Novel Reactions of Alkynes on Dinuclear Ruthenium Centres Bridged by Thiolate Ligands; Syntheses and Characterization of $(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}H)(\mu_2\text{-}SPr^i)[\eta^2\text{-}\mu_2\text{-}Me_3SiC{\equiv}CC({=}CHSiMe_3)C{\equiv}CSiMe_3]Ru(\eta^5\text{-}C_5Me_5)$ and $(\eta^5\text{-}C_5Me_5)Ru(C{\equiv}CTol)(\mu_2\text{-}SPr^i)_2Ru(C{\equiv}CTol)(\eta^5\text{-}C_5Me_5)$

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Paramagnetic complexes $(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}SPr^i)_3Ru(\eta^5\text{-}C_5Me_5)$ **1** and $(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}SPr^i)_2Ru(\eta^5\text{-}C_5Me_5)$ **2** react with $HC{\equiv}CSiMe_3$ to give a novel diamagnetic diruthenium complex $(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}H)(\mu_2\text{-}SPr^i)[\eta^2\text{-}\mu_2\text{-}Me_3SiC{\equiv}CC({=}CHSiMe_3)C{\equiv}CSiMe_3]Ru(\eta^5\text{-}C_5Me_5)$ **3** which easily releases a free alkyne trimer $(Me_3SiC{\equiv}C)_2C{=}CHSiMe_3$ by air oxidation, whereas treatment of **1** with $HC{\equiv}CTol$ affords another diamagnetic diruthenium complex $(\eta^5\text{-}C_5Me_5)Ru(C{\equiv}CTol)(\mu_2\text{-}SPr^i)_2Ru(C{\equiv}CTol)(\eta^5\text{-}C_5Me_5)$ **6**, (Tol = *p*-tolyl).

Transition metal-sulphur cluster complexes have attracted considerable attention as model compounds of both the active sites of natural enzymes and catalytic metal surfaces, as well as catalysts in their own right.[1] During the course of our studies on dinuclear $Ru(\eta^5\text{-}C_5Me_5)$ complexes containing bridging thiolate ligands,[2] we have recently found that the paramagnetic complex $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}SPr^i)_3Ru(\eta^5\text{-}C_5Me_5)$ **1** reacts with H_2 gas or $HC{\equiv}CPh$ on its dinuclear centre to give diamagnetic diruthenium complexes $(\eta^5\text{-}C_5Me_5)RuR(\mu_2\text{-}SPr^i)_2RuR(\eta^5\text{-}C_5Me_5)$ (R = H, $C{\equiv}CPh$).[3] These findings have prompted us to examine the activation and transformation of various organic molecules using the family of dinuclear $Ru(\eta^5\text{-}C_5Me_5)$ compounds possessing bridging thiolate ligands.[4] Here we report the syntheses and crystal structures of novel diruthenium complexes with a perpendicularly oriented bridging alkyne trimmer ligand and with terminal acetylide ligands.

Reaction of $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}SPr^i)_2Ru(\eta^5\text{-}C_5Me_5)$ **2**† with $HC{\equiv}CSiMe_3$ gave the novel diruthenium complex $(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}H)(\mu_2\text{-}SPr^i)[\eta^2\text{-}\mu_2\text{-}Me_3SiC{\equiv}CC({=}CHSiMe_3)C{\equiv}CSiMe_3]Ru(\eta^5\text{-}C_5Me_5)$ **3**‡§ (Scheme 1). Complex **3** was also obtained by analogous treatment of **1**. Fig. 1 shows an ORTEP drawing of **3** having the dinuclear structure, where two Ru atoms are bridged by a $\eta^2\text{-}\mu_2\text{-}Me_3SiC{\equiv}CC({=}CHSiMe_3)C{\equiv}CSiMe_3$ unit derived from three $HC{\equiv}CSiMe_3$ molecules. This, to the best of our knowledge, offers the first example of a transition metal alkyne complex in which an alkyne is combined in such a manner on metal centres. The intramolecular distance between Ru atoms is 2.691(1) Å, corresponding to a Ru–Ru single bond. Recently Tilley reported that treatment of $[(\eta^5\text{-}C_5Me_5)Ru(\mu_3\text{-}Cl)]_4$ **4** with $HC{\equiv}CSiMe_3$ yielded a cyclobutadiene complex $(\eta^5\text{-}C_5Me_5)Ru[\mu_4\text{-}C_4H_2(SiMe_3)_2]Cl$, a ruthenacyclopentadiene complex $(\eta^5\text{-}C_5Me_5)RuCl_2[\eta^2:\eta^4\text{-}\mu_2\text{-}C_4H_2(SiMe_3)_2]Ru(\eta^5\text{-}C_5Me_5)$, and a

