

The Novel Cyclodimerization of Phenylacetylene at a Ruthenium(II) Centre. The Synthesis and X-Ray Structural Characterization of the First Metallacyclopentatriene, $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_4\text{Ph}_2\text{H}_2)\text{Br}]$, and its Facile Conversion into Metallacyclopentadienes

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Cyclodimerization of two molecules of phenylacetylene at the ruthenium(II) centre in $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\eta\text{-C}_8\text{H}_{12})\text{Br}]$ (C_8H_{12} = cyclo-octa-1,5-diene) gives the novel ruthenacyclopentatriene $[(\eta\text{-C}_4\text{H}_5)\text{Ru}(\text{C}_4\text{Ph}_2\text{H}_2)\text{Br}]$ characterized by ^1H and ^{13}C n.m.r. spectroscopy and by X-ray analysis; the triene undergoes facile 'oxidative addition' with donor ligands L (*e.g.* morpholine, trimethyl phosphite, dimethylphenylphosphine) in a bimolecular reaction involving an associative mode of activation to give the ruthenacyclopentadienes $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{L})(\text{C}_4\text{Ph}_2\text{H}_2)\text{Br}]$.

Mechanistic steps involving the formation of metallacycles, and their interconversions and subsequent decay, are implicated in a number of important catalytic transformations.¹ In particular, it has been shown that the cyclodimerization of two molecules of an alkyne at a transition metal centre leads to metallacyclopentadiene complexes¹⁻³ (1), currently favoured as key intermediates in the catalytic cyclo-oligomerization of

alkynes to aromatic compounds.^{2,3} Herein we report on the novel cyclodimerization of phenylacetylene at the ruthenium(II) centre in $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\eta\text{-C}_8\text{H}_{12})\text{Br}]$ (C_8H_{12} = cyclo-octa-1,5-diene), a reaction which does not lead to a metallacyclopentadiene but rather to the first example of a metallacyclopentatriene (2).

The complex $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\eta\text{-C}_8\text{H}_{12})\text{Br}]$ ⁴ (3) reacts with

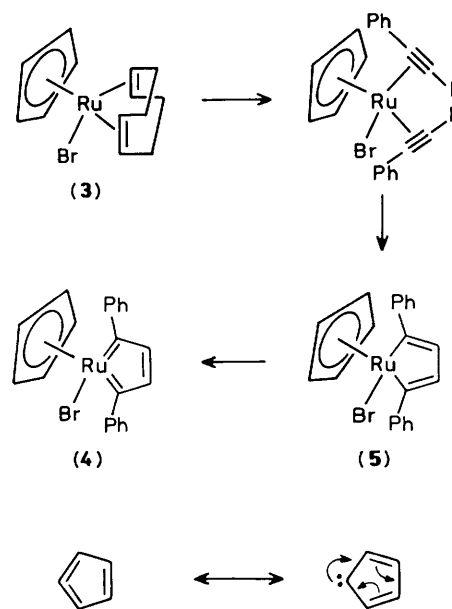


phenylacetylene (mole ratio 1 : 4) in dichloromethane at 0 °C to give a dark green solution. Slow addition of hexane affords green crystals of composition $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_4\text{Ph}_2\text{H}_2)\text{Br}]$ (**4**)[†] (yield 60–70%). In the high-field ^1H n.m.r. spectrum of (**4**) (500.13 MHz, CDCl_3 , 303 K) a sharp singlet is observed for the cyclopentadienyl ligand at δ 5.21. A signal for two magnetically equivalent hydrogen atoms appears at δ 7.82, *downfield* of the phenyl protons which resonate at δ 7.74 (tt, 2H, H_{para}), 7.27 (dd, 4H, H_{ortho}), and 7.19 (m, 4H, H_{meta}). In the $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectrum (125.76 MHz, CDCl_3 , 303 K) a resonance appears at δ 94.5 assignable to the cyclopentadienyl ligand with the expected four resonances for two equivalent phenyl rings appearing at δ 161.7, 128.9, 127.6, and 123.8. Only two further resonances, each accounting for two carbon atoms, are observed, one at δ 156.0 and the other at δ 271.1. The unusual position observed for the two proton resonance downfield of the phenyl proton resonances (suggestive of strong paramagnetic shielding arising from ring current effects in a metallacycle), and the two ^{13}C resonances appearing at δ 156.0 and δ 271.1 (suggestive of metallacycle sp^2 ring carbon atoms⁵ and metal-carbene α -carbon atoms,⁶ respectively) lend support for the formulation of the $\text{C}_4\text{Ph}_2\text{H}_2$ moiety in (**4**) as an unsaturated bis-carbene ligand, and the unit $\{\text{RuC}_4\text{Ph}_2\text{H}_2\}$ as the first example of a metallacyclopentatriene.

