Carbonylation of Benzyne at Polynuclear Ruthenium Centres

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Carbonylation (1 atm, 25 °C) of $[Ru_3(CO)_7(\mu\text{-}PPh_2)_2(\mu_3\text{-}C_6H_4)]$ gives $[Ru_3(CO)_8(\mu\text{-}PPh_2)_2(\mu_3\text{-}C_6H_4CO)]$, arising from linking of μ_3-benzyne with one molecule of CO, while $[Ru_4(CO)_{11}(\mu_4\text{-}PPh)(\mu_4\text{-}C_6H_4)]$ and $[Ru_5(CO)_{13}(\mu_4\text{-}PPh)(\mu_5\text{-}C_6H_4)]$ react with CO (50 atm, 60–100 °C) to afford $[Ru_3(CO)_{10}(\mu_3\text{-}PPh)\{\mu\text{-}C_6H_4(CO)_2\}]$ and/or $[Ru_2(CO)_7\{\mu\text{-}P(Ph)C(O)C_6H_4\}]$, involving linking of μ_4- and μ_5-benzyne with one or two CO molecules; the structures of the products have been established by X-ray diffraction.

We recently described the synthesis of a range of polynuclear ruthenium carbonyl complexes containing μ_3-, μ_4- and μ_5-benzyne, and suggested that these could serve as models for the dissociative chemisorption of benzene on a metal surface.[1,2] We now report the preliminary results of a comparative investigation of the reactivity of benzyne when coordinated in these different ways. Here we describe carbonylation studies, which yield complexes containing benzyne linked with one or two molecules of CO, pointing to possible pathways for organic synthesis with benzene on metal surfaces.

Treatment of the purple μ_3-benzyne complex $[Ru_3(CO)_7(\mu\text{-}PPh_2)_2(\mu_3\text{-}C_6H_4)]$ 1a with CO at room
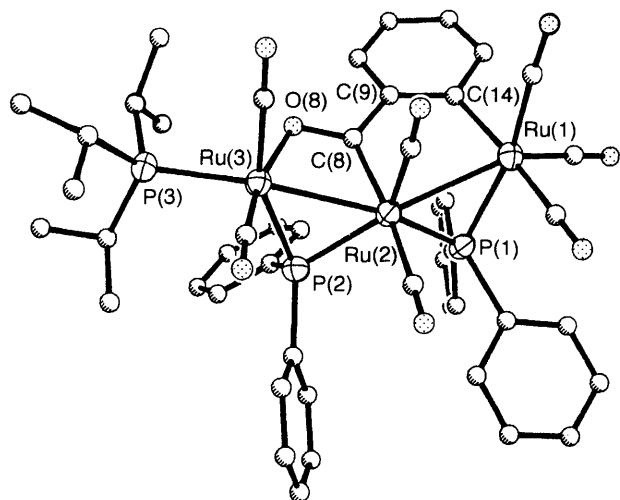
Fig. 1 Molecular structure of **2b**. Important geometric parameters include: bond lengths (Å), Ru(1)–Ru(2) 2.849(1), Ru(1)-P(1) 2.342(2), Ru(1)-C(14) 2.136(9), Ru(2)-Ru(3) 2.783(1), Ru(2)-P(1) 2.367(2), Ru(2)-P(2) 2.365(2), Ru(2)-C(8) 2.033(8), Ru(3)-P(2) 2.364(2), Ru(3)-P(3) 2.388(3), Ru(3)-O(8) 2.170(6), C(8)-O(8) 1.280(10), C(8)-C(9) 1.492(12).

temperature gives yellow [Ru₃(CO)₈(μ-PPh₂)₂(μ₃-C₆H₄CO)] **2a**† quantitatively, within 3 days at 1 atm or 1 day at 2 atm, as shown in Scheme 1. No crystals of **2a** suitable for X-ray diffraction could be obtained but the triisopropylphosphine derivative **2b**,† prepared by carbonylation of **1b**, was amenable to such a study, with the results displayed in Fig. 1.‡
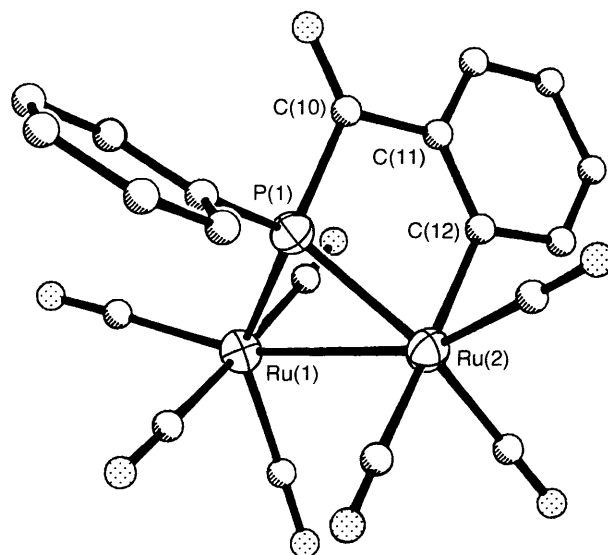

