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A novel non-facial mode of azulene cluster co-ordination. Crystal and molecular structure of the dicarbenoid $Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^1:\eta^1:\eta^1\text{-}C_{10}H_6)$

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Azulene oxidatively added to $Os_3(CO)_{11}(NCCH_3)$ to afford the triosmium cluster $Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^1:\eta^1:\eta^1\text{-}C_{10}H_6)$ **1** in high yield. The organic moiety is bound perpendicularly to the trimetallic plane and acts as a 4e$^-$ donor forming one terminal and one bridging carbene–metal bond. An X-ray diffraction study of **1** was made and full spectroscopic assignment has been made using 1- and 2-D homo- and hetero-nuclear NMR; 2-D ^{13}C EXSY experiments have also allowed the elucidation of the CO exchange process.

Introduction

Co-ordination of aromatic rings to transition metal clusters has extensively been investigated by a number of groups[1] with the aim of developing molecular models for the chemisorption of aromatic compounds on the surface of heterogeneous catalysts. It is well established that such co-ordination reduces the π-electron density leading to unusual nucleophilic substitutions of arenes, thus opening new synthetic strategies.[2] Polycyclic aromatic systems contain a large number of π electrons, formally available for interacting with transition metal clusters, and have been shown to co-ordinate in a wide variety of bonding modes.[3] However, relatively few clusters containing polycyclic arene-derived ligands have been reported.[4] In this paper we report the reaction of the cluster $Os_3(CO)_{11}(NCCH_3)$ with azulene (bicyclo[5.3.0]decapentaene), one of the simplest non-alternate, non-benzenoid, bicyclic aromatic compounds.

Table 1 Selected bond distances (Å) and angles (°) for compound **1**

Os1–Os3	2.8191(5)	C12–C13	1.351(15)
Os1–Os2	2.9818(5)	Os–CO	1.922(1)
Os2–Os3	2.7919(5)	C–O	1.145(1)
Os1–C10	2.123(8)	C14–C15	1.365(13)
Os2–C18	2.179(9)	C15–C16	1.410(13)
Os3–C18	2.185(9)	C16–C17	1.388(13)
C10–C19	1.395(13)	C17–C18	1.480(12)
C10–C11	1.431(12)	C18–C19	1.470(11)
C11–C12	1.400(13)	C15–C19	1.474(13)
C(3)–Os(1)–C(10)	171.1(4)	C(17)–C(18)–C(19)	103.8(7)
Os(1)–C(10)–C(11)	120.6(7)	C(11)–C(10)–C(19)	122.9(8)
Os(1)–C(10)–C(19)	116.5(6)		

Results and discussion

On refluxing a suspension of $Os_3(CO)_{11}(NCCH_3)$ and azulene in n-octane for 1 h one product is obtained, in 65% yield based on reacted $Os_3(CO)_{11}(NCCH_3)$. The analytical data suggest that the reaction proceeds *via* the oxidative addition of azulene to the triosmium cluster giving rise to a derivative of formula $Os_3(\mu\text{-}H)_2(CO)_9(C_{10}H_6)$ **1**. In order to establish the co-ordination mode of the azulene a crystal structure determination of **1** was undertaken.

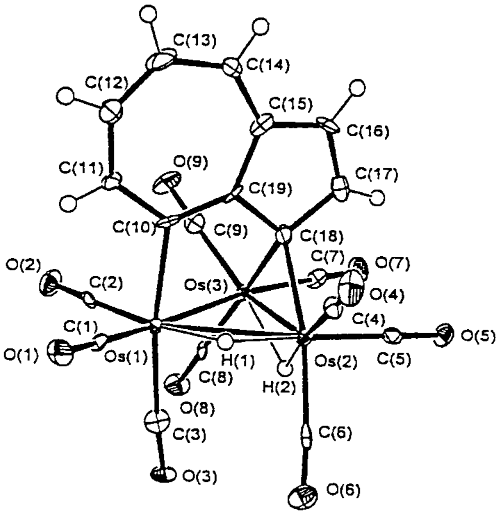

Fig. 1 Solid state structure of compound **1** showing the calculated positions for the hydride atoms.

The molecular structure is shown in Fig. 1 and selected bond lengths and angles are presented in Table 1. Cluster **1** contains the μ_3-azulene ligand bound perpendicularly to the metallic plane through two carbon atoms, C(10) and C(18) with metal–carbon distances of Os(1)–C(10) 2.123(8), Os(2)–C(18) 2.179(9) and Os(3)–C(18) 2.185(9) Å respectively. The bonding of C(18) which bridges Os(2)–Os(3) can be considered as an alkylidene. The Os(1)–Os(2), Os(2)–Os(3) and Os(3)–Os(1) bond lengths are all consistent with the presence of metal–metal bonds. Each osmium atom bears three carbonyl groups and the longest and the shortest metal–metal bonds carry bridging hydrides. The hydride ligands were located by determining the potential energy minima with the program Hydex.[5] As expected the hydride ligand located on the elongated metal–metal bond (Os(1)–Os(2) 2.982 Å) lies in the plane of the triangle whereas that bridging the shortest metal–metal bond (Os(2)–Os(3) 2.792 Å) is located well below this plane.

