C–H Activation of a Coordinated Thiacyclophane: Cyclometallation of 2,11-Dithia[3.3]orthocyclophane by Ruthenium(II)

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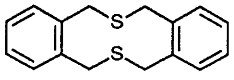
Reaction of (η^6-benzene)ruthenium(II)tris(acetone) solvate with 2,11-dithia[3.3]orthocyclophane leads to coordination of the sulphur donors and deprotonation of a methylene carbon to give the cyclometallated complex $[(\eta^6\text{-}C_6H_6)Ru(o\text{-}C_6H_4CHSCH_2\text{-}o\text{-}C_6H_4CH_2SCH_2)]^+$; an X-ray study shows that cyclometallation occurs at one of two sites in the complex and leads to the formation of a strained three-membered C–Ru–S ring.

The transannular interactions due to the forced proximity of two π systems and the subsequent influence on the chemical and physical properties of cyclophanes has been the subject of much interest for some time.[1] By comparison, the ligating properties of cyclophanes have received relatively little attention. Coordination may occur *via* the aromatic rings of the cyclophane[2] or alternatively it may occur *via* donor atoms included in the cyclophane bridges or in the aromatic rings (*e.g.* pyridinophanes).[3] We report here the C–H activation and subsequent cyclometallation of methylene groups α to the sulphur donors of a thiacyclophane coordinated to an η^6-arene–ruthenium(II) moiety.

$[(\eta^6\text{-}C_6H_6)Ru(o\text{-}C_6H_4CHSCH_2\text{-}o\text{-}C_6H_4CH_2SCH_2)]BF_4$ **1** was prepared by refluxing (η^6-benzene)ruthenium(II)tris(acetone) solvate[4] with 0.75 equiv. of 2,11-dithia[3.3]orthocyclophane[5,6] **2** in acetone under dry N_2 for 4 h. Removal of the solvent followed by recrystallisation from nitromethane–diethyl ether gave orange air-stable crystals of **1**; yield 80% (based on **2**). The same reaction carried out with the selenium analogue of **2**[7] does not give a cyclometallated product. Instead, a compound which analyses as having two selenacyclophanes per (η^6-benzene)ruthenium(II) unit was isolated; yield 75% (based on the selenacyclophane).

Coordination of **2** is *via* the sulphur atoms and a bridge carbon to form a monomeric cation and not *via* the π-ring system as has been reported for non-derivatised cyclophanes.[2] Analytical and NMR data are consistent with this formulation of the complex.† Correlation of proton signals with carbon signals was achieved using a HETCOR experiment, while a DEPT experiment confirmed the presence of a tertiary carbon. Each methylene group has non-equivalent protons giving three AB systems. The axial protons of C(1) and C(2)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† Satisfactory elemental analyses were obtained. m.p. 176 °C (decomp.). **1** is a 1 : 1 electrolyte in $MeNO_2$; $\Lambda = 105\ \Omega^{-1}\ cm^2\ mol^{-1}$. *Spectroscopic data*: HECTOR data, numbering scheme as for X-ray structure. Ha denotes axial, Hb equatorial methylene protons δ (CD_3NO_2) $C(2)H_2$ [Ha: 2.42, d, 1H; Hb: 3.46, d, 1H; $^2J_{HaHb}$ 13.5 Hz; C(2) 23.78], $C(1)H_2$ [Ha: 3.07, d, 1H; Hb: 3.77, d, 1H; $^2J_{HaHb}$ 12.0 Hz; C(1): 30.28], $C(3)H_2$ [Ha: 3.93, d, 1H; Hb: 4.00, d, 1H; $^2J_{HaHb}$ 15.0 Hz; C(2): 36.77], C(4)H [6.12, s, 1H; C(4) 49.33] η^6-C_6H_6 (5.66, s, 6H; C_6 84.81), ^{13}C resonances for C(1), C(2) and C(3) differentiated by comparison with the spectra of related non-cyclometallated derivatives.[8]

(Fig. 1) protrude into the shielding region of the opposite benzene ring, while the axial proton of C(3) is affected by the shielding region of the π-arene. The lower frequency doublets from each AB system are, therefore, assigned to the more shielded axial protons.[9]