Fig. 2 Molecular structure of **4**. Important geometric parameters include: bond lengths (Å), Ru(1)–Ru(2) 2.903(1), Ru(1)-P(1) 2.371(1), Ru(2)-P(1) 2.285(1), Ru(2)-C(12) 2.169(3), P(1)-C(10) 1.878(3), C(10)-O(10) 1.206(4), C(10)-C(11) 1.485(5).

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† The new complexes were characterised by elemental analyses and IR and NMR (¹H, ¹³C{¹H} and ³¹P{¹H}) spectra. *Selected data:* **2a**, yellow powder, ν(CO)/cm⁻¹ (in hexane) at 2085vs, 2069vs, 2026s, 2020m, 2012w, 1996w, 1989m and 1935vw, ¹H NMR (in CD₂Cl₂), δ 7.74–7.64 (m, 2H), 7.52–7.05 (m, 15H), 6.64 (m, 3H), 6.53 (m, 1H) 6.51 (m, 1H), 6.27 (m, 1H) and 5.99 (m, 1H), ¹³C{¹H} NMR (in CD₂Cl₂), δ 278.6 (dd, J_{CP} 8, 5 Hz) (RuC=ORu), ³¹P{¹H} NMR (in CD₂Cl₂), δ 170.8 (d, J_{PP} 27 Hz) and 150.0 (d, J_{PP} 27 Hz).

4, yellow crystals, ν(CO)/cm⁻¹ (in hexane) at 2115m, 2065s, 2048s, 2043s, 2022s, 2004m, 1999m and 1670w, ¹H NMR (in [²H₆]acetone), δ 7.89 (m, 2H), 7.74 (d, J 7 Hz, 1H), 7.61 (t, J 3 Hz, 3H), 7.48 (dt, J 7, 2 Hz, 1H), 7.20 (td, J 7, 2 Hz, 1H) and 7.05 (tdd, J 7, 3, 1 Hz, 1H), ¹³C{¹H} NMR (in CD₂Cl₂), δ 199.8 (d, J_{CP} 55 Hz, PCO), ³¹P{¹H} NMR (in CD₂Cl₂), δ 154.0.

5, orange crystals, ν(CO)/cm⁻¹ (in hexane) at 2112w, 2091m, 2064s, 2043s, 2033m, 2022m, 2017m, 2007vw, 1986w, 1652w and 1501w, ¹H NMR (in CD₂Cl₂), δ 7.67–7.21 (m), ¹³C{¹H} NMR (in CD₂Cl₂), δ 298.4 (s) (RuO=CRu) and 242.4 (d, J_{CP} 45 Hz) {RuC(O)C₆H₄}, ³¹P{¹H} NMR (in CDCl₃), δ 151.2.

‡ *Crystal data* for **2b**: C₄₇H₄₅O₈P₃Ru₃, M = 1134.0, orthorhombic, space group *Pbca* (No. 61), a = 19.448(7), b = 19.568(7), c = 24.135(9) Å, U = 9180(6) Å³, Z = 8, D_c = 1.64 g cm⁻³, λ = 0.71069 Å, μ(Mo-Kα) = 11.1 cm⁻¹, T = 295 K.

For **4**: C₂₀H₉O₈PRu₂, M = 610.398, orthorhombic, space group *Pbca* (No. 61), a = 28.513(3), b = 11.279(1), c = 13.338(1) Å, U = 4289.5(7) Å³, Z = 8, D_c = 1.89 g cm⁻³, λ = 0.71069 Å, μ(Mo-Kα) = 15.0 cm⁻¹, T = 295 K.

For **5**: C₂₄H₉O₁₂PRu₃, M = 823.51, monoclinic, space group *P2₁/c* (No. 14), a = 9.366(2), b = 17.247(2), c = 17.178(3) Å, β = 97.50(1)°, U = 2751.4(8) Å³, Z = 4, D_c = 1.988 g cm⁻³, λ = 0.71069 Å, μ(Mo-Kα) = 17.1 cm⁻¹, T = 295 K.