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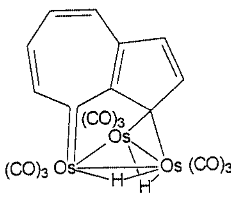
The $C_{10}H_6$ ligand acts as a 4-electron donor allowing the cluster to comply with the '18-electron' rule. The Os(1)–C(10) distance is consistent with the accepted values of M–C distances for terminal carbenes; for instance in $Os_3(\mu\text{-}H)_2(CO)_8[C(Et)NMe_2](\mu_3\text{-}S)$ the Os–C distance of the carbene moiety is 2.10 Å.[6] The presence of a partial double bond between Os(1) and C(10) is in agreement with the position of Os(1), which lies in the same plane as the azulene carbon atoms, giving rise to a novel bonding mode, as shown.



Azulene type ligands usually co-ordinate to metallic moieties through the partition of the π electrons into two sets to form π-cyclopentadienyl and non-cyclic π-dienyl or π-allyl linkages. Although there is a considerable variation in the C–C distances about seven membered rings reported in the literature, the mean values found in **1** do not differ significantly with respect to those reported for the cationic iron–carbene[7] $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(C_7H_4)]^+$ [1.404(42) and 1.398(28) respectively]. Hence the seven membered ring in compound **1** shows no tendency toward an allene structure; also the bond angles about the carbene carbon atom C(10) are within 3° of the idealized value of 120° for sp^2 hybridization.

Spectroscopic characterization of compound **1** was carried out by ^1H and $^{13}C\text{-}\{^1H\}$ NMR, ^1H COSY and ^1H–^{13}C HMQC (heteronuclear multiple quantum correlation) experiments. Low temperature ^1H and ^{13}C NMR data are consistent with the molecular structure found for the crystal persisting in solution. The ^1H COSY NMR spectrum allows the complete assignment of the ligand protons. The one bond ^1H–^{13}C HMQC experiment and the long-range ^1H and ^{13}C data allow the complete assignment of the carbon resonances of the azulene ring. All the spectroscopic data are consistent with the proposed scheme based on a $\mu_3\text{-}\eta^1:\eta^1:\eta^1$ bonding mode of the hydrocarbon to the cluster.

At 283 K the ^{13}C NMR spectrum of the carbonyl region of a ^{13}CO enriched sample shows nine sharp signals at δ 185.1 (d, $^2J_{C,H} = 6.9$), 180.7 (s), 178.3 (s), 177.3 (d, $^2J_{C,H} = 7.6$), 176.5 (s), 172.5 (s), 169.1 (s), 164.5 (dd, $^2J_{C,H} = 10.0$, $^2J_{C,H} = 3.5$) and 162.0 (d, $^2J_{C,H} = 12.3$ Hz) respectively. The ^{13}C chemical shift for the terminal carbene and that for the bridging alkylidene fall at δ 202.95 and 81.95 respectively. On increasing the temperature all of the carbonyl resonances broaden, except for the signal at δ 178.3. A ^{13}C EXSY experiment carried out at 298 K in CD_2Cl_2 (Fig. 2) shows that all COs, except for the resonance at δ 178.26, exchange in a pairwise manner. A variable temperature ^1H NMR study of a toluene solution of compound **1** shows that the two hydride resonances broaden at room temperature and then coalesce at 342 K; from this we have calculated a $\Delta G^\ddagger$ value of 15.8 ± 1.0 kcal mol^{-1}. We believe that this behaviour may be explained by an exchange of the two hydrides around the three edges of the metal triangle. The hydride fluxionality produces an apparent pairwise averaging of the carbonyl groups (except, of course, for the carbonyl which is *trans* to the (C10) carbene atom) and thus the carbonyl framework is rigid on the NMR timescale and the averaging process is solely the result of hydride exchange.

Conclusion

This novel azulene–Os_3 bonding mode is highly stable and stereochemically rigid on the NMR timescale. All previous examples of azulene cluster co-ordination have involved an extensively π-bonded facial interaction. It is also worthy of note that the carbonyl moiety is rigid on the NMR timescale which is very uncommon in $Os_3(CO)_9$ fragments.[8] As far as we know, this is the first example of a carbenic mode of co-ordination of a hydrocarbon moiety without any heteroatom(s) (such as N, O, P or S) stabilizing the ligand–metal interaction(s).