The X-ray crystal structure‡ of **1** confirms sulphur coordination and cyclometallation of a carbon α to one of the sulphurs (Fig. 1). The Ru–C–S three-membered ring that results is highly strained with C–Ru–S 44.3(2)°.[11] The strain in this ring reflects not only the coordination of the sulphur and the adjacent carbon to the metal but also the short C–S distance of 1.698(2) Å between these donors. The short distance indicates an increased C–S bond order. Similar short C–S distances are found in other compounds containing a negatively charged carbon adjacent to an electropositive sulphur, for example in α-sulphonyl carbanions.[12] The arrangement about both S atoms and the cyclometallated C atom deviates considerably from tetrahedral: bond angles range from 61.9(1) to 124.7(3)°. The coordinated thiacyclophane adopts a distorted *anti* conformation in which the benzene rings are 130.6° to each other and fold away from the sulphurs. This is in contrast to an *anti* configuration with the benzene rings essentially parallel proposed for **2** in solution[6,9] and found in the solid state.[9] Molecular mechanical calculations[6,9] indicate, that of three *anti* conformations considered plausible for **2**, the *anti* conformation adopted in the complex is the least favoured in solution. That **2** is able to function as an effective ligand is a consequence of the relatively low barrier to conformational rearrangement[6,9] and the large ring size, which provides sufficient steric flexibility to allow the donor atoms to be accommodated in the coordination sphere of the metal cation.

Compound **1** is disordered (Fig. 1) as a result of the almost equal likelihood of cyclometallation having occurred with either of the methylene carbons, C(3) or C(4), attached to the same benzene ring. Of these two methylene carbon atoms, the one not cyclometallated is approximately the same distance from the Ru [3.232(2) Å] as the methylene carbons on the other ring [3.432(2), 3.245(2) Å]. It is, therefore, very unlikely that any process exists that would allow the interchange of the cyclometallated carbon. Further, variable temperature ^{1}H NMR experiments show no change in the spectra at ⩽84 °C. The presence of this disorder may provide some insight into the mechanism of the C–H activation. CPK models show that the axial H on either C(3) or C(4) can point towards the Ru upon bidentate coordination of **2** *via* the thioether linkages, suggesting a multicentred pathway involving Ru and either H would be possible.[13] In this proposed transition state, the Ru is still coordinatively unsaturated. The reaction would then proceed *via* deprotonation at the α-methylene carbon centre, followed by Ru–C bond formation, to give six coordination.

The cyclometallation can be reversed by the treatment of **1**, in an ethanol–CH_3NO_2 (1 : 1) mixture, with HCl. The product formed is [(η^6-C_6H_6)Ru(*o*-$C_6H_4CH_2SCH_2$-*o*-$C_6H_4CH_2SCH_2$)-Cl]Cl and it is not possible to remove the coordinated Cl from this product and attempt to remake **1**.[8]

