride signals in the range of 15 to -30 ppm.

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[8] Crystal structure analysis for **1**: C$_{20}$H$_8$O$_{13}$Os$_3$Rh$_4$, $M_r = 1438.50$, monoclinic, space group $P2_1/n$ (No. 14), $a = 17.518(3)$, $b = 9.557(2)$, $c = 19.120(3)$ Å, $\beta = 116.53(1)$, $V = 2864.0(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 3.336$ g cm^{-3}, $T = 298$ K, $F(000) = 2560.00$, Mo$_{K\alpha}$ radiation ($\lambda = 0.7107$ Å), μ(Mo$_{K\alpha}$) $= 155.48$ cm^{-1}, dimensions $0.20 \times 0.20 \times 0.25$ mm. 3812 observed diffraction data [$I > 1.50\sigma(I)$] and $R_{int} = 0.067$. Structure solved by direct methods (SHELXS86) and Fourier difference techniques, refined by full-matrix least-squares analysis on F to $R = 0.056$, Rw $= 0.052$, $\omega = 1/\sigma^2$ (F_o). Non-hydrogen atoms were refined anisotrpically. Hydrogen atoms were included but not refined. All calculations were performed on a Silicon-Graphics Computer using the program package TEXSAN. CCDC-196936 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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