

Unusual Ring Opening of Hexamethyl Dewar Benzene in Its Reaction with Triosmium Carbonyl Cluster

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Summary: $Os_3(CO)_{10}(NCMe)_2$ catalyzes the transformation of hexamethyl Dewar benzene (HMDB) to hexamethylbenzene (HMB). This catalytic reaction is in competition with ring opening of the HMDB ligand to give $(\mu-H)_2Os_3(CO)_9(\mu-\eta^3-CH(C_6Me_5))$ (**1**) and $(\mu-H)Os_3(CO)_9(\mu_3-\eta^2-C\equiv C(C_4Me_4Et))$ (**2**).

The coordination chemistry of strained hydrocarbons has fascinated chemists striving to understand the details of structure and reactivity.¹ In particular, benzene is rich with high-energy strained isomers, such as Dewar benzene, prismane, and benzvalene, which interconvert through complex and mysterious rearrangements.² The unsubstituted Dewar benzene is short-lived.³ On the other hand, the hexamethyl Dewar benzene (HMDB) derivative is relatively stable and is prepared conveniently,⁴ which makes it the favorite substance for investigation of the Dewar ring system.⁵ Thermal conversion of HMDB to hexamethylbenzene (HMB) has a measured activation energy of 37 kcal/mol and a half-life of 3 h at 150 °C, despite being exothermic by nearly 60 kcal/mol due to the ring strain and aromaticity.⁶ The high activation energy has been attributed in part to the symmetry forbiddance of the thermal rearrangement.⁷

Metal-assisted rearrangement of HMDB to HMB is known. For instance, isomerization catalyzed by Rh(I) and Pd(II) complexes under thermal conditions,⁸ or under visible light irradiation in the presence of catalytic amounts of $[CpFe(arene)]^+$, has been investigated.⁹ There are various mononuclear transition-metal HMDB complexes in which the HMDB ligand is acting as a chelating η^4 -diolefin,¹⁰ while irradiation of $Fe(CO)_5$ with

HMDB produces the HMB complex $[(\eta^6-C_6Me_6)Fe(CO)_2]_2$.¹¹ In rare cases the HMDB moiety has lost its unity, such as in the reaction of $RhCl_3 \cdot xH_2O$ with HMDB, causing a ring contraction to give $[(\eta^5-C_5Me_5)RhCl_2]_2$.¹² However, the coordination chemistry of HMDB with metal clusters has received little attention. We now report that $Os_3(CO)_{10}(NCMe)_2$ not only catalyzes the conversion of HMDB to HMB but also causes unusual C–H and C–C bond activations of the HMDB ligand to form unique cluster complexes.

Treatment of $Os_3(CO)_{10}(NCMe)_2$ with HMDB (4-fold) at room temperature in methylcyclohexane solvent affords a yellow solution with an IR spectrum¹³ similar to that of $Os_3(CO)_{10}(\eta^4\text{-cyclooctadiene})$ (diene = cyclooctadiene,¹⁴ cyclohexadiene,¹⁵ norbornadiene¹⁶), suggesting that the chelating η^4 -diolefin complex $Os_3(CO)_{10}(\text{HMDB})$ (**3**) is formed. Upon reflux of this mixture under dinitrogen, transformation of HMDB to HMB was observed (path **a**, Scheme 1).¹⁷ This catalytic reaction is in competition with C–H bond activation of the HMDB ligand (path **b**) to give the dihydrido vinylmethylidene cluster $(\mu-H)_2Os_3(CO)_9(\mu-\eta^3-CH(C_6Me_5))$ (**1**)¹⁸ and the acetylide cluster $(\mu-H)Os_3(CO)_9(\mu_3-\eta^2-C\equiv C(C_4Me_4Et))$ (**2**)¹⁹ in 15% and 10% yields, respectively, after separa-

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(17) This catalytic reaction has been followed by ^1H NMR spectroscopy (in C_6D_6) and the degree of HMDB/HMB conversion estimated by integration of the respective signals of reactant and product. A 15% conversion is achieved within 24 h at 80 °C with 5 mol % concentration of $Os_3(CO)_{10}(NCMe)_2$, while the blank test (without adding Os_3 cluster) gives only a 2% conversion.

