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Preliminary communication

The insertion of 1-phenyl-1-propyne into the ruthenaborane cluster $HRu_4(CO)_{12}BH_2$ and the isolation and molecular structure of 1-phenyl-2,3-dimethylazulene

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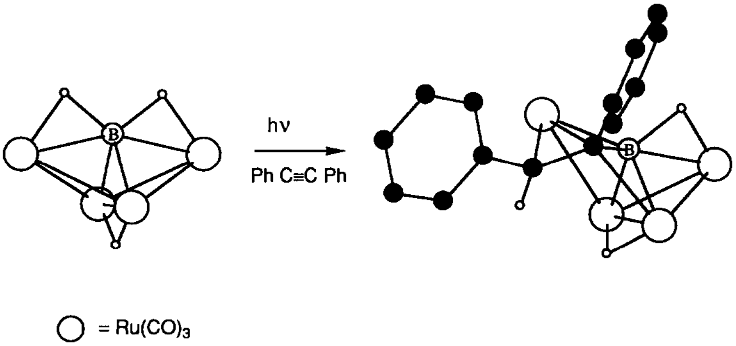
Abstract

Photolysis of the tetraruthenaborane butterfly cluster $HRu_4(CO)_{12}BH_2$ with 1-phenyl-1-propyne yields the cluster product $HRu_4(CO)_{12}B(H)C(Ph)CMeH$. Interestingly, 1-phenyl-2,3-dimethylazulene has also been isolated from the reaction mixture. The formation of this substituted azulene is an example of a novel cyclodimerisation of the alkyne. The crystal structure of 1-phenyl-2,3-dimethylazulene has been determined.

Recently we reported that $HRu_4(CO)_{12}BH_2$, [1,2] **1**, reacts with PhC≡CPh under photolytic conditions to give $HRu_4(CO)_{12}B(H)C(Ph)CHPh$ in which the alkyne has inserted into one Ru_{wing}–Ru_{hinge} bond of the Ru_4-butterfly framework of the metalloborane cluster [3]. The reaction (Scheme 1) was of interest not only because it achieved boron–carbon bond formation while retaining four ruthenium–boron bonding interactions, but also because the nature of the product was significantly



Scheme 1.

0022-328X/91/$03.50

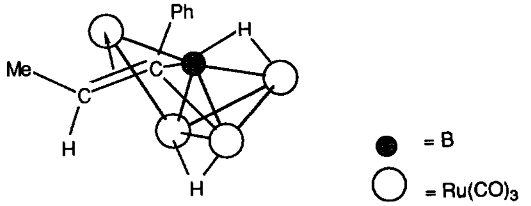


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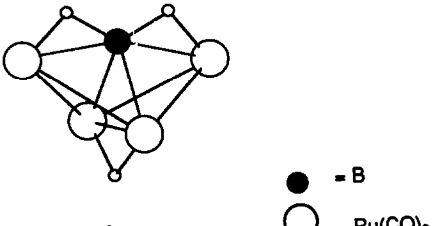
Fig. 1. Proposed structure for $HRu_4(CO)_{12}B(H)(CPh)CMeH$, **2**.

different from that observed in the reactions of PhC≡CPh with the carbide and nitride clusters, $H_2Ru_4(CO)_{12}C$ [4] and $[HRu_4(CO)_{12}N]^-$ [5]. These clusters are isoelectronic with **1**. In extending our investigation of the reactivity of **1** with alkynes, we have observed a novel coupling of two moles of PhC≡CMe to yield a substituted azulene.



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In a typical reaction, 1-phenyl-1-propyne (0.10 ml, 0.8 mmol) was combined with **1** (0.06 g, 0.08 mmol) in a mixture of CH_2Cl_2 (1.0 ml) and CD_2Cl_2 (0.5 ml) and the solution was photolysed in a quartz tube for 15 h. Analysis of the crude reaction mixture by ^{11}B NMR spectroscopy showed the presence of unreacted **1** (δ +109.9) and only one other signal, a doublet at δ +95.5 ($J(BH) = 70$ Hz). This was assigned to $HRu_4(CO)_{12}B(H)C(Ph)CMeH$, **2**, (Fig. 1) on the basis of mass spectral data and similarities between its spectroscopic data [6*] and those of the crystallographically characterised $HRu_4(CO)_{12}B(H)C(Ph)CPhH$ [3]. The orientation of the alkyne fragment and the formation of a $B-C_{Ph}$ rather than a $B-C_{Me}$ interaction (and, consequently, the formation of a CMeH rather than CPhH unit) is deduced from (i) the chemical shift of the methine proton (δ 4.15 in **2** compared to 5.04 in $HRu_4(CO)_{12}B(H)C(Ph)CPhH$ [3] and 5.15 in $HRu_4(CO)_{12}CC(Ph)CPhH$ [4] and (ii) the value of the coupling constant between the methyl and methine protons [7]. $^1H-^1H$ correlation spectroscopy was used to confirm the assignments of the methine and methyl resonances. The yield of **2** ($\approx$ 10%), was less than that of $HRu_4(CO)_{12}B(H)C(Ph)CPhH$ (60% under similar conditions). Separation of the reaction mixture by TLC eluting with hexanes yielded three bands: first, yellow **1**, second, orange **2**, and third, a bright blue fraction identified as 1-phenyl-2,3-dimethylazulene, **3** [8*]. The formation of this isomer, rather than 1,3-dimethyl-2-phenylazulene, has been confirmed by X-ray analysis [9*] but is also apparent from the ^1H

