

Dinuclear ($\eta^5\text{-C}_5\text{Me}_5$)Ru Complexes Triply Bridged by Tellurium or Selenium Ligands—Syntheses and Characterisation of ($\eta^5\text{-C}_5\text{Me}_5$)Ru($\mu_2\text{-RTeTeR}$)($\mu_2\text{-TeR}$) $_2$ Ru($\eta^5\text{-C}_5\text{Me}_5$) and [($\eta^5\text{-C}_5\text{Me}_5$)Ru($\mu_2\text{-SeR}$) $_3$ Ru($\eta^5\text{-C}_5\text{Me}_5$)]Cl (R = Tol, Ph)

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Reactions of [($\eta^5\text{-C}_5\text{Me}_5$)RuCl $_2$] $_2$ **1** with Me $_3$ SiTeR (R = Tol, Ph; Tol = *p*-tolyl) produce diarylditelluride/aryltelluroate-bridged Ru^{II}–Ru^{II} complexes ($\eta^5\text{-C}_5\text{Me}_5$)Ru($\mu_2\text{-RTeTeR}$)($\mu_2\text{-TeR}$) $_2$ Ru($\eta^5\text{-C}_5\text{Me}_5$) **2** (**2a**, R = Tol; **2b**, R = Ph) whereas those with Me $_3$ SiSeR (R = Tol, Ph) yield arylselenolate-bridged Ru^{III}–Ru^{III} complexes [($\eta^5\text{-C}_5\text{Me}_5$)Ru($\mu_2\text{-SeR}$) $_3$ Ru($\eta^5\text{-C}_5\text{Me}_5$)]Cl **3** (**3a**, R = Tol; **3b**, R = Ph); both **2a** and **3a** are fully characterised by X-ray crystallography.

In our continuing studies on transition metal–sulfur cluster complexes, we have recently found that treatment of [($\eta^5\text{-C}_5\text{Me}_5$)RuCl $_2$] $_2$ **1** with various thiolate compounds selectively produces a series of thiolate-bridged dinuclear ($\eta^5\text{-C}_5\text{Me}_5$)Ru complexes^{1,2} which provide bimetallic reaction sites for novel modes of chemical transformations of organic substrates such as alkynes³ and organic halides.^{1c} These findings have prompted us to investigate synthesis and reactivities of dinuclear ($\eta^5\text{-C}_5\text{Me}_5$)Ru family with bridging tellurium or selenium ligands.[†] Here, we report two types of novel diruthenium compounds; Ru^{II}–Ru^{II} complexes with a unique $\mu_2\text{-RTeTeR}$ ligand ($\eta^5\text{-C}_5\text{Me}_5$)Ru($\mu_2\text{-RTeTeR}$)($\mu_2\text{-TeR}$) $_2$ Ru($\eta^5\text{-C}_5\text{Me}_5$) **2** (**2a**, R = Tol; **2b**, R = Ph) and Ru^{III}–Ru^{III} complexes [($\eta^5\text{-C}_5\text{Me}_5$)Ru($\mu_2\text{-SeR}$) $_3$ Ru($\eta^5\text{-C}_5\text{Me}_5$)]Cl **3** (**3a**, R = Tol; **3b**, R = Ph) (Scheme 1).

Complex **1** readily reacts with Me $_3$ SiTeR⁴ (4 equiv. per **1**) in THF at room temp. to give **2**† as a dark-brown crystalline solid. **2a** was further defined by X-ray crystallography.§ The crystal lattice contains two independent but chemically similar formula units. An ORTEP drawing of one of the independent molecules is shown in Fig. 1. Complex **2a** has the dinuclear structure where two ($\eta^5\text{-C}_5\text{Me}_5$)Ru units are bridged by $\mu_2\text{-TolTeTeTol}$ and two $\mu_2\text{-TeTol}$ ligands. Tolyl groups in the $\mu_2\text{-TeTol}$ ligands take *anti* configuration whereas those in the $\mu_2\text{-TolTeTeTol}$ moiety are *syn* to each other. The bond length between two Te atoms in the $\mu_2\text{-TolTeTeTol}$ unit is 2.901(3) Å. The significantly longer Ru–Ru distance of 4.052(3) Å compared with values observed in diruthenium complexes with a Ru–Ru single bond (2.6–2.9 Å)^{1,3} clearly indicates the absence of bonding interaction between the two Ru atoms.

