

Ruthenium–Arene Complexes and Clusters *via* Ultrasound

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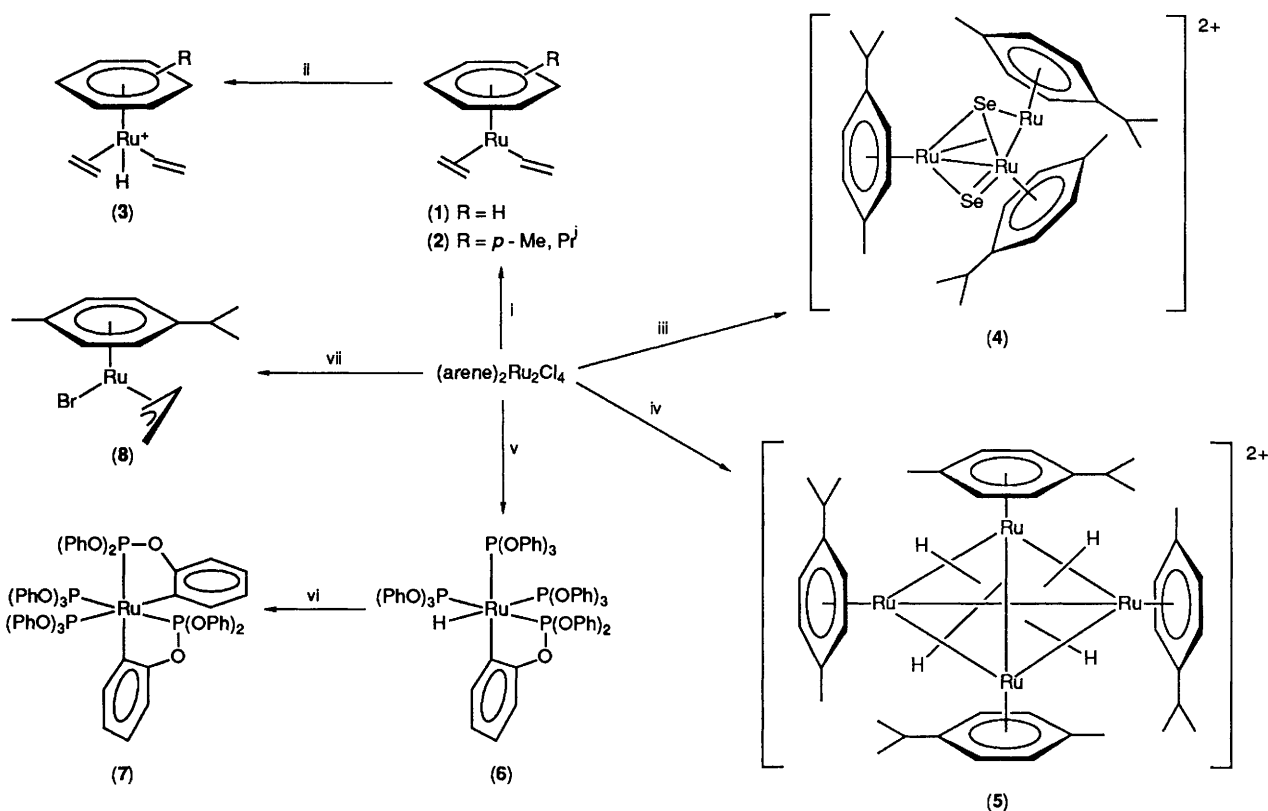
Low-temperature high-power ultrasound provides a versatile method for carrying out heterogeneous reductions allowing the synthesis of new compounds such as $[(C_6H_6)Ru(C_2H_4)_2]$ and $[(cymene)_3Ru_3Se_2]^{2+}$ and new syntheses of known compounds such as $[(cymene)_4Ru_4H_4]^{2+}$

The chemistry of arene–ruthenium compounds is rich and varied¹ in large part owing to the ready accessibility of the $Ru^{II/0}$ redox couple. This makes the class of compound fertile ground for homogeneous catalytic applications. One of the major shortcomings of the chemistry however lies in the difficulty of carrying out mild reduction reactions. The problem lies in finding reagents that will carry out the required electron transfer processes without reacting with the relatively fragile reduction products.