The X-ray crystal structure of (**4**) has been determined.[‡] The structure (Figure 1) confirms the cyclo-dimerization of two molecules of phenylacetylene and the formation of a five-membered ruthenacycle with both phenyl substituents in the α -position. The complex has crystallographic mirror symmetry with the ruthenium, bromine, C(23), and H(23) atoms lying in the mirror plane. The $\{\text{RuC}_4\text{Ph}_2\text{H}_2\}$ metallacycle is close to planar, with the ruthenium atom lying only 0.215 Å out of the C_4 plane. The bond lengths within the metallacycle support a largely delocalized metallacyclopentatriene structure; the Ru–C(1) distance of 1.942(6) Å is close to the Ru=C double bond length range of 1.83–1.91 Å observed in previously reported ruthenium-alkylidene complexes,⁷ and is significantly shorter than the Ru–C single bond length range of 2.030(16)–2.117(9) Å reported for ruthenacyclopentadienes.⁸ The C(1)–C(2) and C(2)–C(2') bond lengths of 1.403(8) and 1.377(12) Å also reflect the proposed metallacyclopentatriene structure but meaningful comparisons with ruthenacyclopentadiene complexes⁸ are difficult to make.

[†] A satisfactory elemental analysis was obtained.

[‡] *Crystal data* for (**4**): $\text{C}_{21}\text{H}_{17}\text{BrRu}$, $M = 450.35$, orthorhombic, space group $\text{Cmc}2_1$, $a = 18.264(3)$, $b = 11.806(2)$, $c = 8.028(2)$ Å, $U = 1731.1(10)$ Å³, $Z = 4$, $D_c = 1.728 \text{ Mg m}^{-3}$, $F(000) = 888$, $\mu(\text{Mo-K}\alpha) = 3.070 \text{ mm}^{-1}$, $\lambda = 0.71069$ Å. The structure was solved by heavy atom (Patterson and difference Fourier) methods and was refined by full matrix weighted least squares [$\sum w|\Delta F|^2$ minimized, $w = \sigma^{-2}(F_o)$] with all non-hydrogen atoms anisotropic. All hydrogen atoms were located in a difference map but only H(2) was freely refined. All other hydrogen atoms were fixed in idealized positions ($d_{\text{C-H}} = 0.95$ Å) and separate common isotropic temperature factors were refined for the phenyl and cyclopentadienyl hydrogen atoms. $R = 0.0391$ and $R_w = 0.0306$ for 1061 unique reflections with $F_o \leq 4\sigma(F_o)$ collected at 295 K on an Enraf-Nonius CAD4F diffractometer. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.



Scheme 1

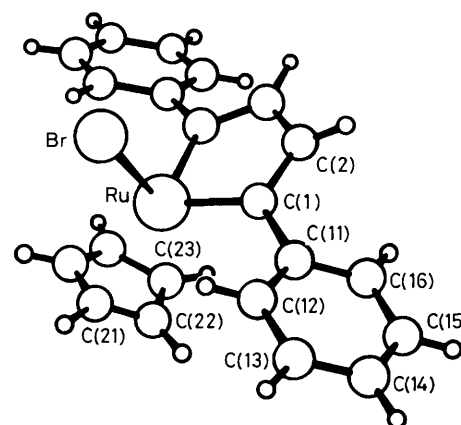
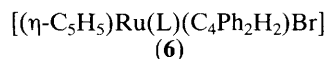


Figure 1. A perspective view of (**4**) showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Ru–Br 2.493(1), Ru–C(1) 1.942(6), Ru–C(21) 2.346(7), Ru–C(22) 2.294(8), Ru–C(23) 2.143(12), C(1)–C(2) 1.403(8), C(2)–C(2') 1.377(12); C(1)–Ru–C(1') 78.7(4), Ru–C(1)–C(2) 117.6(5), C(1)–C(2)–C(2') 112.8(6).