(18) Anal. Calcd for $C_{21}H_{18}O_9Os_3$: C, 25.66; H, 1.83. Found: C, 26.00; H, 1.94. MS (FAB): m/z 990 (M^+ , ^{192}Os). IR (*n*-hexane, $\nu(\text{CO})$): 2120 (w), 2064 (m), 2036 (vs), 2016 (s), 1986 (m), 1958 (m) cm^{-1} . ^1H NMR ($CDCl_3$, 25 °C): δ 6.73 (d, $J = 2$ Hz, 1H), 2.12 (s, 3H), 1.79 (s, 3H), 1.61 (s, 3H), 1.35 (s, 3H), 0.96 (s, 3H), -17.56 (d, $J = 2$ Hz, $\mu\text{-H}$), -18.04 (s, $\mu\text{-H}$). $^{13}\text{C}\{^1\text{H}\}$ NMR ($CDCl_3$, 25 °C): δ 185.0, 178.6, 176.3, 174.7, 174.1, 171.5, 170.7, 170.5, 166.4 (CO), 147.2, 139.9 (MeC=CMe), 134.7, 92.1 ($\mu\text{-CMe=CMe}$), 78.7 ($\mu\text{-CH}$), 66.3, 61.2 (MeC=CMe), 29.9, 12.8, 10.9, 10.2, 10.0 (CH_3). Crystal data for **1**: $C_{21}H_{18}O_9Os_3$, $M_r = 982.94$, monoclinic, space group $P2_1/n$, $a = 14.3985(1)$ Å, $b = 13.9599(1)$ Å, $c = 12.9294(1)$ Å, $\alpha = 90^\circ$, $\beta = 107.8824(4)^\circ$, $\gamma = 90^\circ$, $V = 2473.28(3)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 2.640$ g cm^{-3} , $\mu = 15.420$ mm⁻¹, $F(000) = 1768$, θ range 1.49–27.50°, 299 variables refined with 5673 independent reflections to final R indices ($I > 2\sigma(I)$) of $R1 = 0.0328$ and $wR2 = 0.0793$, and $\text{GOF} = 1.138$.

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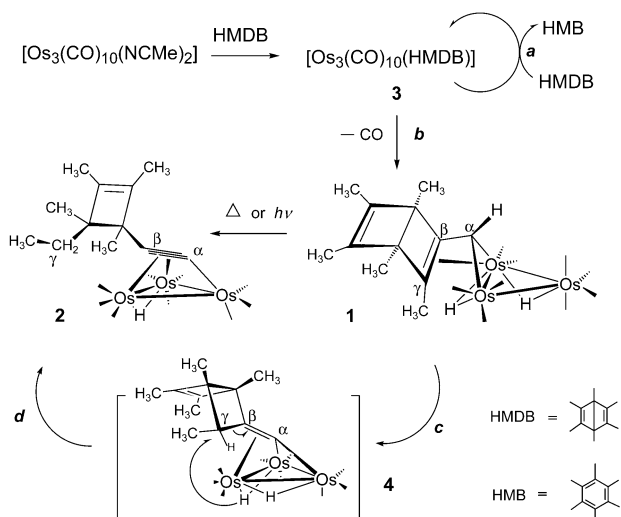
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Scheme 1



tion by TLC and crystallization. The alternative procedure to improve the yields of **1** and **2** to 54 and 13%, respectively, is by adding HMDB dropwise into a hot $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ solution. Compound **1** is likely the precursor of **2**, since heating **1** produces **2** as the major organometallic product. It is worth noting that photoirradiation of **1** also leads to **2** in 62% yield, but with no evidence for the formation of arene clusters²⁰ (via opening of the Dewar benzene ring), as might be expected.