The surprising feature of this structure is a $\mu_2\text{-TolTeTeTol}$ unit formed presumably by coupling of two TeTol ligands at the diruthenium site. Diorganoditellurides most commonly undergo cleavage of their Te–Te bond with formal oxidation of the metal centre to form terminal or bridging telluroate ligands.⁵ The only well-characterized intact coordinated diorganoditelluride complex is (CO) $_3$ Re($\mu_2\text{-PhTeTePh}$)($\mu_2\text{-Br}$) $_2$ Re(CO) $_3$ [Te–Te bond distance; 2.794(5) Å] obtained by displacement of thf in [(CO) $_3$ (thf)Re($\mu_2\text{-Br}$)] $_2$ by

PhTeTePh.^{6,†} Complexes **2** are the first examples of the direct formation of diorganoditelluride from organic telluroates on the well-defined transition metal centre. Furthermore, complexes **2** are possible intermediates for dinuclear reductive elimination of RTeTeR from the diruthenium site.

Similar treatment of **1** with Me $_3$ SiSeR⁷ does not give the selenium analogue of **2**, but produces cationic Ru^{III}–Ru^{III} species **3**.|| The structure of **3a** determined by X-ray diffraction analysis is depicted in Fig. 2.§ Three selenolate ligands

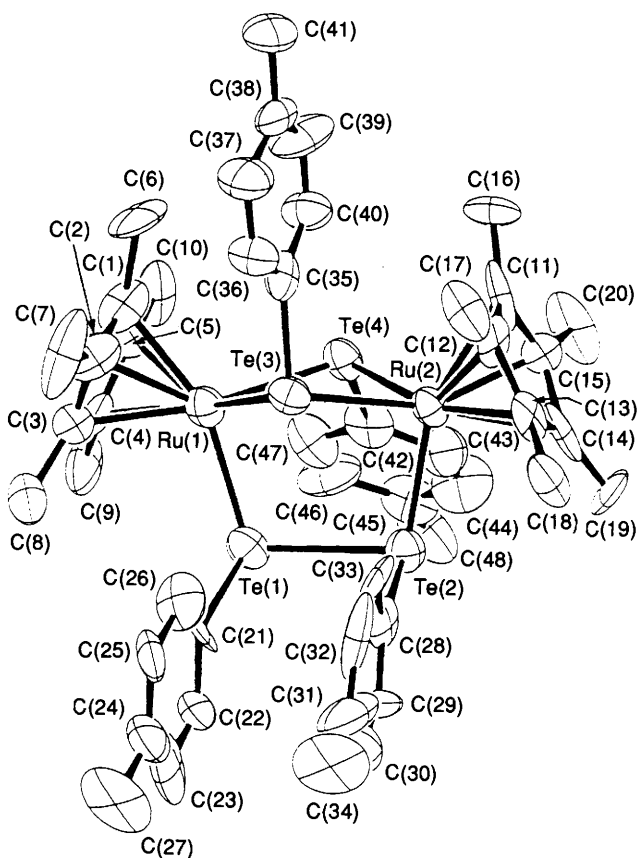
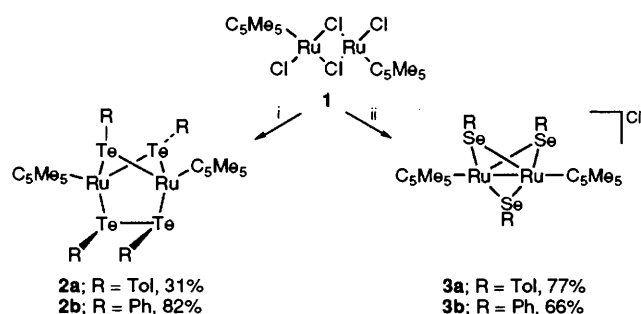


