

A new binding geometry for an *ortho*-xylylene-linked bis(NHC)cyclophane: a ruthenium(II) complex with a chelating (η^1 -NHC) $_2$: η^6 -arene ligand

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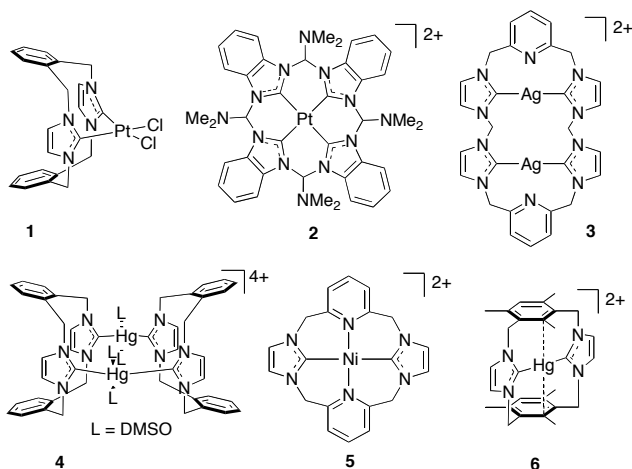
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Using two different reaction procedures, a Ru(II) complex has been isolated that contains an *ortho*-xylylene-linked bis(NHC)cyclophane (NHC = *N*-heterocyclic carbene) that binds to the Ru centre through two carbene carbons and one of the arene rings in a η^6 -mode.

Cyclophanes have been of interest since the studies of Cram and Steinberg in the 1950s.¹ Azolium-cyclophanes are a subset of this class of macrocyclic compounds, containing azolium groups as part of the macrocyclic structure, and have been of interest in more recent times.² Like cyclophanes generally, azolium-cyclophanes have been of interest for diverse reasons, including their synthetic challenges, potential for host-guest chemistry (in particular anion recognition),³ dynamic conformational behaviour,⁴ and, for cyclophanes involving imidazolium- or benzimidazolium-components, their potential to act as precursors to NHC metal complexes.⁵⁻¹⁰

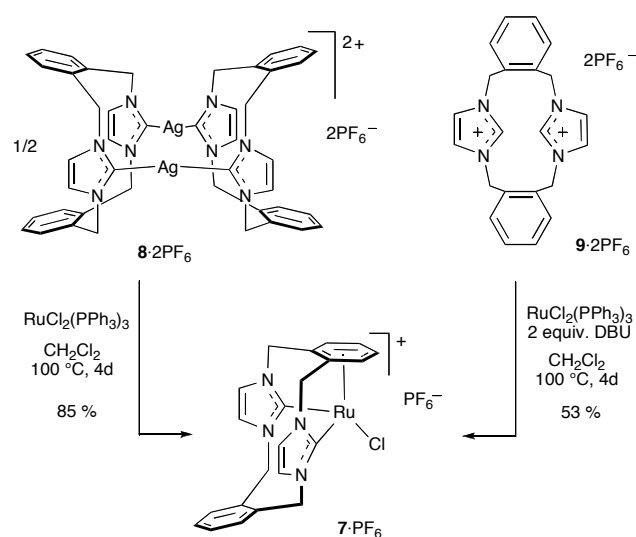


NHC-cyclophane ligands display a broad range of coordination modes. The most common metal binding mode involves coordination *via* only the carbene carbons of the NHC component of the macrocycle. In such cases the cyclophanes can chelate a single metal with two or more NHCs (e.g. **1**⁷ and **2**⁸ respectively) or form dinuclear complexes (e.g. **3**⁹ and **4**¹⁰). In examples where the cyclophane structure consists of *ortho*-xylylene linked NHCs (e.g. **1** and **4**), the xylylene groups are invariably directed away from the metal centre.^{5, 7, 10, 11} The inclusion of additional donor groups in the cyclophane structure can result in binding modes involving the NHCs and the additional

groups (e.g. **5**¹²) and in some cases there are close metal-arene contacts dictated by the cyclophane structure but which are not "bonding" interactions (e.g. **6**¹⁰ and a related Hg complex incorporating a 9,10-bis(imidazolylmethyl)anthracene-based ligand¹³).

Here we report the first case where two NHCs and an arene, which constitute part of a single cyclophane macrocyclic structure, simultaneously bind to one metal centre (Scheme 1).

