Novel Reactions of Alkynes on a Coordinatively Unsaturated Diruthenium Centre Bridged by Thiolate Ligands. Syntheses and Crystal Structures of Dinuclear Ruthenacyclopentenyl Complexes

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The coordinatively unsaturated complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}SPr^i)_2Ru(\eta^5\text{-}C_5Me_5)]$ **1** reacts with HC≡CR {R = Tol (p-MeC$_6$H$_4$) or $\overline{C{=}CH[CH_2]_3CH_2}$} to form novel dinuclear ruthenacyclopentenyl complexes **2** and **3**, respectively, both of which have been fully characterized by X-ray crystallography.

Considerable attention has recently been focused on transition metal–sulfur cluster complexes as model compounds of both active sites of natural enzymes and catalytic metal surfaces, as well as catalysts in their own right.[1] In our continuing studies on dinuclear Ru(η^5-C$_5$Me$_5$) complexes possessing bridging thiolate ligands,[2,3] we have sought to develop novel modes of activation and transformation of organic molecules on the well-defined thiolate-bridged diruthenium centre. Here we report the syntheses and crystal structures of novel dinuclear ruthenacyclopentenyl complexes obtained by treatment of the coordinatively unsaturated complex **1**† with HC≡CR (R = Tol, $\overline{C{=}CH[CH_2]_3CH_2}$).

Results are summarized in Scheme 1.‡ Complex **1** readily reacted with HC≡CTol (3 equiv.) at room temperature to form

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† This complex is an extremely air-sensitive diamagnetic compound and is readily oxidized to form an unidentified paramagnetic species. The paramagnetic character of **1** claimed previously[5] must be due to a small amount of this impurity formed by accidental contact with air. Details on the syntheses and structures of the complexes $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}SR)_2Ru(\eta^5\text{-}C_5Me_5)]$ will be reported elsewhere. Recently Kölle *et al.* independently reported the synthesis and crystal structure of $[(\eta^5\text{-}C_5Me_4Et)Ru(\mu_2\text{-}SEt)_2Ru(\eta^5\text{-}C_5Me_4Et)]$.[7]

‡ Elemental analyses of complex **2**, **3**, **5** and **6** gave satisfactory results. Detailed spectroscopic data for these novel complexes were available to referees as Supplementary Material.

Complex **2**: after removal of the solvent from the reaction solution, the resulting dark-brown residue was purified by chromatography on silica gel with benzene–hexane (2:1) as eluent. The solvent was evaporated from a single brown band to give **2** in 24% yield. Crystals suitable for an X-ray structural analysis were obtained from toluene–acetonitrile.

Complex **3**: this compound was prepared analogously (yield 25%). Crystals suitable for an X-ray structural analysis were obtained from benzene–acetonitrile.

Complex **5**: selected spectroscopic data: IR (KBr) ν(C≡N)/cm^{-1} 2062s; ^{1}H NMR (C$_6$D$_6$) δ 6.46, 5.57 (s, 1H each, H^a and H^b), 2.30 (s, 1H, H^c), 2.47, 2.11, 1.96 (s, 3H each, C$_6$H$_4$*Me*), 1.97, 1.54 (s, 15H each, C$_5$*Me*$_5$) and 1.09 (s, 9H, CN*Bu*^{t}).

Complex **6**: selected spectroscopic data; IR (KBr) ν(C≡N)/cm^{-1} 2058s; ^{1}H NMR (C$_6$D$_6$) δ 6.34 (s, 1H, H^a), 6.30, 5.56 (br s, 1H each, H^b and H^c), 1.95, 1.52 (s, 15H each, C$_5$*Me*$_5$) and 1.09 (s, 9H, CN*Bu*^{t}).