We have been examining the use of ultrasound for carrying out organometallic reactions and in particular have been examining reactions in which novel products, unobtainable by

conventional thermal or photochemical methods, may be made.² We now report that ultrasound is particularly suitable for the heterogeneous reduction reactions required to produce a range of new ruthenium–arene complexes, both mononuclear and polynuclear, as well as providing convenient access to known complexes. The ultrasonic conditions seem to be particularly appropriate for making the more reactive, and hence interesting, members of a series of complexes when thermal methods can be used to generate the more robust complexes.

Ultrasound creates reaction conditions that are different from conventional thermal or photochemical reactions.³ In



Scheme 1. R = C₆H₆ or *p*-MeC₆H₄CHMe₂. *Reagents and conditions:* i, Zn, ultrasound, 263 K, CH₂Cl₂, C₂H₄ (2 atm), 4 h; ii, CF₃CO₂H, 193 K, CD₂Cl₂; iii, Zn, ultrasound, 263 K, Se, CH₂Cl₂; iv, Zn, ultrasound, 263 K, CH₂Cl₂, H₂ (2 atm); v, Zn, ultrasound, 273 K, thf, then P(OPh)₃, 273 K; vi, 293 K, CH₂Cl₂; vii, Zn, ultrasound, 273 K, thf, then allyl bromide, 293 K.

particular, cavitation collapse adjacent to a surface provides a mechanical abrading and mixing that is particularly useful when heterogeneous conditions are necessary. Additionally, the severity of the cavitation collapse increases with decreasing temperature. The two factors combine to make reduction reactions at low temperatures particularly favourable.

When [(C₆H₆)₂Ru₂Cl₄] is placed in CH₂Cl₂ with zinc dust under an atmosphere of ethylene (2 bar) and subjected to ultrasound[†] at -10 °C (Scheme 1) the product, [(C₆H₆)Ru(C₂H₄)₂] (1),[‡] may be isolated in 50% yield as white sublimable crystals that are moderately air stable. The

related complex containing the cymene ligand (2) can be made using exactly the same approach in similar yield, indicating the generality of the reaction for alkyl-substituted benzene-containing complexes. This compares with the more conventional synthesis of [(C₆Me₆)Ru(C₂H₄)₂] which is only successful for this (the most stable) member of the series.^{4a}

The complex (1) is an important member of the class of compounds (cyclic polyene)M(ethylene)₂ which have been studied for nearly 30 years.^{4b} The compounds are readily characterised by ¹H NMR spectroscopy. A variable temperature experiment performed on (1) gave no indication of ethylene rotation. This contrasts with the fluxionality involving ethylene rotation that was originally measured for [(C₅H₅)Rh(C₂H₄)₂].⁵ Presumably the increased electron density of the ruthenium system, and consequent increased π-back donation, increases the rotational energy barrier for ruthenium relative to rhodium.

The increased electron density on the ruthenium complex is also reflected in the observation of a metal hydride complex [(C₆H₆)RuH(C₂H₄)₂]⁺ (3) upon protonation of (1).⁶ This makes the ruthenium system directly comparable to [(C₅Me₅)RhH(C₂H₄)(PMe₃)]⁺ and not [(C₅Me₅)Rh(η²-CH₂CH₃)(C₂H₄)₂]⁺ which contains an agostic C-H-M interaction.⁷

In the presence of a better π-accepting ligand such as CO, the ultrasonic reaction leads to arene substitution and Ru(CO)₅ is formed in moderate yield.⁸ Thermal decomposition to Ru₃(CO)₁₂ provides an unusual route to the carbonyl complex that does not require the use of an autoclave.⁹

Cluster-formation reactions are also possible under the ultrasonic conditions. When the zinc reduction reaction is carried out in the presence of selenium, [(cymene)₃Ru₃Se₂]²⁺ (4) may be isolated in 25% yield. The yield is 50% in the

[†] Preparations were carried out using a Vibracell VC500 ultrasonic generator made by Sonics Materials operating at 20 kHz.

[‡] *Spectroscopic data:* (1) ν_{CH} (Nujol mull) 2965 and 2925 cm⁻¹; ¹H NMR δ (CDCl₃), 5.35 (s, 6H, C₆H₆), 2.30 and 0.54 (m, 8H, C₂H₄).