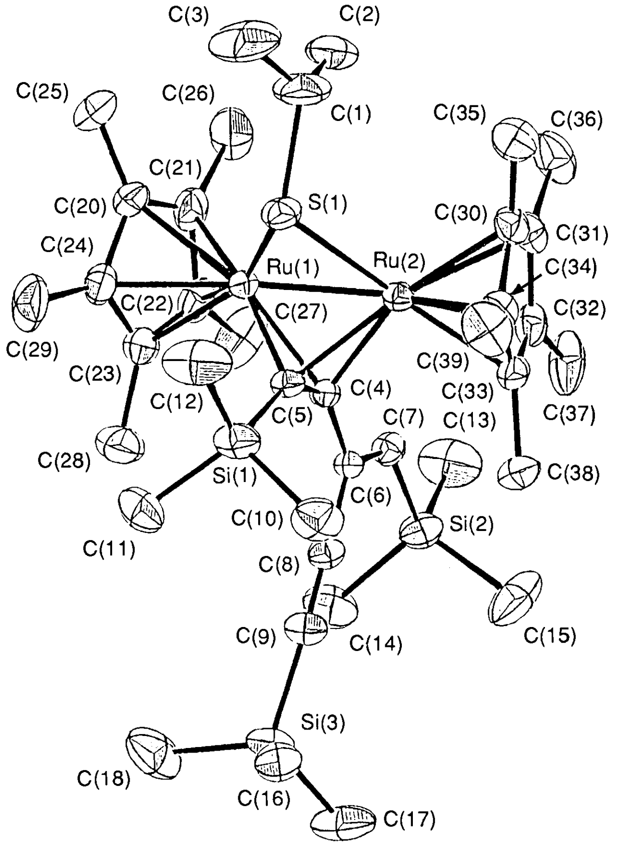

Fig. 1 ORTEP drawing of **3**. Important bond distances (Å): Ru(1)–Ru(2) 2.691(1), Ru(1)–S(1) 2.374(2), Ru(2)–S(1) 2.366(3), Ru(1)–C(4) 2.101(8), Ru(1)–C(5) 2.190(7), Ru(2)–C(4) 2.089(6), Ru(2)–C(5) 2.188(7), C(4)–C(5) 1.316(9); bond angles (°): Ru(1)–S(1)–Ru(2) 69.19(7), Ru(1)–C(4)–Ru(2) 79.9(2), Ru(1)–C(5)–Ru(2) 75.9(2), C(4)–C(5)–Si(1), 145.2(5), C(5)–C(4)–C(6), 140.4(5).

