Co-ordination of Benzyne at Tetra- and Penta-Ruthenium Centres: A Model for Dissociative Chemisorption of Benzene on a Stepped Metal (111) Surface

Selby A. R. Knox, Brian R. Lloyd, A. Guy Orpen, Josep M. Viñas, and Martin Weber

Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K.

Heating [$Ru_3(CO)_{11}(PPh_3)$] in toluene yields complexes [$Ru_4(CO)_{11}(\mu_4$-PPh)(μ_4-η^4-C_6H_4)] and [$Ru_5(CO)_{13}(\mu_4$-PPh)(μ_5-η^6-C_6H_4)], structurally identified by *X*-ray diffraction, in which benzyne is co-ordinated at tetra- and penta-ruthenium centres respectively; the latter provides a model for the dissociative chemisorption of benzene at a step site on a metal (111) surface.

Muetterties suggested[1] in 1982 that the dissociative chemisorption (C–H bond cleavage) observed[2] for benzene on a stepped metal (111) surface is due to its η^6-co-ordination parallel to one terrace of the surface allowing a close approach of its hydrogens to the step atoms of a second terrace (see Figure 8 of ref. 1). We describe here the synthesis and structural characterisation of complexes in which benzyne is co-ordinated in an unprecedented fashion at tetra- and penta-ruthenium centres. The five metal atoms of the latter are in the arrangement of a step site on a (111) surface (see Figure 1) and the complex can be viewed as a model for the aftermath of benzene C–H activation on such a surface, in close accord with Muetterties' suggestion.

When [$Ru_3(CO)_{11}(PPh_3)$] is heated in toluene for 18 h three complexes are formed: triruthenium [$Ru_3(CO)_7(\mu$-$PPh_2)_2(\mu_3$-η^2-C_6H_4)](**1**),[3,4] containing μ_3-benzyne (30% yield), tetraruthenium [$Ru_4(CO)_{11}(\mu_4$-PPh)(μ_4-η^4-C_6H_4)] (**2a**),† containing μ_4-benzyne (33%), and pentaruthenium [$Ru_5(CO)_{13}(\mu_4$-PPh)(μ_5-η^6-C_6H_4)](**3**),† containing μ_5-benzyne (7%). Similarly, thermolysis of [$Ru_3(CO)_{11}(PPh_2Me)$] and [$Ru_3(CO)_{11}(PPh_2CH_2NPh_2)$] gives (**2b**) and (**2c**), respectively, but [$Os_3(CO)_{11}(PPh_3)$] does not provide an analogue of (**2**) or (**3**).[5] The generation of benzyne by thermolysis of a tertiary phenylphosphine complex is not without precedent,[3–7] and may occur *via ortho*-metallation followed by phosphorus–carbon bond cleavage.[8] Only one example exists of a polynuclear benzyne complex being derived from benzene itself.[9,10]

The molecular structures of (**2a**), (**2c**), and (**3**) have been determined by *X*-ray diffraction studies,‡ and the results for one molecule of (**2a**) and for (**3**) are summarised in Figures 2

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† The new complexes were characterised by elemental analyses and i.r. and n.m.r. (^{1}H and ^{31}P) spectra. Selected data: (**2a**), red crystals, ν(CO) (in hexane) at 2083w, 2049m, 2042s, 2027m, 2023m, 1997mw, 1980w, and 1826w cm^{-1}, ^{1}H n.m.r. (in [$^2H_6$]acetone, δ values in p.p.m.), δ 6.65 (2H, m) and 7.15 (2H, m) (benzyne protons, AA'BB' system), ^{31}P{^{1}H} n.m.r. (in $CDCl_3$, δ 411.6 p.p.m. (**3**), red crystals, ν(CO) (in hexane) at 2085vw, 2060vs, 2049m, 2042w, 2025m, 2018m, 2013s, 1982vw, and 1966vw cm^{-1}, ^{1}H n.m.r. (in [$^2H_6$]acetone), δ5.49 (2H, m) and 5.83 (2H, m) (benzyne protons, AA'BB' system), ^{31}P{^{1}H} n.m.r. (in $CDCl_3$), δ 423.7 p.p.m.