Fig. 1 An ORTEP drawing of **2a**. Selected bond distances: Ru(1)–Te(1), 2.540(3), Ru(1)–Te(3), 2.681(3); Ru(1)–Te(4), 2.668(3); Ru(2)–Te(2), 2.540(3); Ru(2)–Te(3), 2.698(3); Ru(2)–Te(4), 2.667(3); Te(1)–Te(2), 2.901(3) Å; bond angles: Te(1)–Ru(1)–Te(3), 93.02(10); Te(1)–Ru(1)–Te(4), 88.84(10); Te(3)–Ru(1)–Te(4), 77.43(8); Te(2)–Ru(2)–Te(3), 90.66(9); Te(2)–Ru(2)–Te(4), 91.42(9); Te(3)–Ru(2)–Te(4), 77.15(8); Ru(1)–Te(1)–Te(2), 103.16(9); Ru(1)–Te(1)–C(21), 96.1(7); Te(2)–Te(1)–C(21), 96.1(7); Ru(2)–Te(2)–Te(1), 102.86(9); Ru(2)–Te(2)–C(28), 96.4(6); Te(1)–Te(2)–C(28), 96.4(6); Ru(1)–Te(3)–Ru(2), 97.75(9); Ru(1)–Te(3)–C(35), 104.6(7); Ru(2)–Te(3)–C(35), 103.3(7); Ru(1)–Te(4)–Ru(2), 98.85(9); Ru(1)–Te(4)–C(42), 107.7(8); Ru(2)–Te(4)–C(42), 110.3(9)°



Scheme 1 Reagents: i, Me $_3$ SiTeR, THF; ii, Me $_3$ SiSeR, CH $_2$ Cl $_2$

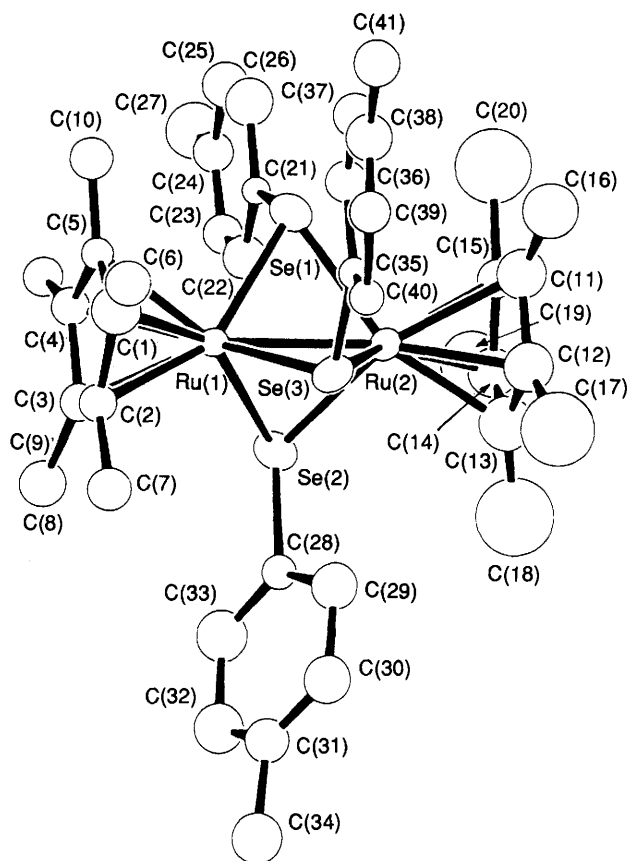


Fig. 2 An ORTEP drawing of a cationic part of **3a**. Selected bond distances: Ru(1)–Ru(2), 2.685(3); Ru(1)–Se(1), 2.461(4); Ru(1)–Se(2), 2.466(4); Ru(1)–Se(3), 2.446(4); Ru(2)–Se(1), 2.449(4); Ru(2)–Se(2), 2.465(4); Ru(2)–Se(3), 2.447(4) Å; bond angles: Ru(2)–Ru(1)–Se(1), 56.6(1); Ru(2)–Ru(1)–Se(2), 56.98(10); Ru(2)–Ru(1)–Se(3), 56.75(10); Ru(1)–Ru(2)–Se(1), 57.07(10); Ru(1)–Ru(2)–Se(2), 57.0(1); Ru(1)–Ru(2)–Se(3), 56.7(1); Se(1)–Ru(1)–Se(2), 93.1(1); Se(1)–Ru(1)–Se(3), 94.2(1); Se(2)–Ru(1)–Se(3), 91.3(1); Se(1)–Ru(2)–Se(2), 93.4(1); Se(1)–Ru(2)–Se(3), 94.5(1); Se(2)–Ru(2)–Se(3), 91.3(1); Ru(1)–Se(1)–Ru(2), 66.3(1); Ru(1)–Se(1)–C(21), 113.5(7); Ru(2)–Se(1)–C(21), 114.7(8); Ru(1)–Se(2)–Ru(2), 66.0(1); Ru(1)–Se(2)–C(28), 107.8(7); Ru(2)–Se(2)–C(28), 112.5(8); Ru(1)–Se(3)–Ru(2), 66.6(1); Ru(1)–Se(3)–C(35), 111.6(8); Ru(2)–Se(3)–C(35), 112.1(7)°