Organotriosmium cluster systems are known to undergo a variety of transformations in which the organic moiety is changed by proton transfers to and/or from the metal framework,²¹ such as activation of benzene C–H bonds to form the benzyne complex $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_6\text{H}_4)$.²² Apparently, compound **1** is derived from **3** via double C–H bond activation of a HMDB methyl group on the triosmium framework, concomitant with a CO loss and a change of the diene bonding mode to an η^2 feature. Nevertheless, direct C–H bond activation of the HMDB molecule onto the metal cluster without precoordination cannot be excluded under the thermal conditions. The reaction pathways from **1** to **2** appear to be greatly complicated, which involve opening of a cyclobutene ring and various hydrogen atom migrations. A plausible mechanism is depicted in paths **c** and **d** of Scheme 1. Presumably, a hydrogen 1,3-shift from the alkylidene carbon (α) to the alkene carbon (γ) occurs to generate the $\mu_3\text{-}\eta^2$ -vinylidene intermediate **4**, followed by $\text{C}_\beta\text{-C}_\gamma$ bond scission and hydrogen migration to the

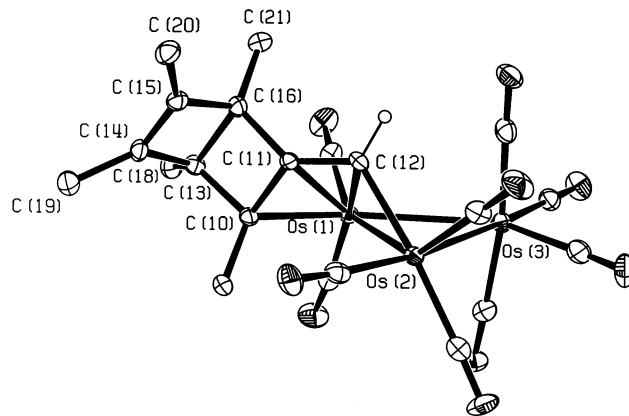


Figure 1. Molecular structure of **1** (ORTEP diagram). Selected bond lengths (Å): Os(1)–Os(2) = 2.8730(3), Os(1)–Os(3) = 3.0550(4), Os(2)–Os(3) = 2.8855(3), Os(1)–C(12) = 2.250(6), Os(1)–C(11) = 2.259(6), Os(1)–C(10) = 2.217(6), Os(2)–C(12) = 2.141(6), C(10)–C(11) = 1.489(8), C(11)–C(12) = 1.378(9), C(10)–C(13) = 1.549(9), C(13)–C(14) = 1.524(9), C(13)–C(16) = 1.583(9), C(14)–C(15) = 1.345(9), C(15)–C(16) = 1.510(9), C(11)–C(16) = 1.533(9). Selected bond angles (deg): Os(1)–Os(2)–Os(3) = 64.080(9), Os(1)–Os(3)–Os(2) = 57.761(8), Os(2)–Os(1)–Os(3) = 58.158(8), Os(1)–C(12)–Os(2) = 81.7(2), Os(1)–C(12)–C(11) = 72.6(4), Os(2)–C(12)–C(11) = 121.6(5), C(12)–C(11)–C(10) = 129.0(6), C(12)–C(11)–C(16) = 134.7(6), C(10)–C(11)–C(16) = 93.4(5), C(11)–C(16)–C(13) = 87.3(5), C(16)–C(13)–C(10) = 89.2(5), C(13)–C(10)–C(11) = 90.1(5), C(13)–C(14)–C(15) = 93.5(5), C(14)–C(15)–C(16) = 95.5(5), C(15)–C(16)–C(13) = 85.1(5), C(16)–C(13)–C(14) = 85.8(5), C(11)–C(16)–C(15) = 109.1(5), C(10)–C(13)–C(14) = 111.3(5), C(13)–C(14)–C(19) = 132.0(6), C(15)–C(14)–C(19) = 134.4(6), C(14)–C(15)–C(20) = 135.1(6), C(16)–C(15)–C(20) = 129.4(6).