‡ *Crystal data*. For (**2a**): $C_{23}H_9O_{11}PRu_4$, M = 896.41, triclinic, space group $P\bar{1}$ (No. 2), a = 9.326(2), b = 15.884(3), c = 18.796(4) Å, α = 88.80(2), β = 77.37(2), γ = 88.64(2)°, U = 2715.8(7)Å^3, Z = 4, D_c = 2.19 g cm^{-3}, λ = 0.71069 Å, μ(Mo-K_α) = 22.56 cm^{-1}, T = 295 K.

For (**2c**): $C_{30}H_{16}NO_{11}PRu_4$, M = 1004.05, monoclinic, space group $P2_1/n$ (No. 14), a = 9.650(2), b = 19.571(5), c = 17.558(4) Å, β = 101.47(2)°, U = 3250(2) Å^3, Z = 4, D_c = 2.05 g cm^{-3}, λ = 0.71069 Å, μ(Mo-K_α) = 18.97 cm^{-1}, T = 295 K.

For (**3**): $C_{25}H_9O_{13}PRu_5$, M = 1053.56, monoclinic, space group $P2_1/n$ (No. 14), a = 10.037(2), b = 18.311(3), c = 16.425(2) Å, β = 102.20(1)°, U = 2950.5(7) Å^3, Z = 4, D_c = 2.37 g cm^{-3}, λ = 0.71069 Å, μ(Mo-K_α) = 25.73 cm^{-1}, T = 295 K.

Data were collected for each structure using Nicolet R3m diffractometers (graphite monochromated Mo-K_α *X*-radiation), for unique portions of reciprocal space in the range $4<2\theta<50°$. The structures were solved by heavy-atom methods (Patterson and Fourier) and refined by least squares. Final residuals (R) were 0.050, 0.029, and 0.034 for 4992, 5040, and 4335 unique, observed [$I > 1.5\sigma(I)$], absorption-corrected intensities for (**2a**), (**2c**), and (**3**), respectively. Atomic co-ordinates, bond lengths and angles, and vibrational parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

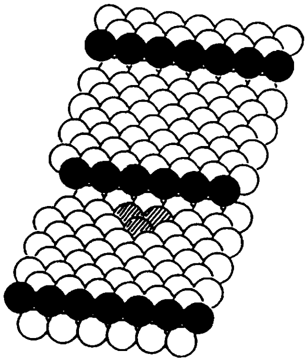


Figure 1. Representation of a stepped metal (111) surface. The step atoms are shown black. The three shaded atoms and adjacent pair of step atoms comprise a five-atom step site of the type found in complex (**3**).