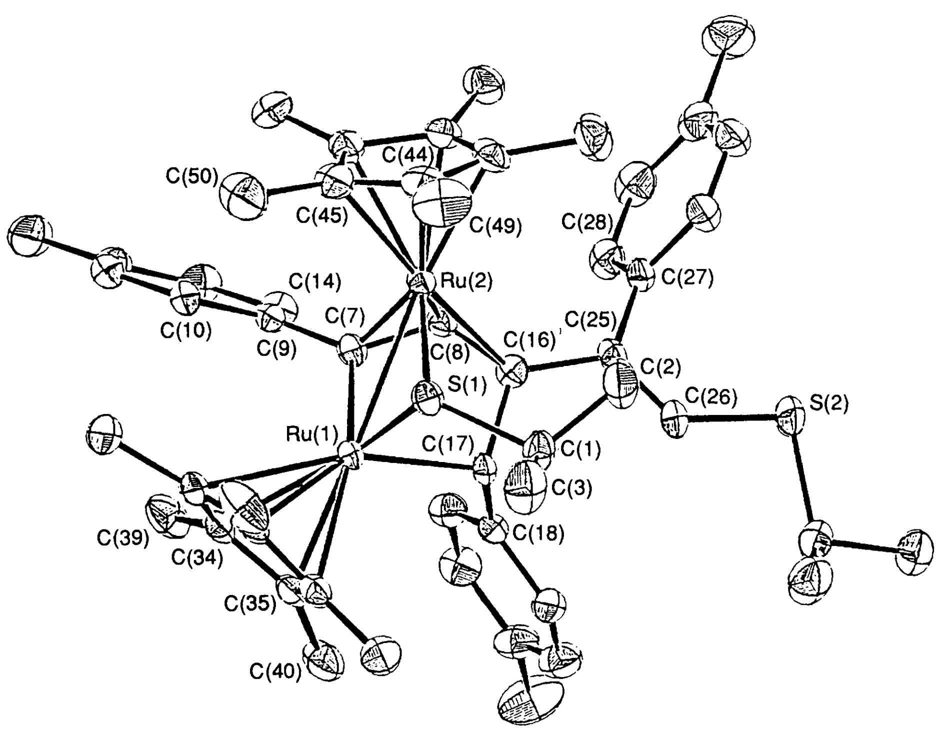
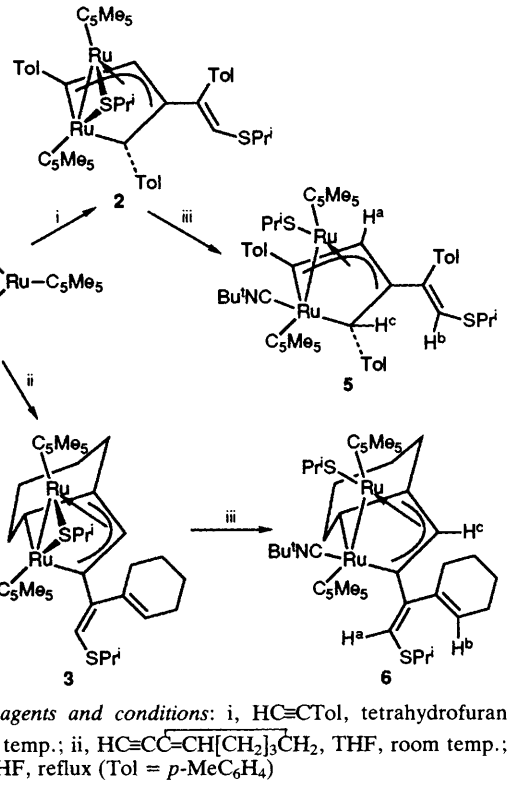


Fig. 1 ORTEP drawing of **2**. Important bond distances: Ru(1)–Ru(2), 2.779(1); Ru(1)–C(7), 2.079(8); Ru(1)–C(17), 2.154(6); Ru(2)–C(7), 2.189(7); Ru(2)–C(8), 2.162(8); Ru(2)–C(16), 2.378(9); C(7)–C(8), 1.445(9); C(8)–C(16), 1.40(1); C(16)–C(17), 1.54(1) Å; bond angles: Ru(1)–C(7)–C(8), 114.9(6); Ru(1)–C(7)–C(9), 123.5(5); Ru(1)–C(17)–C(16), 114.4(5); C(7)–Ru(1)–C(17), 77.7(3); C(7)–C(8)–C(16), 113.8(7); C(8)–C(7)–C(9), 118.4(6); C(8)–C(16)–C(17), 112.1(7); C(8)–C(16)–C(25), 122.2(8); C(17)–C(16)–C(25), 117.4(8)°.