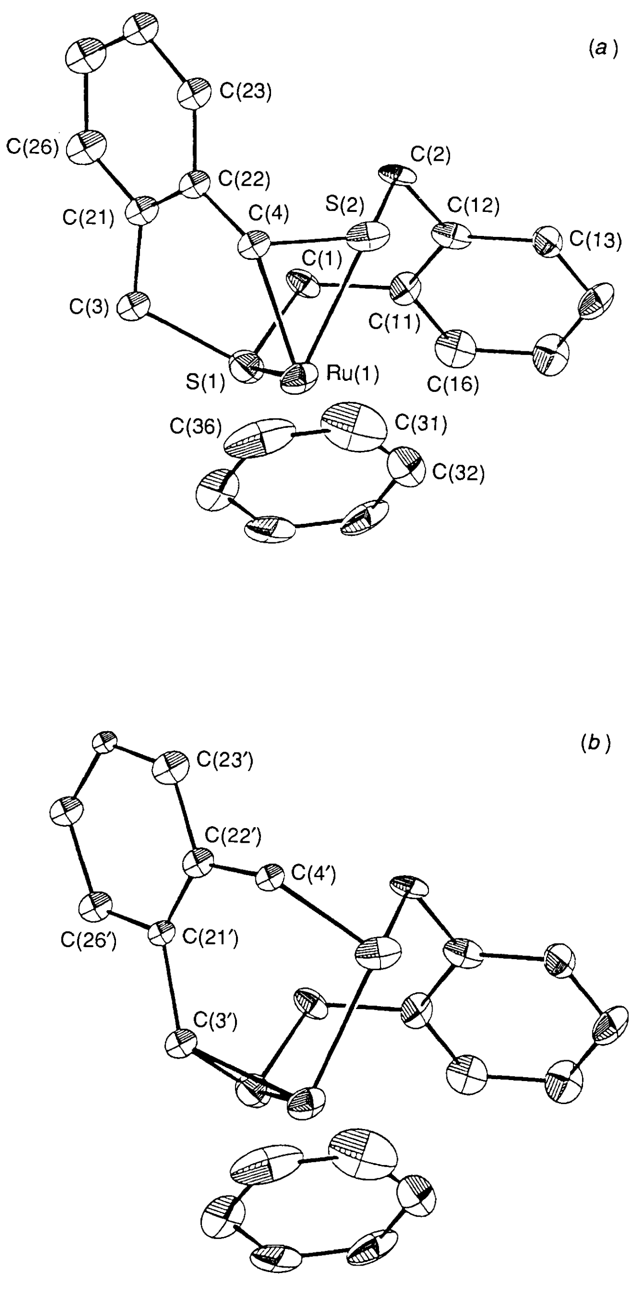

Fig. 1 ORTEP view of **1** [site occupancy factor for (*a*) is 0.58(2)]. Thermal ellipsoids are drawn at the 50% probability level. H atoms and anion omitted. Selected distances (Å) and angles (°) [values are given for (*a*) but those for (*b*) are similar]: Average Ru(1)–C(arene), 2.21(2); Ru(1)–C(4), 2.143(1); Ru(1)–S(1), 2.331(2); Ru(1)–S(2), 2.333(2); S(2)–C(4), 1.698(2); S(1)–C(3), 1.888(2); S(2)–C(2), 1.827(7); C(4)–Ru(1)–S(2), 44.3(1); Ru(1)–S(2)–C(4), 61.9(1); Ru(1)–S(2)–C(2), 116.4(2); C(4)–S(2)–C(2), 113.7(3); Ru(1)–S(1)–C(3), 100.2(1); S(1)–Ru(1)–S(2), 101.3(1); S(2)–C(4)–C(22), 115.3(4); S(1)–C(3)–C(21), 115.5(4).

Activation of a C–H bond, α to a thioether coordinated to a transition metal centre is uncommon, although it has been reported previously.[14] However, the present example, which results in M–C bond formation, and the presence of very strained coordination is unique. Further investigations of the chemistry involving thia- and selena-cyclophane systems with the η^6-arene–ruthenium(II) moiety and other metals are now in progress.

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‡ *Crystal data* for [$C_{22}H_{21}S_2Ru$]BF_4: monoclinic $P2_1/c$, a = 12.188(4) Å, b = 13.374(3) Å, c = 13.891(3) Å, β = 115.29(2)°, V = 2047.3(8) Å^3, Z = 4, T = 153 K, D_m = 1.70(5) g cm^{-3}, D_c = 1.74 g cm^{-3}, size 0.22 × 0.18 × 0.33 mm, μ(Mo-Kα) = 9.92 cm^{-1}, 2θ limits 4–50°, 200 variables refined with 2173 unique data ($I > I\sigma$) (Nicolet P3 diffractometer) to R = 0.0635 and R_w = 0.0492. The structure was solved using SHELXS-86[10] and refined using SHELX-76.[10] All benzene rings were constrained to be regular hexagons with bond lengths fixed at 1.395 Å. With the exception of disordered atoms, all non-H atoms were refined anisotropically. The disorder of ring C(21)–C(26) and the methylene carbons C(3) and C(4) was successfully modelled by allowing two sites for this *o*-xylyl group. The site occupancy factor for this group was refined to 0.58(2). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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