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* Reference number with asterisk indicates a note in the list of references.

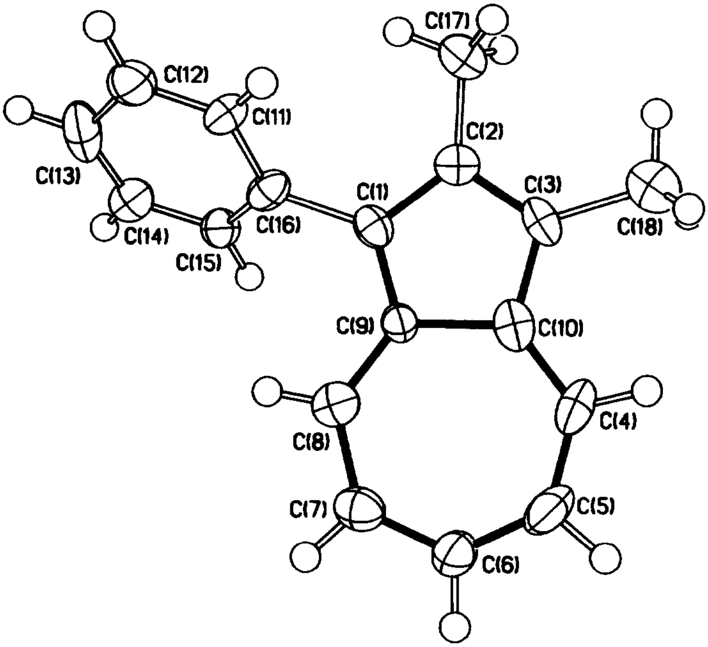
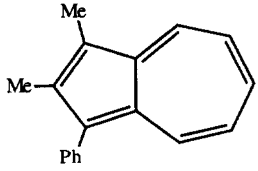


Fig. 2. Molecular structure and labelling scheme for 3: C(1)–C(2) = 1.397(11), C(1)–C(9) = 1.358(12), C(2)–C(3) = 1.379(12), C(3)–C(10) = 1.431(13), C(9)–C(10) = 1.535(10), C(4)–C(10) = 1.360(14), C(4)–C(5) = 1.390(15), C(5)–C(6) = 1.367(13), C(6)–C(7) = 1.389(12), C(7)–C(8) = 1.431(13), C(8)–C(9) = 1.385(12) Å.

NMR spectrum of **3**. Each proton attached to the seven-membered ring of 1-phenyl-2,3-dimethylazulene is unique whereas in 1,3-dimethyl-2-phenylazulene, there are only three environments. The region between δ 8.5 and 6.5 in the ^{1}H NMR spectrum of **3** consists of two doublets and two apparent triplets in addition to a multiplet in the typical region for phenyl resonances. Integration of this region implies that the resonance for one the ring protons is masked by those of the phenyl substituent.



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A crystal of **3** of X-ray quality was grown from hexane at −20 °C and the molecular structure is shown in Fig. 2. The geometrical parameters that define the bicyclic framework in **3** are similar to those in azulene [10,11] and 2-phenylazulene [12] but in both these molecules, the structures were disordered. The distance of 1.535(10) Å for the transannular interaction C(9)–C(10) is indicative of a single bond whereas other intra-ring distances are consistent with a conjugated system.

There are no significant deviations from planarity for the atoms which make up the bicyclic system. The plane of the phenyl ring lies at 55.1° with respect to the plane of the azulene rings.

Compound **3** is formally a dimer of $PhC\equiv CMe$ [13*] but one in which one C–C bond of a phenyl ring has been activated allowing ring expansion to give a seven-membered ring. One mole $PhC\equiv CMe$ is identified as forming part of the five-membered ring. Precedent for this type of self-assembly comes from the formation of 1,2,3-triphenylazulene from $PhC\equiv CPh$ in the presence of $AlCl_3$ and 2,4-dinitrobenzenesulfenyl chloride [14,15]. Interestingly, we do not observe the formation of 1,2,3-triphenylazulene during the reaction of $PhC\equiv CPh$ with **1**. Other cyclodimerisation reactions have been observed in the presence of transition metal species [16], but the formation of a substituted azulene under the specified conditions would appear to be a novel observation. The yield in which **3** is obtained is, however, variable (1 to 10% yield) and this fact has prompted us to examine the reaction more closely. Test reactions show that **3** is formed in trace amounts simply by photolysing $PhC\equiv CMe$ alone in CH_2Cl_2 or in the presence of other ruthenaborane based clusters, namely $Ru_3(CO)_9BH_5$ and $HRu_3(CO)_9B_2H_5$. Further studies on this and related systems are in progress.

