

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

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

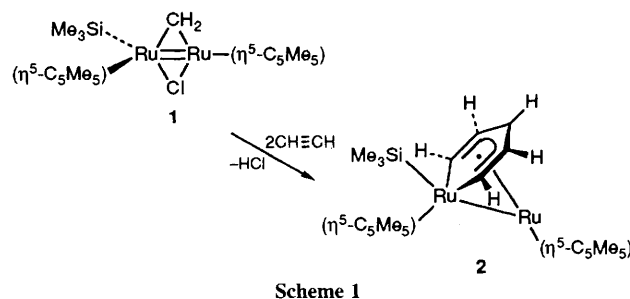
The synthesis and reactivity of metallacycles have been areas of intense research due in part to the role of such compounds in many catalytic reactions.¹ Metallabenzene (or metallacyclohexatriene) rings are some of the most interesting metallacycles of the transition elements because they have been implicated as intermediates *en route* to a variety of cyclopentadienyl complexes²⁻⁴ and similar structures have been implicated as intermediates in alkyne 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 $[\text{Mo}_2(2,4\text{-C}_7\text{H}_{11})(2,4\text{-C}_7\text{H}_9)(\text{CO})_5]$ 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 ¹H and ¹³C NMR spectra of the first unsubstituted metallabenzene complex $[\text{Ru}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\eta^2,\eta^5\text{-C}_5\text{H}_5)(\text{SiMe}_3)]$.

We have recently described the reaction of $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ with $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}]_4$, in which alkylation of the ruthenium centre is followed by C-Si bond cleavage to give the unusual methylene/silyl complex $[\text{Ru}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-CH}_2)(\text{SiMe}_3)\text{Cl}]$ **1**.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 $\text{HC}\equiv\text{CH}$ 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 $[\text{Ru}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\eta^2,\eta^5\text{-C}_5\text{H}_5)(\text{SiMe}_3)]$ **2** (Scheme 1). The ¹H NMR spectrum of **2** exhibits resonances for the ruthenabenzene ring protons at δ 9.75 (dd, ³*J*_{HH} 6.0, ⁴*J*_{HH} 1.0 Hz), δ 4.94 (dd, ³*J*_{HH} 7.0, ³*J*_{HH} 6.0 Hz) and δ 4.32 (tt, ³*J*_{HH} 7.0, ⁴*J*_{HH} 1.0 Hz), which can be assigned to the *ortho*, *meta* and *para* protons, respectively. The ¹³C NMR spectrum shows resonances for

the ruthenabenzene *ortho*, *meta* and *para* carbons at δ 177.0 (dd, ¹*J*_{CH} 140, ²*J*_{CH} 7 Hz), δ 86.8 (dd, ¹*J*_{CH} 156, ²*J*_{CH} 6 Hz) and δ 83.4 (d, ¹*J*_{CH} 164 Hz), respectively.

When **1** is treated with DCCD in toluene, the [²H₄] isotopomer $[\text{Ru}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\eta^2,\eta^5\text{-C}_5\text{HD}_4)(\text{SiMe}_3)]$ is obtained. One of the two hydrogen atoms of the bridging methylene group is retained in the product, and ¹H 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 of the ligands. The two ruthenium centres are connected by a single Ru-Ru bond with Ru(1)-



[‡] Crystal data for $\text{C}_{28}\text{H}_{44}\text{Ru}_2\text{Si}$ [-75°C , Enraf-Nonius CAD4]: orthorhombic, space group *Pnma*, with $a = 21.973(7)$, $b = 13.676(4)$, $c = 8.888(4)$ Å, $U = 2671(2)$ Å³, $Z = 4$, $D_c = 1.519$ g cm⁻³, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 11.67$ cm⁻¹, $R_F = 0.023$, $R_wF = 0.027$ for 247 variables and 2350 data with $I > 2.58 \sigma(I)$. The data were corrected for Lorentz and polarization effects, absorption, and secondary extinction; the structure was solved by direct-methods (SHELX-86). All non-hydrogen atoms were refined anisotropically; hydrogen atom positions were refined with independent isotropic thermal coefficients. 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.

[†] Along with the ruthenabenzene complex **2**, we have isolated and characterised $[\text{Ru}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\eta^2,\eta^4\text{-C}_4\text{H}_4)\text{Cl}_2]$ ¹⁸ and $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\eta^6\text{-C}_6\text{H}_6)\text{Cl}]$ ¹⁹ from the reaction.

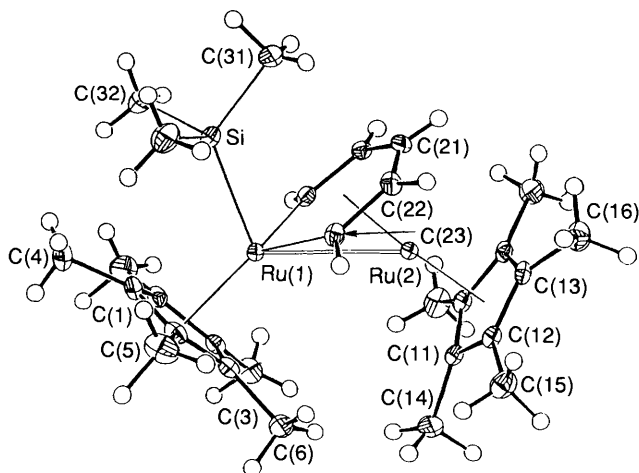


Fig. 1 ORTEP diagram of the molecular structure of $[\text{Ru}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\eta^2,\eta^5\text{-C}_5\text{H}_5)(\text{SiMe}_3)]$ **2**. The 35% probability density surfaces are shown.

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 ($\eta^5\text{-C}_5\text{Me}_5$) group, σ -bonded to the SiMe_3 group [$\text{Ru}(1)\text{-Si}$ 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 π -bonding. Ru(2) is bound to the other ($\eta^5\text{-C}_5\text{Me}_5$) group and is π -bonded to the RuC_5H_5 ruthenabenzene 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,^{11–15} the C(*ortho*)–C(*meta*) and C(*meta*)–C(*para*) bond distances of 1.417(3) and 1.406(4) Å in the RuC_5H_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_5H_5 ring is not exactly planar: Ru(1) is 0.32 Å out of the C_5H_5 plane and the dihedral angle between the C(*ortho*)–Ru(1)–C(*ortho*) unit and the C_5H_5 fragment is 12.9°.

The present molecule adds to the small number of known metallabenzene complexes, and its isolation, *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.

We thank the National Science Foundation (Grant CHE 89-21757) for support of this work, and Teresa Prussak-Wieckowska for assistance with the X-ray crystallographic determination. W. L. acknowledges receipt of a University of Illinois Department of Chemistry Fellowship and G. S. G. acknowledges receipt of a Camille and Henry Dreyfus Teacher–Scholar Award and an A. P. Sloan Foundation Research Fellowship.

Received, 29th September 1992; Com. 2/05238E

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