Scheme 1 *Reagents and conditions*: i, HC≡CTol, tetrahydrofuran (THF), room temp.; ii, $HC{\equiv}C\overline{C{=}CH[CH_2]_3CH_2}$, THF, room temp.; iii, Bu^{t}NC, THF, reflux (Tol = *p*-MeC$_6$H$_4$)

a novel dinuclear ruthenacyclopentenyl complex **2**. Fig. 1 shows an ORTEP drawing of the dinuclear structure of **2**; two Ru atoms are bridged by an η^2:η^3-μ_2-C(Tol)CHC(CTol=CH-SPr^i)CHTol moiety derived from a μ_2-SPr^i ligand and three HC≡CTol molecules.§ Two alkyne molecules form a five-membered metallacycle with Ru(1), a part of which [C(7), C(8) and C(16)] is bound to Ru(2) *via* an η^3-allyl type coordination. The intramolecular distance between the two Ru atoms is 2.779(1) Å, corresponding to an Ru–Ru single bond.

The most remarkable feature of **2** is the unique dinuclear ruthenacyclopentenyl structure resulting from incorporation of three HC≡CTol molecules into the diruthenium centre in **1** accompanied by ring closure. To the best of our knowledge, this is the first example of any kind of transformation in which alkynes are converted to form a metallacycle having such a specific structure. Another interesting point to note is the

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§ The structures were solved by direct methods and refined by least-squares from intensity data collected using Mo-Kα X-radiation (λ = 0.7107 Å) in the ω ($2\theta < 30°$) or the ω–2θ ($2\theta > 30°$) scan mode on a Rigaku AFC-6A diffractometer for complex **2** or a Mac MXC-18 diffractometer for complex **3** respectively. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Crystal Data for **2**: $C_{53}H_{68}S_2Ru_2$, M = 971.49, triclinic, space group $P\bar{1}$, a = 12.832(8), b = 13.132(7), c = 16.888(8) Å, α = 73.62(4), β = 80.75(4), γ = 60.78(4)°, U = 2382 Å^3, Z = 2, D_c = 1.354 g cm^{-3}, μ (Mo-Kα) = 7.385 cm^{-1}, $F(000)$ = 1012. Final $R(R_w)$ = 0.057 (0.070) for 6597 unique observed [$F_o > 3\sigma(F_o)$], absorption-corrected intensities with $3 < 2\theta < 50°$.

Crystal Data for **3**: $C_{42}H_{64}S_2Ru_2$, M = 835.32, triclinic, space group $P\bar{1}$, a = 12.235(6), b = 13.925(6), c = 11.904(5) Å, α = 92.73(3), β = 91.48(4), γ = 89.55(4)°, U = 2025(1) Å^3, Z = 2, D_c = 1.37 g cm^{-3}, μ (Mo-Kα) = 8.568 cm^{-1}, $F(000)$ = 872. Final R (R_w) = 0.072 (0.078) for 5805 unique observed [$F_0 > 3\sigma(F_0)$], absorption-corrected intensities with $3 < 2\theta < 50°$.