Data were collected for each structure using Nicolet R3m diffractometers (graphite monochromated Mo-Kα X-radiation), for unique portions of reciprocal space in the range $4 < 2θ < 50°$. The structures were solved by heavy-atom methods (Patterson and Fourier) and refined by least-squares analysis. Final residuals (R) were 0.048, 0.027 and 0.027 for 4700, 3424 and 4824 unique, observed [$I > 2σ(I)$, $I > 1.5σ(I)$, $I > 2σ(I)$], absorption-corrected intensities for **2b**, **4** and **5**, respectively. Atomic coordinates, bond lengths and angles, and vibrational parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.
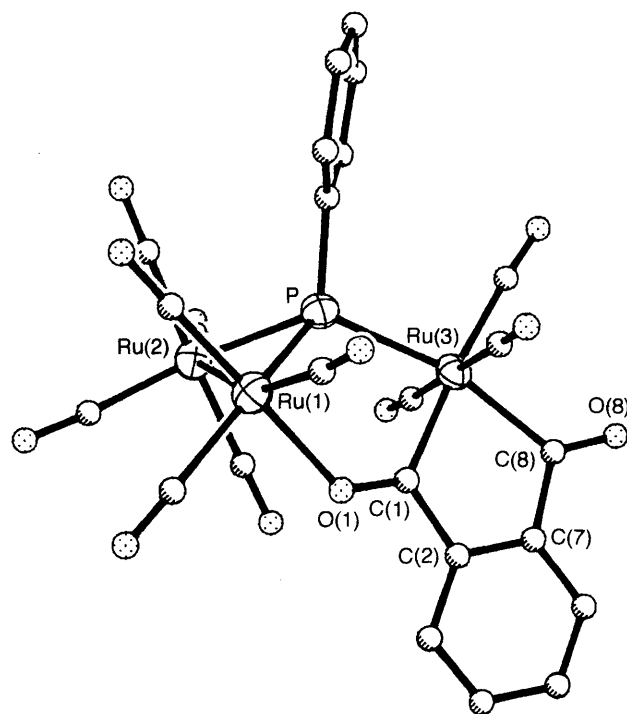

Fig. 3 Molecular structure of **5**. Important geometric parameters include: bond lengths (Å), Ru(1)-Ru(2) 2.836(1), Ru(1)-P 2.338(1), Ru(1)-O(1) 2.145(2), Ru(2)-P 2.416(1), Ru(3)-P 2.443(1), Ru(3)-C(1) 2.067(4), Ru(3)-C(8) 2.115(4), C(1)-O(1) 1.249(4), C(1)-C(2) 1.484(5), C(7)-C(8) 1.493(6), C(8)-O(8) 1.201(5).

The structural investigation reveals that two molecules of CO are incorporated upon carbonylation of the complexes **1**, resulting in the opening of a Ru–Ru bond and the formation of a novel *ortho*-metallated benzoyl ligand, which triply bridges the triruthenium unit in μ-acyl fashion, *via* the coordination of the carbonyl oxygen. The expectation that the benzoyl ligand arose from migratory insertion into a Ru–benzyne σ-bond was confirmed when treatment of **1a** with ¹³CO at 25 °C gave **2a**
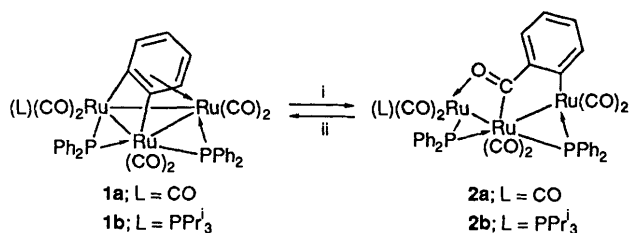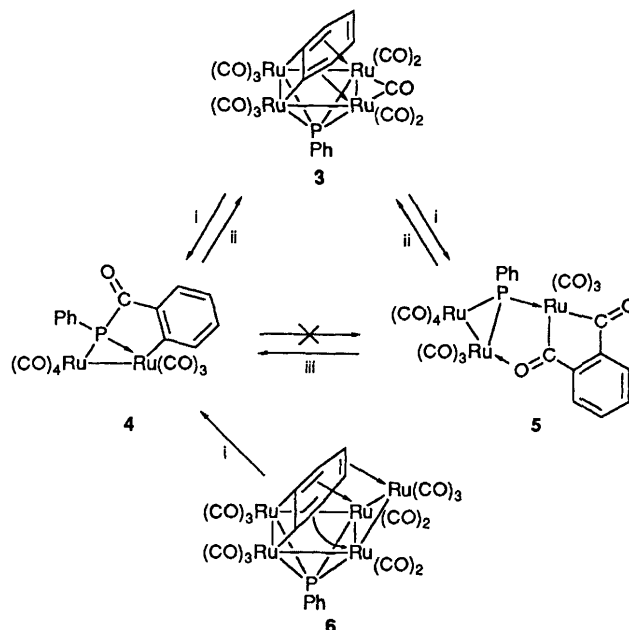
Scheme 1 *Reagents and conditions*: i, CO (1 atm, 3 days); ii, hexane reflux

Scheme 2 *Reagents and conditions*: i, CO (50 atm, 60–100 °C); ii, toluene reflux; iii, UV

with the label confined to terminal carbonyl sites, clearly shown by ^{13}C NMR monitoring of the distinctive benzoyl CO signal at δ 279. Although this indicates that the insertion is irreversible at room temperature, **1b** is regenerated smoothly when **2b** is warmed in hexane.