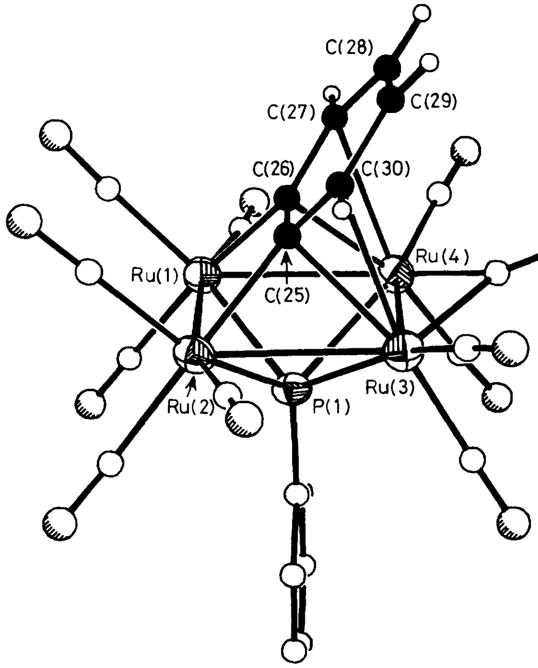


Figure 2. Molecular structure of one of two crystallographically distinct molecules of (**2a**). Important geometric parameters include: bond lengths (Å) [length in second molecule, length in (**2c**)], Ru(1)–Ru(2) 2.943(1) [2.932(1), 2.921(1)], Ru(2)–Ru(3) 2.896(1) [2.918(1), 2.927(1)], Ru(3)–Ru(4) 2.791(1) [2.805(1), 2.816(1)], Ru(1)–Ru(4) 2.891(1) [2.910(2), 2.875(1)], Ru(1)–P(1) 2.352(3) [2.344(3), 2.359(1)], Ru(2)–P(1) 2.353(3) [2.354(4), 2.356(1)], Ru(3)–P(1) 2.425(3) [2.444(3), 2.423(1)], Ru(4)–P(1) 2.446(3) [2.432(3), 2.469(1)], Ru(1)–C(26) 2.108(10) [2.100(11), 2.115(4)], Ru(2)–C(25) 2.110(10) [2.122(10), 2.117(3)], Ru(3)–C(25) 2.294(9) [2.309(12), 2.301(4)], Ru(4)–C(26) 2.299(10) [2.317(13), 2.292(4)], Ru(3)–C(30) 2.656(11) [2.583(12), 2.634(4)], Ru(4)–C(27) 2.689(11) [2.619(14), 2.592(4)], C(25)–C(26) 1.455(15) [1.460(16), 1.447(5)], C(26)–C(27) 1.395(14) [1.419(18), 1.391(5)], C(27)–C(28) 1.399(18) [1.394(20), 1.427(6)], C(28)–C(29) 1.3630(20) [1.355(25), 1.344(6)], C(29)–C(30) 1.405(16) [1.373 (20), 1.407(6)], C(25)–C(30) 1.403(16) [1.393(14), 1.380(9)].

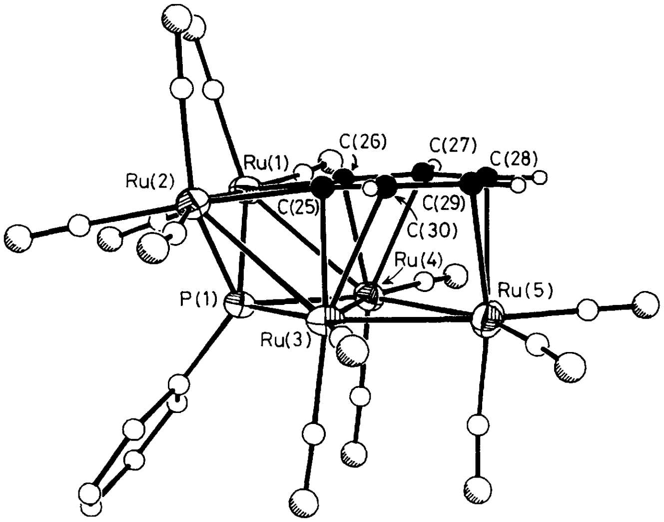
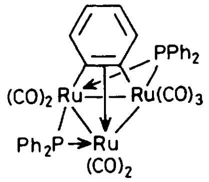


Figure 3. Molecular structure of (**3**). Important geometric parameters include: bond lengths (Å), Ru(1)–Ru(2) 2.902(1), Ru(2)–Ru(3) 2.905(1), Ru(3)–Ru(4) 2.865(1), Ru(1)–Ru(4) 2.897(1), Ru(3)–Ru(5) 2.769(1), Ru(4)–Ru(5) 2.783(1), Ru(1)–P 2.379(1), Ru(2)–P 2.386(2), Ru(3)–P 2.378(2), Ru(4)–P 2.381(2), Ru(1)–C(26) 2.097(6), Ru(2)–C(25) 2.116(6), Ru(3)–C(25) 2.234(5), Ru(4)–C(26) 2.251(6), Ru(3)–C(30) 2.391(5), Ru(4)–C(27) 2.391(6), Ru(5)–C(28) 2.427(6), Ru(5)–C(29) 2.398(7), C(25)–C(26) 1.451(9), C(26)–C(27) 1.395(9), C(27)–C(28) 1.441(10), C(28)–C(29) 1.394(10), C(29)–C(30) 1.443(10), C(25)–C(30) 1.380(9).