The ruthenium(II) complex **7**·PF₆ was prepared using two distinct synthetic pathways. The reaction of the silver complex **8**·2PF₆ with RuCl₂(PPh₃)₃ in dichloromethane, with the unusual reaction conditions of heating at 100 °C in a sealed flask, afforded **7**·PF₆ in 85% yield after 4 days (Scheme 1).[‡] Alternatively, the reaction of the imidazolium salt **9**·2PF₆ with RuCl₂(PPh₃)₃ and DBU (1,8-diazabicycloundec-7-ene) in dichloromethane at 100 °C in a sealed flask for 4 days afforded **7**·PF₆ in 53% yield (Scheme 1). Importantly, the complex **7** is not formed if the reaction mixtures are not heated to 100 °C. For example, when a mixture of **8**·2PF₆ and RuCl₂(PPh₃)₃ was heated in dichloromethane at reflux for 6 days, a mixture of unidentified products was obtained, but complex **7** was not present (as indicated by ¹H NMR spectroscopy). "Free carbene" methods commonly used for the synthesis of ruthenium complexes proved unsuccessful for synthesis of **7**. For example, reaction



Scheme 1 Synthesis of **7**·PF₆

of the imidazolium cation **9** with a strong base [NaH/*t*-BuOK(cat.)] followed by the addition of RuCl₂(PPh₃)₃ afforded only complex mixtures of products.

The salt **7**·PF₆ was isolated as a red-brown solid, which precipitated from the reaction mixtures. The hexafluorophosphate salt is soluble in polar organic solvents such as acetonitrile, DMSO and DMF but does not appreciably dissolve in lower polarity organic solvents such as dichloromethane, THF or benzene. A by-product from the silver-transfer reaction, AgCl(PPh₃)₃, was isolated as crystals from the filtrate.[‡] It is common in silver-NHC transfer reactions for the silver halide by-product to precipitate from the reaction mixture, leaving the desired complex in solution. Advantageously in our case, the free triphenylphosphine generated as the reaction proceeds, coordinates to the AgCl forming the soluble by-product AgCl(PPh₃)₃, and allows facile isolation of the insoluble **7**·PF₆ in high purity.

The ¹H and ¹³C NMR spectra of solutions of **7**·PF₆ in *d*₆-DMSO display sharp resonances which are consistent with an *ortho*-xylylene-linked bis(NHC) cyclophane ligand locked in a single conformation.^{5, 7} The signals corresponding to the benzylic protons appear as two pairs of doublets, *i.e.*, two AX patterns. One pair of doublets is due to the *exo* and *endo* benzylic protons of the Ru-bound xylylene group, the other pair to the *exo* and *endo* benzylic protons of the free xylylene group. The signals attributed to the aryl protons on the xylylene groups appear as two AA'XX' patterns; one set is appreciably upfield from the other (δ 6.10 and 6.84 vs 7.36 and 7.75), the upfield shift being consistent with a xylylene ring being π -bound to the ruthenium centre. The ¹H NMR spectra did not change as the sample was heated from room temperature to 125 °C, consistent with the complex remaining rigid (*i.e.*, no exchange process, such as interchange of the π -bound and free xylylene environments) over this temperature range. The ¹³C NMR spectrum displayed a signal at δ 181 which is attributed to the carbene carbon bound to the ruthenium centre.

The solid-state structure of **7**·PF₆ has an asymmetric unit with a single molecule, devoid of crystallographic symmetry. The dimensions, however, conform closely to the requirements of the *quasi*-mirror plane which contains X(3) (the centroid of the ring C(31-36)), Ru, Cl and the bisector of the ligand 'bite' (Fig. 1). The ruthenium atom is essentially four-coordinated by the chlorine atom, the pair of imidazole-carbene donors, and the centroid of one of the bridging xylylene aromatic rings: (χ^2 (C₆ plane) = 58). The other xylylene ring is folded away from the metal atom in an *anti* conformation, with the C₆/C₆ interplanar dihedral angle being 45.70(7)°. Although the parameters of the ruthenium environment are essentially unremarkable, they are very likely influenced by the presence and nature of the ligand which envelops most of the coordination sphere. Notable features are as follows: (a) The chlorine atom is contacted by a pair of benzylic hydrogen atoms (Fig. 1). (b) The η^6 -bound xylylene ring is appreciably canted by virtue of one edge being tethered by the pair of imidazole rings, the difference between Ru-C associated with that edge and its opposite being 0.2₃ Å (Fig. 1). This constraint is reflected further in (c) the angles at the

benzylic carbon atoms, those 'within' the tridentate ligand at C(2,3) being 106.3(2)° (x2), those 'without' (at C(1,4)) being 112.7(2), 111.4(2)°. Further, (d), very considerable asymmetries are found in the exocyclic angles at the coordinated carbene atoms, Ru-C-N 'within' the ligand being 115.7(1), 115.4(1)°, *cf.* those 'without' 140.0(2)° (x2). Despite this suggestion of considerable strain, the ruthenium atom lies closely coplanar with the C₃N₂ imidazole planes (δ Ru 0.018(4), 0.031(4) Å). Close Cl...H intermolecular contacts are found, one to a (coordinated) xylylene ring hydrogen (Cl...H(35)(2-x, 1-y, 1-z) 2.7₃ Å) and one to an imidazole hydrogen (Cl...H(44)(x, 1/2-y, z-1/2) 2.6₄ Å).