A mechanism to account for the formation of (**4**) is outlined in Scheme 1. Cyclo-octadiene substitution in (**3**) by donor ligands has been established to be a facile process.⁴ Cyclo-dimerization of two molecules of phenylacetylene together with concomitant oxidative addition to the metal atom would be expected, on the basis of numerous precedents,¹ to form initially a co-ordinatively unsaturated 16-electron ruthenium(IV)–metallacyclopentadiene complex (**5**). In interpreting the conversion of (**5**) into the formally 18-electron ruthenium(II)–metallacyclopentatriene (**4**), (**5**) is best likened to cyclopentadienylidene [shown below (**5**); Scheme 1] which could undergo a redistribution of electrons to give cyclopentatriene [below (**4**)]. In a similar manner, participation of a pair of ruthenium-based electrons would give the 'metalla-allene' or metallacyclopentatriene (**4**).

The most important implication of such a relationship between (**4**) and (**5**) is that the provision of a pair of electrons

by a donor ligand to the metal atom in (4) should obviate the need for the triene structure, with a reversion to a metallacyclopentadiene, this time, however, forming the saturated 18-electron complex $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{L})(\text{C}_4\text{Ph}_2\text{H}_2)\text{Br}]$.



Indeed, treatment of (4) with a single molar equivalent of the donor ligands morpholine, trimethyl phosphite, or dimethylphenylphosphine in CDCl_3 (25 °C) rapidly generates species which on the basis of their ^1H and $^{13}\text{C}\{^1\text{H}\}$ n.m.r. characteristics are formulated as the metallacyclopentadiene complexes $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{L})(\text{C}_4\text{Ph}_2\text{H}_2)\text{Br}]$ (6) [$\text{L} = \text{HN}(\text{CH}_2\text{CH}_2)_2\text{O}$, $\text{P}(\text{OMe})_3$, or PMe_2Ph]. In a typical example (6) [$\text{L} = \text{HN}(\text{CH}_2\text{CH}_2)_2\text{O}$],[§] it is the marked upfield shift of the metallacycle protons to δ 7.01, and the appearance of ^{13}C resonances at δ 201.3 and δ 142.3 assignable to C_α and C_β respectively which are the most indicative of the triene into diene conversion.⁵ The conversion (4) \rightarrow (6) represents a novel organometallic transformation and for this reason we have briefly investigated the kinetics of the reaction of (4) with $\text{P}(\text{OMe})_3$ and PMe_2Ph in acetone by u.v.-visible spectrophotometry. The rate law, established under pseudo-first-order conditions, takes the form $-\text{d}[(4)]/\text{d}t = k_{\text{obs}}[(4)]$ where $k_{\text{obs}} = k_1[\text{L}]$. The specific rate constants at 25 °C are $k_1 = 3.8$ and $757 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $\text{L} = \text{P}(\text{OMe})_3$ and PMe_2Ph respectively. The activation parameters associated with k_1 (temperature range 15–35 °C) are $\Delta H^\ddagger = 4.67 [8.24] \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -44.7 [-20.08] \text{ cal K}^{-1} \text{ mol}^{-1}$ (1 cal = 4.184 J), for PMe_2Ph and, in square brackets, $\text{P}(\text{OMe})_3$. The observed second-order kinetics, the large negative values of ΔS^\ddagger , and the marked effect of the nature of the entering nucleophile on the reaction rate constant, strongly favour a bimolecular reaction involving an associative mode of activation. Particularly

noteworthy too are the very low activation enthalpies for the conversion of (4) into (6), consistent with the expectation that this should be a low-energy process.

In conclusion, the results presented here describe a hitherto unanticipated product of the cyclodimerization of two molecules of alkyne at a transition metal centre. The factor which probably most influences the formation of the metallacyclopentatriene rather than the expected metallacyclopentadiene is the unsaturation ensuing at the ruthenium centre following cyclo-octadiene displacement and alkyne cyclo-dimerization. This suggests that metallacyclopentatrienes should be stabilized at a range of transition metal centres which satisfy criteria similar to $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\eta\text{-C}_8\text{H}_{12})\text{Br}]$.

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[§] ^1H N.m.r. (CDCl_3 , 303 K, 500.13 MHz): δ 7.20 (m, 6H, Ph), 7.17 (m, 3H, Ph), 7.10 (m, 6H, Ph), 7.01 (s, 2H, CH), 5.01 (s, 5H, C_5H_5), 4.02 (t, 2H, CH_2), 3.63 (t, 2H, CH_2), 3.43 (t, 2H, CH_2), and 2.43 (t, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ n.m.r. (CDCl_3 , 303 K, 125.76 MHz): δ 201.3 (C_α), 151.7 (C,Ph), 142.3 (C_β), 127.4, 126.2, 125.6 (C,Ph), 92.4 (C_5H_5), 82.2, 71.0, 68.3, and 49.5 (CH_2).