coordinate to two Ru atoms almost symmetrically so that the Ru–Ru vector is on a pseudothreefold axis. The intramolecular distance between two Ru atoms is 2.684(3) Å, corresponding to a Ru–Ru single bond.^{1,3}

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Footnotes

† In contrast to the well-developed iron chemistry, far fewer works have been reported until recently on organoruthenium complexes with telluroate,^{8c} telluride,⁹ selenolate⁸ and selenide¹⁰ ligands.

‡ After removal of the solvent, the resulting solid was chromatographed on silica gel with benzene:hexane (2:1). Evaporation of the solvent from a single dark-brown band gave a dark-brown solid which was recrystallized from benzene–acetonitrile to afford **2** as columnar crystals. **2a**: Yield, 31%, ¹H NMR (C₆D₆) δ 7.68–6.50 (m, 16H, aryl), 2.25 (s, 6H, μ₂-MeC₆H₄TeTeC₆H₄Me), 2.19, 1.96 (s, 3H each, μ₂-TeC₆H₄Me), 1.77 (s, 30H, η⁵-C₅Me₅); **2b**: Yield, 82%, ¹H NMR (C₆D₆) δ 7.70–6.72 (m, 20H, aryl), 1.70 (s, 30H, η⁵-C₅Me₅).

§ *Crystal data* for **2a**: C₄₈H₅₈Te₄Ru₂, *M* = 1347.53, triclinic, space group *P*1, *a* = 17.270(3), *b* = 23.498(3), *c* = 12.836(2) Å, α = 96.76(1), β = 102.55(2), γ = 102.881(10)°, *U* = 4880(1) Å³, *Z* = 4, *D*_c = 1.834 g cm⁻³, μ(Mo–Kα) = 29.93 cm⁻¹, *F*(000) = 2568. Final *R*(*R*_w) = 0.065(0.044) for unique observed [*I* > 3σ(*I*)] 6471 absorption-corrected intensities with 3 < 2θ < 55°.

3a: C₄₁H₅₁ClSe₃Ru₂·CH₂Cl₂, *M* = 1101.24, triclinic, space group *P*1, *a* = 10.961(2), *b* = 19.776(3), *c* = 10.593(2) Å, α = 100.47(1), β = 99.31(1), γ = 74.89(1)°, *U* = 2164.2(6) Å³, *Z* = 2, *D*_c = 1.690 g cm⁻³, μ(Mo–Kα) = 34.35 cm⁻¹, *F*(000) = 1088. Final *R*(*R*_w) = 0.098(0.073) for unique observed [*I* > 3σ(*I*)] 3598 absorption-corrected intensities with 3 < 2θ < 55°.

The structures were solved by heavy-metal methods and refined by full-matrix least-squares from intensity data collected using Mo–Kα radiation (λ = 0.7107 Å) in ω–2θ scan mode on a Rigaku-AFC7R diffractometer. Atomic coordinates, anisotropic displacement parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ Two R groups in the μ₂-RTeTeR unit in **2** are *syn* to each other whereas two phenyl groups in the μ₂-PhTeTePh ligand in (CO)₃Re(μ₂-PhTeTePh)(μ₂-Br)₂Re(CO)₃ take *anti* configuration.

|| After removal of the solvent, the resulting solid was washed with hexane and recrystallized from CH₂Cl₂–Et₂O. **3a**: Yield 77%, ¹H NMR (CDCl₃) δ 7.22, 7.11 (d, 6H each, *J* 10.8 Hz, aryl), 2.33 (s, 9H, C₆H₄Me), 1.51 (s, 30H, η⁵-C₅Me₅); **3b**: Yield 66%, ¹H NMR (CDCl₃) δ 8.20–7.27 (m, 15H, aryl), 1.50 (s, 30H, η⁵-C₅Me₅).

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