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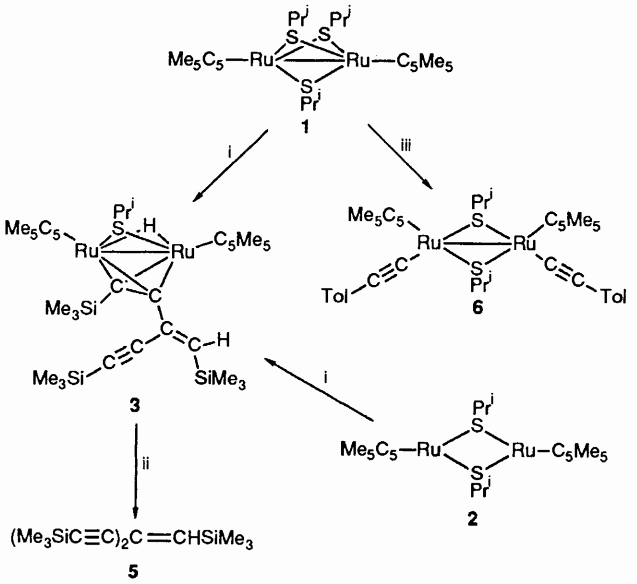
† This paramagnetic air-sensitive complex can be prepared by treatment of $(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}OMe)_2Ru(\eta^5\text{-}C_5Me_5)$ with Me_3SiSPr^i in tetrahydrofuran (THF), or $[(\eta^5\text{-}C_5Me_5)Ru(\mu_3\text{-}Cl)]_4$ with $NaSPr^i$ in MeOH. Details of the syntheses and structure of a series of compounds of the form $(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}SR)_2Ru(\eta^5\text{-}C_5Me_5)$ will be published elsewhere.

‡ The formation of Pr^iSH in the reaction mixture was observed by GLC analysis. After removal of the solvent, the resulting brown residue was purified by chromatography on alumina eluting with hexane. The solvent was evaporated from a single wine-red band which eluted to yield **3**. Recrystallization from benzene–acetonitrile gave **3** as columnar crystals in 41% yield. ^1H NMR (C_6D_6) δ 6.71 (s, 1H, $C{=}CHSiMe_3$), 1.82 (s, 30H, C_5Me_5), 1.10 (d, 6H, *J* 6.7 Hz, $SCHMe_2$), 0.64 (s, 9H, $SiMe_3$), 0.53 (s, 9H, $SiMe_3$), 0.31 (s; 9H, $SiMe_3$), −15.9 (s, 1H, $Ru(\mu_2\text{-}H)Ru$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 145.01, 135.63 (C^6 and C^7), 115.81, 109.40, 97.69, 92.74 (acetylenic and vinylic), 92.35(C_5Me_5), 35.44($SCHMe_2$), 25.95($SCHMe_2$), 11.23 (C_5Me_5), 3.12 ($SiMe_3$), −0.11 ($SiMe_3$), −1.11($SiMe_3$). The existence of a μ_2-hydrido ligand is strongly suggested by the large dihedral angle of 218.50° between two planes defined by two Ru atoms and S(1), or C(4), although the hydrogen atom was not located by the structural analysis.

§ *Crystal_data* for **3**: $C_{38}H_{66}Si_3SRu_2$, $M = 841.51$, triclinic, space group $P\bar{1}$, $a = 11.632(3)$, $b = 21.161(6)$, $c = 11.167(3)$ Å, $\alpha = 103.51(3)$, $\beta = 121.48(2)$, $\gamma = 72.16(2)°$, $U = 2222$ Å^3, $Z = 2$, $D_c = 1.257$ g cm^{-3}, μ(Mo-Kα) = 8.13 cm^{-1}, $F(000) = 880$. Final R (R_w) = 0.047 (0.061) for 6504 unique observed $[I > 3\sigma(I)]$, absorption-corrected intensities with $3 > 2\theta > 50°$. The structures were solved by direct methods and refined by least-squares analysis from intensity data collected using Mo-Kα X-radiation ($\lambda = 0.7107$ Å) in ω ($2\theta < 30°$) and ω-2θ ($2\theta > 30°$) scan mode on a Rigaku AFC-6A diffractometer. 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.



Scheme 1 *Reagents*: i, HC≡CSiMe$_3$, THF; ii, THF, under air; iii, HC≡CTol, benzene (Tol = *p*-tolyl)

triruthenium cluster $(\eta^5\text{-}C_5Me_5)_3Ru_3(\mu_2\text{-}Cl)_2(\mu_3\text{-}Cl)(\eta^2\text{-}\mu_2\text{-}HC{\equiv}CSiMe_3)$.[5] It is noteworthy that completely different products are formed depending upon the type of $(\eta^5\text{-}C_5Me_5)Ru^{II}$ species **2** and **4**.