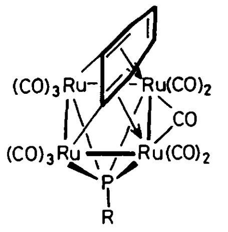
and 3 respectively. The structures of the second molecule of (**2a**) and of (**2c**) are essentially identical to that shown in Figure 2, with the replacement of Ph by CH_2NPh_2 in (**2c**). In all these molecules a square Ru_4 unit is capped on one side, approximately symmetrically, by a μ_4-phosphinidene ligand. On the other side benzyne functions as a six-electron donor in (**2**) and as an eight-electron donor in (**3**), bridging all the metal atoms. The benzyne co-ordination modes are best represented as in the diagrams, *i.e.* as *ortho*-dimetallated benzene. Thus Ru(1) and Ru(2) lie close to the C_6 plane in each case and show Ru–C σ-bond distances which are considerably shorter than the π-bonded Ru(3)–C and Ru(4)–C distances. In (**2**) the η^2-interactions between the benzyne and Ru(3), Ru(4) are rather asymmetric, with the bridging carbons [C(25) and C(26)] showing the shorter distances. The flexibility of this bonding mode is reflected in the varying angle between the Ru_4 and C_6 planes [54.7 and 49.0° in (**2a**) (two molecules), 50.9° in (**2c**)]. In (**3**) the benzyne ligand is further η^2-bonded to Ru(5), and the complex may be viewed as formally related to (**2a**) through replacement of the bridging carbonyl by an isolobal $Ru(CO)_3L$ fragment (L = η^2-double bond of benzyne). The benzyne ligand shows considerable localisation of multiple bonding in the way indicated in the diagrams; thus in each complex C(25)–C(26) is the longest C–C bond and for (**2**) C(28)–C(29) is the shortest.

The view of complex (**3**) given in Figure 3 emphasises the η^2,η^2,η^2-co-ordination of benzyne to the triruthenium unit Ru(3)Ru(4)Ru(5), similar to the bonding of benzene in the complex $[Os_3(CO)_9(C_6H_6)]$.[11] The most striking feature of (**3**), however, is that the five metal atoms mimic a step-site on a (111) surface (see Figure 1), where Ru(3)Ru(4)Ru(5) are in one terrace and Ru(1)Ru(2) are step atoms in the first row of the next. In the light of this observation, and Muetterties' intuition, it is attractive to envisage that the approach of benzene on a metal (111) surface to exposed, low-co-ordinate, step atoms will result in the activation of two *ortho*-CH bonds, to generate benzyne chemisorbed as in (**3**).

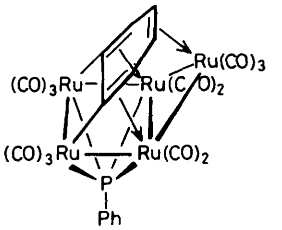
The complexes (**1**) and (**2**) may likewise be regarded as models for the dissociative chemisorption of benzene on metal (111) and (100) surfaces respectively. The consequences for



(**1**)



(**2a**) R = Ph
(**2b**) R = Me
(**2c**) R = CH_2NPh_2



(**3**)

the reactivity of co-ordinated benzyne of the different bond localisations in (**1**) (free diene unit) and (**2**) (free mono-ene) are under investigation; both species react readily with alkynes.

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