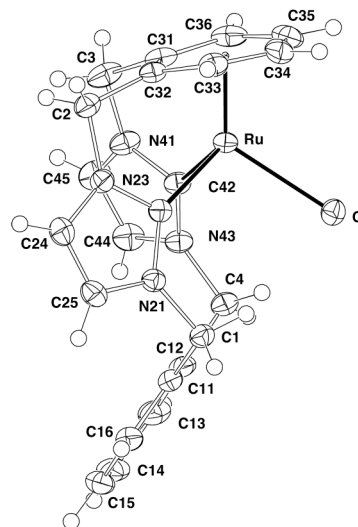
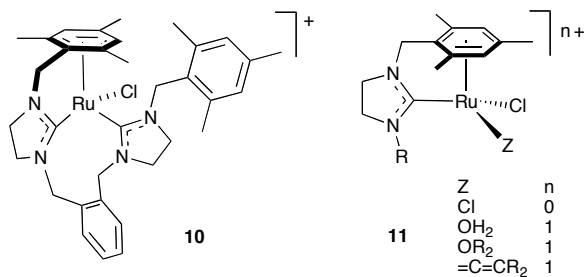


Fig. 1 Projection of the cation **7**. 50% probability amplitude displacement ellipsoids; hydrogen atoms have an arbitrary radius of 0.1 Å. Selected bond distances (Å) and angles (°): Ru-C(31) 2.091(2), Ru-C(32) 2.094(2), Ru-C(33) 2.274(2), Ru-C(34) 2.330(2), Ru-C(35) 2.333(2), Ru-C(36) 2.271(2), Ru-X(3) 1.666 [X(3) is the centroid of the ring C(31-36)], Ru-Cl 2.4304(5), Ru-C(22) 2.038(2), Ru-C(42) 2.034(2), X(3)-Ru-Cl 122.7, X(3)-Ru-C(22) 122.8, X(3)-Ru-C(42) 122.9, Cl-Ru-C(22) 99.71(6), Cl-Ru-C(42) 99.27(6), C(22)-Ru-C(42) 82.56(8), Cl...H(1B) 2.5₇, Cl...H(4A) 2.5₆, H(2B)...H(3A) 2.0₄.

The structure of **7** represents a unique binding mode for NHC-linked cyclophanes bound to any type of metal. Amongst the ruthenium literature the chelating (η^1 -NHC)₂: η^6 -arene binding mode is a rare structure, the only other example having been reported recently (**10**·PF₆).¹⁴ In the case of **10**·PF₆ the chelating (η^1 -NHC)₂: η^6 -arene motif involves a "terminal" arene of the ligand and not the xylylene ring that bridges the two NHC ligands, as in the case of **7**·PF₆. Presumably, coordination of the terminal mesityl arene is favoured over coordination of the bridging xylylene ring in the case of **10**, as coordination of the xylylene group would impose considerable strain in the complex (*cf.* **7**). There are a small number of examples of ruthenium complexes in the literature with a chelating η^1 -NHC: η^6 -arene motif (*e.g.* **11**).¹⁵

The unique structure exemplified by **7** promises some interesting chemistry. We are currently investigating the properties of **7** and related cyclophane-NHC complexes of Ru, such as their ligand exchange reactions, catalytic activity (*e.g.* in hydrogenation), and biological activity.



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Notes and references

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† Electronic Supplementary Information (ESI) available: For crystallographic data in CIF format see DOI: 10.1039/b000000x/

‡ Selected experimental, spectroscopic data, and crystallographic data: 7-PF₆ Method A: In a nitrogen-filled drybox, a solution of RuCl₂(PPh₃)₃ (83 mg, 87 mmol) in dichloromethane (3 mL) was added to a suspension of the silver complex 8-2PF₆⁺ (55 mg, 43 mmol) in dichloromethane (5 mL). The mixture was sealed in a thick-walled flask fitted with a Youngs tap and heated at 100 °C for 4 d. The resulting red brown solid was collected, washed with diethyl ether (2 x 5 mL), dichloromethane (2 x 5 mL) and dried under vacuum. Yield 45 mg, 85%. Colourless crystals deposited from the filtrate were shown by an X-ray study to be [ClAg(PPh₃)₃]-2CH₂Cl₂ (to be discussed elsewhere; CCDC 730740).