In contrast to **1** the μ$_4$-benzyne complex [Ru$_4$(CO)$_{11}$-(μ$_4$-PPh)(μ$_4$-C$_6$H$_4$)] **3** is stable to CO at 1 atm, but under 50 atm at 60 °C the cluster fragments to give [Ru$_2$-(CO)$_7$\{μ-P(Ph)C(O)C$_6$H$_4$\}] **4**† and [Ru$_3$(CO)$_{10}$(μ$_3$-PPh)\{μ-C$_6$H$_4$(CO)$_2$\}] **5**† in 20 and 60% yields, respectively; at the same pressure but higher temperature (100 °C) the yields of **4** and **5** are reversed, at 60 and 20%. Treatment of the μ$_5$-benzyne complex [Ru$_5$(CO)$_{13}$(μ$_4$-PPh)(μ$_5$-C$_6$H$_4$)] **6** with CO at 50 atm and 100 °C also resulted in cluster fragmentation, affording [Ru$_3$(CO)$_{12}$] and **4** in good yield, but giving no **5**. The structures of **4** and **5** have been established by X-ray diffraction and the results are shown in Fig. 2 and 3.‡

Both **4** and **5** arise from the linking of CO with benzyne. However, while one CO is involved in **4**, and is also attached to the phosphinidene ligand, in **5** two CO molecules have inserted into the Ru–benzyne σ-bonds to form a phthaloyl ligand. As in **2**, one of these carbonyls functions as a μ-acyl, but now bridging an open edge of a ruthenium triangle. The effect of bridging on the acyl is to lengthen the C–O distance and shorten the Ru–C distance relative to the values for a σ-bound acyl [Ru–C = 2.033(8) and 2.067(4) Å for the μ-acyls in **2b** and **5**, 2.155(4) Å for the σ-acyl in **5**; C–O 1.280(10) and 1.249(4) Å for the μ-acyls in **2b** and **5**, 1.201(5) Å for the σ-acyl in **5**], suggesting a contribution from a carbene form [Ru=C(Ar)–O⁻ *cf.* Ru–C(Ar)=O] to the bonding.

The presence of the μ-acyl units in **2** and **5** makes it seem plausible that a complex containing a benzoyl ligand of the type found in **2** is an intermediate in the formation of the phthaloyl species **5**. The conditions under which the optimum yields of **4** and **5** are obtained (see above) indicate that at 60 °C this benzoyl undergoes a second CO insertion preferentially, to give **5**, but that at 100 °C C–P bond formation dominates, leading to **4**. This situation is consistent with reversible CO insertion and, in confirmation, heating **5** in toluene at reflux for 1 h regenerated **3** in 60% yield, completing a remarkably efficient Ru$_4$⇌Ru$_3$ restructuring given the complexity of this pair of molecules. The C–P bond formation step is also reversible, in that heating **4** in toluene produces **3** in 20% yield. Formally, complex **4** differs from **5** in being short of 'Ru(CO)$_4$' and this unit is actually ejected on UV photolysis of **5**, giving a 25% yield of **4**. However, treatment of **4** with the 'Ru(CO)$_4$' source [Ru(CO)$_4$(C$_2$H$_4$)] does not regenerate **5**.

We are currently seeking to determine the conditions under which the carbonylated benzyne ligands are removed from the ruthenium complexes as organic molecules. Treatment of **4** and **5** with bromine then water or with hydroxide does result in the destruction of the complexes and the formation of carbonyl-containing organics but so far neither benzoic nor phthalic acid has been unequivocally identified as a product. More promisingly, bubbling hydrogen through a refluxing toluene solution of **5** generates the known complex [Ru$_3$-H$_2$(CO)$_9$(μ$_3$-PPh)]³ in 60% yield, with phthalaldehyde as the likely fate of the phthaloyl ligand.

This work suggests that following the dissociative chemisorption (C–H bond cleavage) of benzene on a metal surface,[4] reaction with CO will generate carbonyl-containing species of the types found in **2** and **5**, as precursors of useful organic molecules.

References

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