The First Unsubstituted Metallabenzene Complex \([\text{Ru}_2(\eta^5-C_5\text{Me}_5)_2(\eta^2,\eta^5-C_5\text{H}_5)](\text{SiMe}_3)\]

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Treatment of the silyl/methylene complex \([\text{Ru}_2(\eta^5-C_5\text{Me}_5)_2(\mu-\text{CH}_2)](\text{SiMe}_3)\text{Cl}]\) with acetylene gives the first unsubstituted metallabenzene complex \([\text{Ru}_2(\eta^5-C_5\text{Me}_5)_2(\eta^2,\eta^5-C_5\text{H}_5)](\text{SiMe}_3)\text{]}\), which has been characterised by NMR spectroscopy and X-ray crystallography.

The synthesis and reactivity of metallacycles have been areas of intense research due in part to the role of such compounds in many catalytic reactions.\(^1\) Metallabenzene (or metallacyclohexatriene) rings are some of the most interesting metallacycles of the transition elements because they have been implicated as intermediates en route to a variety of cyclopentadienyl complexes\(^2^-^4\) and similar structures have been implicated as intermediates in alkyn oligomerization processes.\(^5^-^7\)

Equally interesting is the question of whether such metallabenzenes exhibit aromatic properties.\(^8\) Stable sulfide- or thiol-substituted osmabenzene complexes have been obtained via a cyclization reaction from two molecules of acetylene and an osmium–thiocarbonyl complex.\(^9^-^10\) A dimethyl substituted molybdabenzene complex \([\text{Mo}_2(2,4-C_7\text{H}_9)(\text{C}_2\text{H}_4)](\text{CO})_3]\)\(^11\) and a family of dimethyl substituted iridabenzene complexes have been prepared by α-H abstraction from the two terminal carbon centres of 2,4-dimethylpentadienyl groups.\(^12^-^15\) More recently, a dimethyl substituted ruthenabenzene complex has also been prepared in the same way.\(^16\) We report here the synthesis, single crystal X-ray structure, and \(^1\)H and \(^13\)C NMR spectra of the first unsubstituted metallabenzene complex \([\text{Ru}_2(\eta^2,\eta^5-C_5\text{H}_5)](\text{SiMe}_3)\text]\).

We have recently described the reaction of \(\text{Mg(CH}_2\text{SiMe}_3)_2\) with \([\text{Ru}(\eta^5-C_5\text{Me}_5)_2]\text{Cl}_2,\) in which alkylation of the ruthenium centre is followed by C-Si bond cleavage to give the unusual methylene/silyl complex \([\text{Ru}(\eta^5-C_5\text{Me}_5)_2(\mu-\text{CH}_2)](\text{SiMe}_3)\text{Cl}]\).\(^17\) In the course of exploring the reactivity of this methylene/silyl compound, we have found that treatment of 1 with 1 atm (1 atm = 101325 Pa) of \(\text{HGCH}\) in toluene gives several products,\(^†\) one of which is the result of elimination of HCl and incorporation of 2 equiv. of HCCH. This product has been identified as the unusual metallabenzene complex \([\text{Ru}_2(\eta^2,\eta^5-C_5\text{Me}_5)_2(\eta^2,\eta^5-C_5\text{H}_5)](\text{SiMe}_3)\text]\) (Scheme 1). The \(^1\)H NMR spectrum of 2 exhibits resonances for the ruthenabenzene ortho, meta and para carbons at δ 177.0 (dd, \(j_{1,2}\text{H} 140, j_{3,4}\text{H} 7\) Hz), δ 86.8 (dd, \(j_{1,2}\text{H} 156, j_{3,4}\text{H} 6\) Hz) and δ 83.4 (d, \(j_{1,2}\text{H} 164\) Hz), respectively.