The free alkyne trimer $(Me_3SiC{\equiv}C)_2C{=}CHSiMe_3$ **5** can easily be released from **3** by air oxidation in almost quantitative yield.¶ Previously $HC{\equiv}CSiMe_3$ was shown to oligomerise to afford a mixture of linear products, $Me_3SiCH{=}CHC{\equiv}CSiMe_3$ and $Me_3SiCH{=}CHCH{=}C(SiMe_3)C{\equiv}CSiMe_3$ in the presence of $Ni(acac)_2$–$AlEt_3$–PPh_3 catalyst.[6] (Hacac = pentane-2,4-dione.) It is of great interest that oligomerisation of $HC{\equiv}CSiMe_3$ on the dinuclear ruthenium centre in **1** and **2** proceeds fully regioselectively to form the acyclic, branched trimer **5** as a single product.

The reaction of HC≡CTol on the diruthenium centre in **1** and **2** occurs in quite a different manner. Thus, treatment of **1** with HC≡CTol yielded the terminal diacetylide complex $(\eta^5\text{-}C_5Me_5)Ru(C{\equiv}CTol)(\mu_2\text{-}SPr^i)_2Ru(C{\equiv}CTol)(\eta^5\text{-}C_5Me_5)$ **6**, which was spectroscopically characterized|| (Scheme 1), whereas reaction of **2** with HC≡CTol gave another diruthenium complex **8**. Spectroscopic data indicates that three alkyne molecules are incorporated into the diruthenium system. Further studies are in progress on the structure of **8**, reactivities of **3**, **6** and **8**, as well as the mechanism for the formation of these complexes.

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¶ *Mass spectroscopy* (high resolution) calcd. for $C_{15}H_{28}Si_3$ m/z = 292.1545 (M^+), found m/z = 292.1522 (M^+); ^1H NMR ($CDCl_3$) δ 6.61 (s, 1H, C=C*H*SiMe$_3$), 0.21 (S, 9H, SiMe$_3$), 0.19 (s, 9H, SiMe$_3$), 0.18 (s, 9H, SiMe$_3$).

|| After removal of the solvent, the resulting brown solid was purified by chromatography on alumina eluting with benzene–hexane (2 : 1). The solvent was evaporated from the single brown band which eluted to yield **6**. Recrystallization from benzene–acetonitrile gave **6** as cubic brown crystals in 32% yield. IR (KBr) ν(C≡C) cm^{-1} 2100 s; ^1H NMR (C_6D_6) δ 7.36 (d, 4H, *J* 7.9 Hz, aryl), 6.98 (d, 4H, *J* 7.9 Hz, aryl), 5.03 (sep, 2H, *J* 6.7 Hz, SC*H*Me$_2$), 2.15 (s, 6H, C$_6$H$_4$*Me*), 1.69 (s, 30H, C$_5$Me$_5$), 1.66 (d, 12H, *J* 6.7 Hz, SCH*Me*$_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 132.69, 131.06, 128.06 (aryl), 115.74 (C≡*C*Tol), 107.55 (*C*≡CTol), 98.59 (*C*$_5$Me$_5$), 41.01 (S*C*HMe$_2$), 24.49 (SCH*Me*$_2$), 21.16 (C$_6$H$_4$*Me*), 10.72 (C$_5$*Me*$_5$).

Complex **6** has also been defined by an X-ray crystal structure determination. Preliminary results ($R = 0.99$, $R_w = 0.11$) confirm the structure sketched in Scheme 1. Complex **6** has the doubly bridged dinuclear structure with a terminal acetylide ligand on each Ru atom. Two acetylide ligands are in mutually *cis* configuration. The coordination geometry of C_5Me_5 and SPr^i groups around the Ru atoms in **6** is similar to that observed in $(\eta^5\text{-}C_5Me_5)Ru(H)(\mu_2SPr^i)_2Ru(H)(\eta^5\text{-}C_5Me_5)$ **7**,[3] so that the previously proposed terminal dihydride structure of **7** has now been indirectly confirmed.