7-PF₆ Method B: In a nitrogen-filled drybox, 1,8-diazabicycloundec-7-ene (DBU, 15 μL, 100 mmol) was added to a suspension of imidazolium cyclophane salt 9-2PF₆⁺ (25 mg, 40 mmol) and RuCl₂(PPh₃)₃ (38 mg, 40 mmol) in dichloromethane (8 mL). The mixture was sealed in a thick-walled flask fitted with a Youngs tap and heated at 100 °C for 4 d. A red solution with red brown solid resulted. The red brown solid was collected, washed with diethyl ether (2 x 5 mL), dichloromethane (2 x 5 mL) and dried under vacuum. Yield 13 mg, 53%.

Analytically pure samples of 7-PF₆ and crystals suitable for X-ray diffraction studies were obtained by diffusion of vapours between neat benzene and a solution of the complex in acetonitrile. δ_{H} (500.1 MHz; *d*₆-DMSO) 4.52 (2H, d, *J* = 14 Hz, 2 x benzylic CHH), 4.83 (2H, d, *J* = 14 Hz, 2 x benzylic CH'H'), 5.15 (2H, d, *J* = 14 Hz, 2 x benzylic CHH), 6.09-6.11 (2H, AA' part of AA'XX' pattern, 2 x Ar CH, Ru bound Ar), 6.58 (2H, d, *J* = 14 Hz, benzylic CH'H'), 6.83-6.85 (2H, XX' part of AA'XX' pattern, 2 x Ar CH, Ru bound Ar), 7.35-7.36 (2H, AA' part of AA'XX' pattern, 2 x Ar H), 7.44 (2H, d, *J* = 2 Hz, 2 x imidazolyl H4 or H5), 7.54 (2H, d, *J* = 2 Hz, 2 x imidazolyl H5 or H4), 7.74-7.76 (2H, XX' part of AA'XX' pattern, 2 x Ar H); δ_{C} (125.8 MHz; *d*₆-DMSO) 48.4 (CH₂), 49.0 (CH₂), 122.1 (imidazolyl C4' or C5'), 122.4 (imidazolyl C4' or C4'), 100.8 (Ar CH), 102.5 (Ar CH), 129.2 (Ar CH), 132.0 (Ar CH), 136.2 (Ar C), 166.2 (Ar C) and 181.0 (C-Ru); (Found: C, 43.42; H, 3.68; N, 9.31. Calc. for C₂₂H₂₀N₄RuClPF₆·0.5(CH₃CN)·0.1(C₆H₆): C, 43.59; H, 3.43; N, 9.69%).

Crystal data for data 7-PF₆ C₂₂H₂₀ClN₄RuPF₆, *M* = 621.9. Monoclinic, space group *P*2₁/*c* (*C*_{2h}⁵, No. 14), *a* = 10.9815(6), *b* = 13.6028(8), *c* = 15.4744(9) Å, β = 95.016(1)°, *V* = 2302.7(2) Å³. *D*_c (*Z* = 4) = 1.794 g cm⁻³. CCDC 729839. Full sphere of 'low'-temperature CCD area-detector diffractometer data was measured (ω -scans, $2\theta_{\text{max}} = 58^\circ$; monochromatic Mo K α radiation, $\lambda = 0.71073$ Å; *T* ca. 170 K) yielding 17962 reflections, these merging to 5735 unique (*R*_{int} = 0.020) after 'empirical'/multiscan absorption correction ($\mu_{\text{Mo}} = 0.94$ mm⁻¹, specimen: 0.15 x 0.15 x 0.012 mm, *T*_{min,max} = 0.90) which were used in the full matrix least squares refinement on *F*², refining anisotropic displacement parameters for the non-hydrogen atoms, hydrogen atom treatment following a riding model (reflection weights: $(\sigma^2(F_o^2) + (0.0336P)^2 + 2.33P)^{-1}$ ($P = (F_o^2 + 2F_c^2)/3$)). 5150 reflections with *I* > 2σ(*I*) were considered 'observed'. *R*1 = 0.029, *wR*2 = 0.072. Neutral atom complex scattering factors were employed within the SHELXL 97 program.¹⁷

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