γ -carbon to afford **2**. Complexes containing a $\mu_3\text{-}\eta^2$ -vinylidene ligand are known in many cluster systems.^{21,23} Besides, equilibration of vinylidene and acetylide species has been postulated for chemisorption of acetylene on the Pt(111) surface.²⁴

The ¹H NMR spectrum of **1** displays five singlets in the range δ 2.12–0.96 for the inequivalent methyl groups and a 1 H doublet at δ 6.73 for the alkylidene proton, which is coupled with the bridging hydride resonance at δ –17.56 (J = 2 Hz), while the other bridging hydride appears as a singlet at δ –18.04. The molecular structure of **1** is depicted in Figure 1. The two hydride ligands were not located but are believed to span the Os(1)–Os(3) and Os(1)–Os(2) edges, where the Os(1)–Os(3) distance of 3.0550(4) Å is significantly longer than the other intermetallic distances Os(1)–Os(2) = 2.8730(3) Å and Os(2)–Os(3) = 2.8855(3) Å. The coordinated portion of the organic ligand can be described as a vinylmethylidene. The methylidene carbon C(12) bridges the Os(1)–Os(2) edge asymmetrically with the bond lengths C(12)–Os(2) = 2.141(6) Å and C(12)–Os(1) = 2.250(6) Å. The dihedral angle between the triosmium plane and the Os(1)–C(12)–Os(2) plane is 108.3°. The vinyl C(10)=C(11) group is coordinated to Os(1) in the exo side, with a C(10)–Os(1) distance of

(19) Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_9\text{Os}_3$: C, 25.66; H, 1.83. Found: C, 25.20; H, 1.60. MS (FAB): m/z 990 [M^+ , ¹⁹²Os]. IR (*n*-hexane, $\nu(\text{CO})$): 2100 (w), 2072 (vs), 2048 (s), 2012 (vs), 2000 (s), 1978 (m) cm^{-1} . ¹H NMR (CDCl_3 , 25 °C): δ 1.78 (s, 3H), 1.62 (s, 3H), 1.45 (s, 3H), 1.14 (s, 3H, Me), 1.03 (q, 2H, Et), 0.89 (t, 3H, Et), –22.99 (s, $\mu\text{-H}$). Crystal data for **2**: $\text{C}_{21}\text{H}_{17}\text{O}_9\text{Os}_3$, M_r = 983.95, monoclinic, space group $P2_1/n$, a = 9.5373(1) Å, b = 42.8440(4) Å, c = 12.2112(1) Å, α = 90°, β = 103.2851(5)°, γ = 90°, V = 4856.16(8) Å³, Z = 8, ρ_{calcd} = 2.692 g cm^{-3} , μ = 15.707 mm^{-1} , $F(000)$ = 3544, θ range 1.78–27.50°, 596 variables refined with 11 006 independent reflections to final R indices ($I > 2\sigma(I)$) of R_1 = 0.0429 and wR_2 = 0.0936, and GOF = 1.151.

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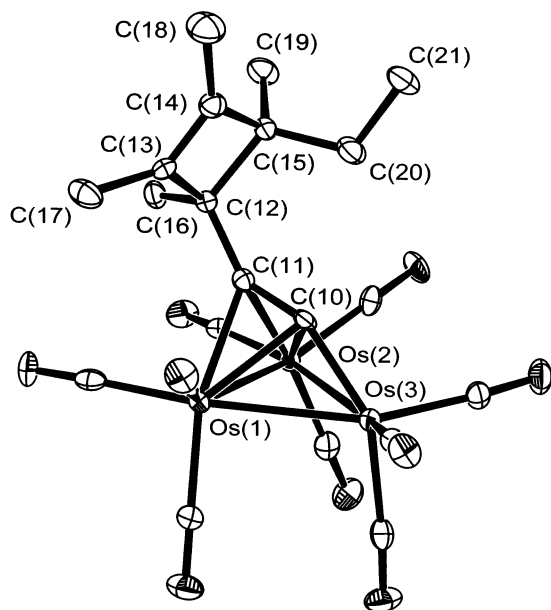