(2) ¹H NMR δ (CDCl₃), 5.03 (m, 4H, MeC₆H₄CHMe₂), 2.39 (sept, 1H, MeC₆H₄CHMe₂), 2.08 (s, 3H, MeC₆H₄CHMe₂), 1.23 (d, 6H, MeC₆H₄CHMe₂), 1.87 and 0.57 (m, 8H, C₂H₄).

(3) ¹H NMR 193 K, δ (CD₂Cl₂), 6.25 (s, 6H, C₆H₆), 3.21, 2.19, 1.61, and 0.63 (m, 8H, C₂H₄), -10.59 (s, 1H, RuH).

(4) ¹H NMR δ (CD₃COCD₃) 6.27 (m, 4H, MeC₆H₄CHMe₂), 2.73 (sept, 1H, MeC₆H₄CHMe₂), 2.49 (s, 3H, MeC₆H₄CHMe₂), 1.43 (d, 6H, MeC₆H₄CHMe₂).

(6) ¹H NMR δ (CDCl₃), 7.5–6.5 (m, 59H, Ph) and -8.42 (m, 1H, RuH); ³¹P{¹H} NMR δ (CDCl₃), δ 162.6, 138.2, 137.4, and 125.8 ppm, *J*_{P-*trans*} 630 Hz, *J*_{P-*cis*} 51, 50, 43 and 41 Hz.

(8) ¹H NMR δ (CDCl₃), 5.28 (m, 4H, MeC₆H₄CHMe₂), 3.90 (m, 1H, CH₂CHCH₂), 3.75 and 2.64 (d, 4H, CH₂CHCH₂), 2.80 (sept, 1H, MeC₆H₄CHMe₂), 2.12 (s, 3H, MeC₆H₄CHMe₂), and 1.33 (d, 6H, MeC₆H₄CHMe₂).

Satisfactory microanalyses have been obtained for all new compounds.

reaction mixture. This cluster is directly comparable to the recently reported sulphur analogue¹⁰ and is also electrochemically active, undergoing two reversible one-electron reduction processes at -0.46 and -0.71 V *versus* the standard calomel electrode (sce).§

Using similar conditions but with an atmosphere of hydrogen (2 bar), a tetranuclear cluster, [(cymene)₄Ru₄H₄]²⁺ (5),¹¹ can be isolated.¶ In this case multiple electron-transfer processes are accessible, and reversible processes occur at -0.42 and -1.09 V *versus* the sce. We are currently investigating this reaction further, because, when the reaction mixture is monitored by ¹H NMR spectroscopy, a number of other hydrido species, that are as yet uncharacterised, can be observed.

We have attempted to explore the fate of the reaction when a poor ligand for the zero-valent ruthenium centre is present. When the reaction is carried out in tetrahydrofuran (thf), an intense purple colour develops in the solution, but no identifiable compound can be detected spectroscopically. However this intermediate can be trapped by a range of substrates.

When the reaction mixture is treated with P(OPh)₃, arene substitution occurs at room temperature leading to formation of moderate yields (30%) of (6). The isolation of this complex is another indication of the mild conditions under which the ultrasonic reaction takes place because conventional amalgam reduction of [RuCl₂{P(OPh)₃}₄] leads to (7)¹² and not (6). The product (6) may be converted quantitatively to (7) by

§ All electrochemical measurements were made using cyclic voltammetry in a solution of 0.1 M NEt₄BF₄ in acetonitrile at room temperature and using ferrocene as an internal calibrant. Reversibility criteria used were those outlined in 'Instrumental Methods in Electrochemistry,' Southampton Electrochemistry Group, Wiley, 1985, p. 185.

¶ The isolated yield of this cluster is currently lower than that of the selenium cluster, and experiments to optimise the yield are being carried out.

simply allowing the reaction mixture to warm to room temperature. Curiously the ruthenium complex (6) is a different isomer from the known osmium complex analogue.¹²

Treatment of the reaction mixture with allyl bromide leads to a simple oxidative addition reaction and the product (8) may be isolated (22% yield) as a red oil. The related benzene complex has been reported.¹³ A ¹H NMR spectral study has demonstrated that the complex exists in CHCl₃ solution with the allyl ligand predominantly in the *endo*-conformation.

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