When 1 is treated with DCCD in toluene, the \([\text{HL}]\) isomerism \([\text{Ru}_2(\eta^2,\eta^5-C_5\text{Me}_5)_2(\eta^2,\eta^5-C_5\text{H}_5)](\text{SiMe}_3)\text]\) is obtained. One of the two hydrogen atoms of the bridging methylene group is retained in the product, and \(^1\)H NMR spectroscopy shows that it appears in the ortho position of the ruthenabenzene ring. The absence of hydrogen in the para position of the ruthenabenzene ring strongly suggests that elimination of HCl takes place after the insertion of two acetylene molecules into the Ru–CH2–Ru unit of the methylene/silyl complex.

The ruthenabenzene nature of 2 has been confirmed by a single crystal X-ray structure determination (Fig. 1). The molecule has a symmetry plane that passes through Ru(1), Ru(2), and the centres of all the ligands. The two ruthenium centres are connected by a single Ru–Ru bond with Ru(1)–Ru(2) = 2.58 Å, Ru(1)–C(1) = 1.75 Å, Ru(2)–C(2) = 1.79 Å, C(1)–C(2) = 1.39 Å, and C(3)–C(4) = 1.34 Å. The bond lengths and angles are consistent with those of other metallabenzene complexes.

\(^†\) Along with the ruthenabenzene complex 2, we have isolated and characterised \([\text{Ru}_2(\eta^2,\eta^5-C_5\text{Me}_5)_2(\eta^2,\eta^5-C_5\text{H}_5)](\text{SiMe}_3)\text{Cl}]\) and \([\text{Ru}[\eta^5-C_5\text{Me}_5](\eta^5-C_5\text{H}_5)](\text{SiMe}_3)\text{]}\) from the reaction.
The ORTEP diagram of the molecular structure of \([\text{Ru}_2(\eta^5-\text{CSMe}_5)\eta^5-\text{CSH}_5(\text{SiMe}_3)]\) \(2\). The 35\% probability density surfaces are shown.

Ru(2) 2.898 (1) Å; alternatively, \(2\) can be formulated as a zwitterionic species with a dative metal–metal bond to achieve 18-electron counts on both ruthenium centres. One of the ruthenium centres, Ru(1), is bonded to a \(\eta^5\)-CSMe\(_5\) group, \(\sigma\)-bonded to the SiMe\(_3\) group [Ru(1)-Si 2.426(1) Å], and forms the sixth vertex of the metallabenzene ring; the two sigma Ru(1)-C distances of 1.970(3) Å to the metallabenzene ring are shorter than expected for a single bond and suggest that there is partial metal-carbon \(\pi\)-bonding. Ru(2) is bound to the other \(\eta^5\)-CSMe\(_5\) group and is \(\pi\)-bonded to the RuC\(_5\)H\(_5\) ring; the Ru(2)-C distances to the metallabenzene ring are 2.290(3), 2.175(3) and 2.134(4) Å to the ortho, meta and para carbon atoms, respectively. Like previously known substituted metallabenzene complexes, the C(ortho)-C(meta) and C(meta)-C(para) bond distances of 1.417(3) and 1.406(4) Å in the RuC\(_5\)H\(_5\) ring are essentially equal, and are consistent with a completely delocalised structure. Owing presumably to the constraints of the Ru-Ru bond, the RuC\(_5\)H\(_5\) ring is not exactly planar: Ru(1) is 0.32 Å out of the C\(_5\)H\(_5\) plane and the dihedral angle between the C(ortho)-Ru(1)-C(ortho) unit and the C\(_5\)H\(_5\) fragment is 12.9°.

The present molecule adds to the small number of known metallabenzene complexes, and its isolation, \(\text{via}\) the reaction of an alkylidene ligand with two equiv. of an alkyne, represents a new synthetic route to such complexes. The reactivity of this first unsubstituted metallabenzene complex is of interest: so far, the molecule appears remarkably robust and does not react with Lewis bases such as PMe\(_3\). Further studies of the reactivity of \(2\) are underway.

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References