Figure 2. Molecular structure of **2** (ORTEP diagram). Selected bond lengths (Å): Os(1)–Os(2) = 2.8337(6), Os(1)–Os(3) = 2.8322(5), Os(2)–Os(3) = 2.8433(6), Os(1)–C(10) = 2.255(9), Os(1)–C(11) = 2.28(1), Os(2)–C(10) = 2.25(1), Os(2)–C(11) = 2.30(1), Os(3)–C(10) = 1.98(1), C(10)–C(11) = 1.32(1), C(11)–C(12) = 1.50(1), C(12)–C(13) = 1.54(2), C(13)–C(14) = 1.34(1), C(14)–C(15) = 1.51(2), C(15)–C(12) = 1.63(1). Selected bond angles (deg): Os(1)–Os(2)–Os(3) = 59.85(1), Os(1)–Os(3)–Os(2) = 59.91(1), Os(2)–Os(1)–Os(3) = 60.24(1), Os(1)–C(10)–Os(2) = 77.9(3), Os(1)–C(11)–Os(2) = 76.4(3), Os(3)–C(10)–C(11) = 152.4(8), Os(1)–C(11)–C(12) = 133.5(7), Os(2)–C(11)–C(12) = 133.5(7), C(10)–C(11)–C(12) = 142.5(9), C(11)–C(12)–C(13) = 116.8(9), C(12)–C(13)–C(14) = 95.2(9), C(13)–C(14)–C(15) = 95.6(9), C(14)–C(15)–C(12) = 85.4(8), C(15)–C(12)–C(13) = 83.6(7).

2.217(6) Å and C(11)–Os(1) distance of 2.259(6) Å. The Dewar benzene framework remains intact, such that the two cyclobutene rings are each planar with a dihedral angle of 109.7° between the two planes and the C(10)–C(11), C(13)–C(16), and C(14)–C(15) edges are parallel to each other, giving a ladder-shaped (or trapezoid) configuration.

The IR absorptions in the carbonyl region of **2** show a pattern similar to that recorded for $[(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CR})]$.²⁵ The ¹H NMR spectrum presents four singlets in the range δ 1.78–1.14 for the methyl groups, a 2H quartet at δ 1.03 and a 3H triplet at δ 0.89 for the ethyl group, and a singlet at δ –22.99 for the bridging hydride. The molecular structure of **2** is shown in Figure 2. The bridging hydride ligand was not located but is believed to span the Os(1)–Os(2) edge. The overall molecule consists of a triangular Os₃(CO)₉ moiety, which is capped on one face by a $\mu_3\text{-}\eta^2$ -cyclobutenylacetylide ligand. The Os₃ triangle is nearly isosceles, with Os(1)–Os(2) = 2.8337(6) Å, Os(1)–Os(3) = 2.8322(5) Å, and Os(2)–Os(3) = 2.8433(6) Å. The acetylide C(10)≡C(11) group formally forms a σ bond to Os(3) and π -bonds to the atoms Os(1) and Os(2). The Os(3), C(10), C(11), and C(12) atoms are about coplanar (torsion angle 178.1°), with the bond angles Os(3)–C(10)–C(11) = 152.4(8)° and C(10)–C(11)–C(12) = 142.5(9)°. The cyclobutene ring is slightly twisted, as indicated by the torsion angles C(12)–C(13)–C(14)–C(15) = 3.06° and C(17)–C(13)–C(14)–C(18) = 3.69°. The alkyl groups connected to the C(12) and C(15) atoms are essentially eclipsed, which should cause considerable steric repulsions and might account for the lengthened C(12)–C(15) single-bond distance of 1.63(1) Å (cf. C(13)–C(16) = 1.583(9) Å in **1**).

In summary, the transformation from hexamethyl Dewar benzene to a cyclobutenylacetylide moiety in **2** is unprecedented and of interest within the context of the chemistry of strained hydrocarbons. It may provide an attractive general strategy for the activation of related bicyclobutene systems, which are applicable to organic synthesis.

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Supporting Information Available: Complete tables of crystallographic data, positional parameters, bond lengths, and bond angles of **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>. OM030281U

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