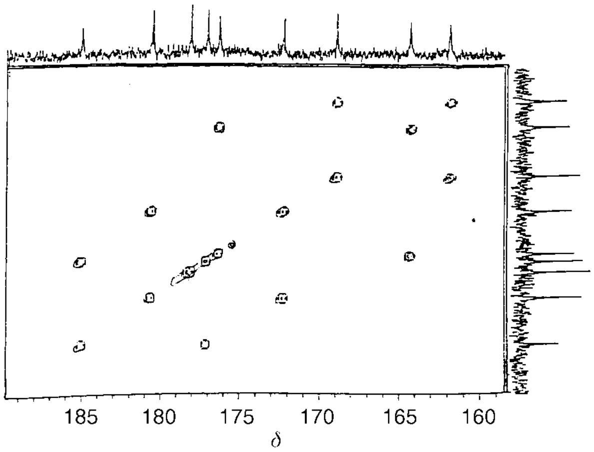


Fig. 2 Contour plot of a ^{13}C 2D-EXSY experiment (carbonyl region, 100.25 MHz, CD_2Cl_2, 298 K, $t_m = 0.5$ s) for a ^{13}CO enriched sample of compound **1**.

Experimental

In a three neck round bottom flask 0.10 g of $Os_3(CO)_{11}(NCCH_3)$[9] was suspended in 50 cm^3 of n-octane under nitrogen. The suspension was taken to reflux and then azulene 0.014 g was added. The solution was kept refluxing for 1 h. After all $Os_3(CO)_{11}(NCCH_3)$ had reacted, as shown by thin layer chromatography, the solvent was evaporated under vacuum and unchanged azulene was sublimed off using a cold finger apparatus. The yellow-orange solid residue was loaded onto silica TLC plates (Silica gel 60 F_{254}, 2 mm thickness, eluent pentane). One product was recovered, as deep yellow-orange crystals in 65% yield. Crystals of $Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^1:\eta^1:\eta^1\text{-}C_{10}H_6)$ **1** were recovered from a saturated n-heptane solution at 0 °C. Calc. for $C_{19}H_8O_9Os_3$: C, 23.98; H, 0.85. Found: C, 24.26; H, 0.88%. IR (ν(CO), n-pentane): 2103m, 2073s, 2046vs, 2026m, 2019m, sh, 2001w, 1987w and 1972m cm^{-1}. ^1H NMR (CD_2Cl_2, −50 °C, 400 MHz): δ −13.99, −14.55, 8.76 (H^{11}, d, $^3J = 9.75$), 8.32 (H^{14}, d, $^3J = 9.75$), 7.57 (H^{17}, d, $^3J = 4.2$), 7.51 (H^{13}, t, $^3J = 9.75$), 7.34 (H^{12}, t, $^3J = 9.75$) and 7.07 (H^{16}, d, $^3J = 4.2$ Hz). ^{13}C NMR (CD_2Cl_2, −50 °C, 100 MHz): 202.9 (C^{10}), 183.6 (C^{19}), 175.2 (C^{17}, $^1J = 159.9$), 155.3 (C^{11}, 160.2 , $^1J = 155.9$), 152.5 (C^{15}), 136.6 (C^{14}, $^1J = 124.1$), 135.4 (C^{13}, $^1J_{CH} = 154.51$), 134.6 (C^{12}, $^1J_{CH} = 152.59$), 122.4 (C^{16}, $^1J = 165.3$ Hz) and 81.9 (C^{18}).

X-Ray crystallographic studies of compound 1

Orange-yellow crystals of compound **1** were obtained by slow evaporation of pentane solutions. Suitable crystals were mounted in oil droplets, which solidified at the data collection temperature, on a Nonius ^{Kappa}CCD diffractometer. The crystals were indexed and data collection strategy determined by the Nonius 'Collect' program.[10] Data were integrated and merged, corrected for Lorentz and polarization effects and for the effects of absorption using the programs DENZO-SMN and Scalepack.[11] The structures were solved by direct methods and all non-hydrogen atoms of the clusters refined anisotropically (SHELXL 97),[12] while hydrogen atoms were included in calculated positions and allowed to ride on the atoms to which they were attached, with thermal parameters tied to those of the parent atom. Details of the crystal data

Table 2 Crystallographic data for cluster **1**

Chemical formula	$C_{19}H_8O_9Os_3$
Formula weight	950.85
Crystal system	Triclinic
Space group	$P\bar{1}$
T/K	293(2)
a/Å	8.392(3)
b/Å	8.835(5)
c/Å	15.125(9)
α/°	83.38(3)
β/°	86.21(3)
γ/°	68.71(3)
V/Å^3	1037.5(9)
Z	2
λ(Mo-Kα)/Å	0.71070
μ/mm^{-1}	16.120
Reflections collected	8242
Independent reflections	4758 [R(int) = 0.0722]
Final $R1$, $wR2$ indices [$I > 2\sigma(I)$]	0.0420, 0.0974
(all data)	0.0536, 0.1023

and of the data collection and structure solution and refinement are in Table 2.

CCDC reference number 186/1982.

See http://www.rsc.org/suppdata/dt/b0/b002399j/ for crystallographic files in .cif format.

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