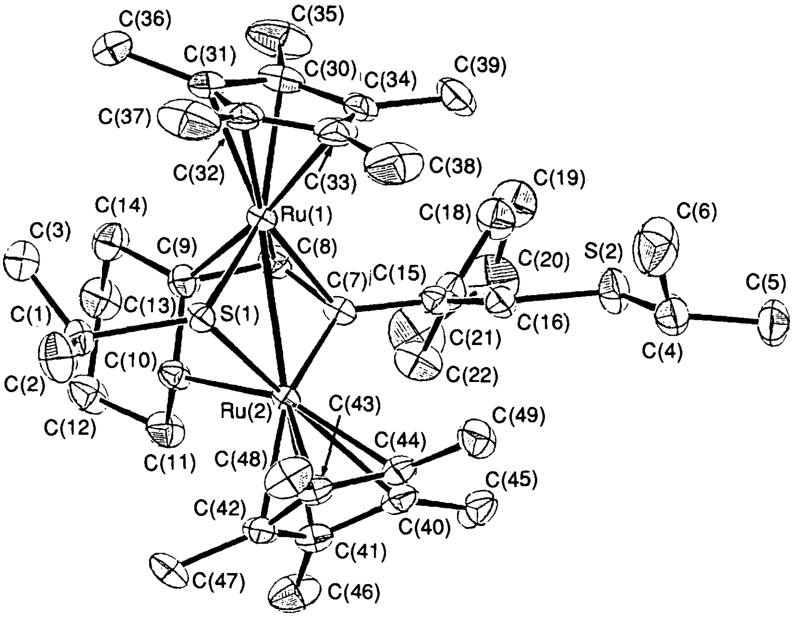

Fig. 2 ORTEP drawing of **3**. Important bond distances: Ru(1)–Ru(2), 2.796(2); Ru(1)–C(7), 2.223(8); Ru(1)–C(8), 2.143(8); Ru(1)–C(9), 2.239(8); Ru(2)–C(7), 2.073(8); Ru(2)–C(10), 2.143(8); C(7)–C(8), 1.45(1); C(8)–C(9), 1.45(1); C(9)–C(10), 1.53(1) Å; bond angles: Ru(2)–C(7)–C(8), 114.4(5); Ru(2)–C(7)–C(15), 128.6(7); Ru(2)–C(10)–C(9), 104.6(5); C(7)–Ru(2)–C(10), 78.5(3); C(7)–C(8)–C(9), 113.6(7); C(8)–C(7)–C(15), 116.3(8); C(8)–C(9)–C(10), 110.2(7); C(8)–C(9)–C(14), 118.7(8); C(10)–C(9)–C(14), 117.3(8)°.

formal insertion of alkyne molecules into the Ru–S bond in **1**. Although several mono- and di-nuclear thiolate compounds have been reported to undergo insertions of alkynes into the M–S bond, these reactions are strictly limited to those with fluorinated alkynes, *e.g.*, $CF_3C{\equiv}CCF_3$.[4]

Reaction of **1** with $HC{\equiv}C\overline{C{=}CH[CH_2]_3C}H_2$ yielded another type of dinuclear ruthenacyclopentenyl complex **3**. In this case, two alkyne molecules are incorporated into the diruthenium centre in **1**. An ORTEP drawing of **3** is shown in Fig. 2.§ The five-membered metallacycle in **3** [Ru(2), C(7), C(8), C(9) and C(10)] is formed by the conjugated en-yne unit in one alkyne molecule and Ru(2), apparently owing to the original C=C bond being located suitably for ring closure. The intramolecular distance of 2.796(2) Å between the two Ru atoms indicates an Ru–Ru single bond.

Previously we reported that a unique oxidative trimerisation of $HC{\equiv}CSiMe_3$ readily proceeds on the diruthenium site in both **1** and the related paramagnetic complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}SPr^i)_3Ru(\eta^5\text{-}C_5Me_5)]$ **4** to form a novel bridging alkyne complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}H)(\mu_2\text{-}SPr^i)\{\eta^2\text{-}\mu_2\text{-}Me_3SiC{\equiv}CC({=}CHSiMe_3)C{\equiv}CSiMe_3\}Ru(\eta^5\text{-}C_5Me_5)]$.[5] Results described herein clearly demonstrate that reactions of **1** with terminal alkynes are surprisingly sensitive to the alkyne substituent.[6]

Further studies are in progress aimed at inducing additional transformations of **2** and **3**. Preliminary results have shown that complex **2** and **3** reacted quantitatively with Bu^tNC in refluxing tetrahydrofuran (THF) to give **5** and **6**, respectively (Scheme 1). Both **5** and **6** were spectroscopically characterized.

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6 In sharp contrast, treatment of complex **4** with terminal alkynes yields a series of dinuclear terminal diacetylide complexes $[(\eta^5\text{-}C_5Me_5)Ru(C{\equiv}CR)(\mu_2\text{-}SPr^i)_2Ru(C{\equiv}CR)(\eta^5\text{-}C_5Me_5)]$, which show unusual reactivities towards electrophiles: H. Matsuzaka, Y. Hirayama, M. Nishio, Y. Mizobe and M. Hidai, *Organometallics*, in the press.

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