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References and notes

1 A.K. Chipperfield, C.E. Housecroft and A.L. Rheingold, Organometallics, 9 (1990) 681.

2 F.-E. Hong, D.A. McCarthy, J.P. White III, C.E. Cottrell and S.G. Shore, Inorg. Chem., 29 (1990) 2874.

3 A.K. Chipperfield, B.S. Haggerty, C.E. Housecroft and A.L. Rheingold, J. Chem. Soc., Chem. Commun., 1174 (1990).

4 T. Dutton, B.F.G. Johnson, J. Lewis, S.M. Owen and P.R. Raithby, J. Chem. Soc., Chem. Commun., 1423 (1988).

5 M. Blohm and W.L. Gladfelter, Organometallics, 5 (1986) 1049.

6 $HRu_4(CO)_{12}B(H)C(Ph)CMeH$, **2**: 250 MHz ^1H NMR (CD_2Cl_2, 298 K) δ 7.5–7.2 (m, 5H, *Ph*), 4.15 (quartet, $J(HH) = 6.4$ Hz, *Me*), 1.91 (doublet, $J(HH) = 6.3$ Hz, C*H*), −7.4 (br. quartet, $J(BH) = 70$ Hz, Ru–*H*–B), −19.3 (s, Ru–*H*–Ru); 128 MHz ^{11}B NMR (CD_2Cl_2, 298 K) δ +95.5 (d, $J(BH) = 70$ Hz); IR (hexane, cm^{-1}) ν(CO) 2106w, 2098m, 2078m, 2071m, 2059vs, 2045s, 2027vs, 2021m, 2016m, 2001m, 1990m, 1960w; FAB-MS (NOBA matrix) m/z M^+ 875, ($M^+ - 12CO$) 539 (isotopic pattern agrees with that simulated for **2**).

7 J.W. Emsley, J. Feeney and L.H. Sutcliffe, High Resolution NMR Spectroscopy, Pergamon Press, Oxford, 1st edn., Vol. 2, p. 725.

8 1-Phenyl-2,3-dimethylazulene, **3**: 250 MHz ^1H NMR (CD_2Cl_2, 298 K) δ 8.21 (d, $J(HH) = 9.3$ Hz, 1H), 8.06 (d, $J(HH) = 9.7$ Hz, 1H), 7.5–7.25 (m, 6H), 7.07 (t, $J(HH) = 9.7$ Hz, 1H), 6.98 (t, $J(HH) = 9.5$ Hz, 1H), 2.61 (s, 3H), 2.52 (s, 3H); FAB-MS (NOBA matrix) m/z M^+ 232 (isotopic pattern agrees with simulated for $C_{18}H_{16}$).

9 Crystallographic data for **3**: $C_{18}H_{16}$, orthorhombic, *Pbca*, $a = 17.359(6)$, $b = 7.779(3)$, $c = 19.423(9)$ Å, $V = 2622.9(20)$ Å^3, $Z = 8$. Of 1451 data collected from a weakly diffracting crystal (Nicolet R3m, $4° \leqslant 2\theta \leqslant 45°$, $T = 295$ K), 704 were observed. With all carbon atoms anisotropic and hydrogen atom positions idealised, $R(f) = 7.95\%$, $R(wf) = 8.89\%$. Complete tables of bond distances and

angles, atomic coordinates and structure factors may be obtained from one of the authors (A.L.R.) and have been deposited with the Cambridge Crystallographic Data Centre.

10 J.M. Robertson, H.M.M. Shearer, G.A. Sim and D.G. Watson, Acta Crystallogr., 15 (1962) 1.

11 G.S. Pawley, Acta Crystallogr., 18 (1965) 560.

12 B.D. Sharma and J. Donohue, Nature, 192 (1961) 863.

13 In view of the nature of the products **3**, the purity of the PhC≡CMe (Aldrich) was confirmed by ^{1}H NMR spectroscopy.

14 S.J. Assony and N. Kharasch, J. Am. Chem., Soc., 80 (1958) 5978.

15 K. Hafner, Angew. Chem., 70 (1958) 419.

16 M.J. Winter, in F.R. Hartley and S. Patai (Eds.), The Chemistry of the Metal–Carbon Bond, Wiley, Chichester, 1985, Vol. 3.