

Transformation of dimethyl acetylenedicarboxylate to bis(methylcarboxylate)vinylidene at a diruthenium centre: unprecedented 1,2-migration of a CO₂Me group

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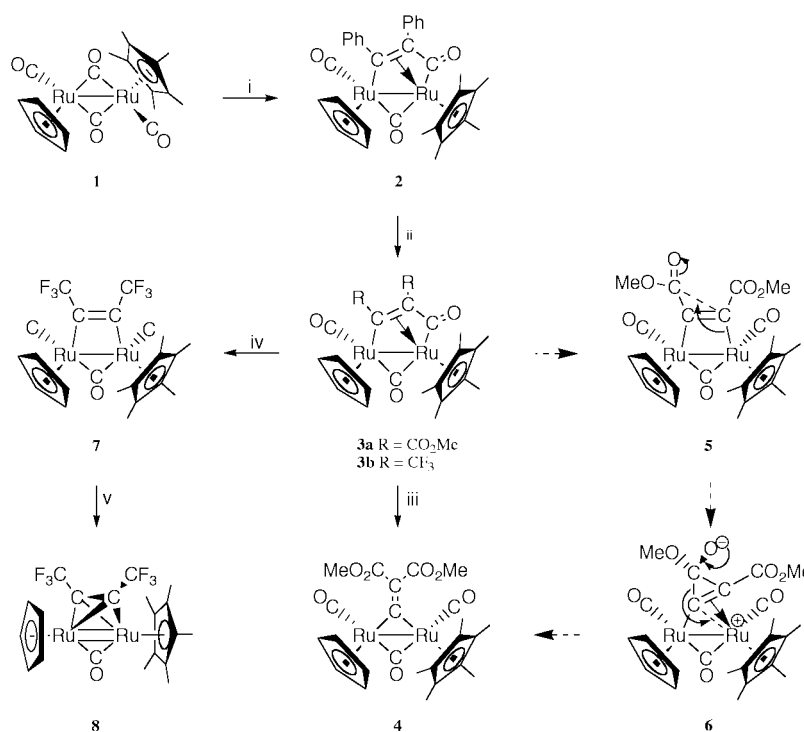
Dimethyl acetylenedicarboxylate is shown to rearrange at a diruthenium centre to give a μ -C=C(CO₂Me)₂ vinylidene complex in high yield *via* a 1,2-CO₂Me shift within a diruthenacyclopentenone species, a transformation proposed to occur *via* a zwitterionic μ -cyclopropenyl intermediate stabilised by the Cp* ligand.

In accord with the well established ability of hydrogen and trimethylsilyl to migrate, alkynes are known to undergo both 1,2-H and 1,2-SiMe₃ shifts within the coordination sphere of a transition metal to give vinylidene ligands.^{1,2} Thus, for example, we have shown that the μ -vinylidene complex [Ru₂(CO)₂(μ -CO)(μ -C=CH₂)(η -C₅H₅)₂]³ may be synthesised by treatment of the dimetallacyclopentenone species [Ru₂(CO)(μ -CO){ μ - η^1 : η^3 -C(O)C₂Ph₂}(η -C₅H₅)₂] with ethyne and that the reaction proceeds *via* initial alkyne exchange, forming the corresponding dimetallacyclopentenone complex. However, reaction with dimethyl acetylenedicarboxylate (MeO₂CC \equiv CCO₂Me) did not involve such a migration, giving instead the expected dimetallacyclobutene complex [Ru₂(CO)₂(μ -CO){ μ - η^1 : η^1 -(MeCO₂)C=C(CO₂Me)}(η -C₅H₅)₂]⁴ showing the usual form of coordination of this alkyne at a dinuclear metal centre. We now report that dimethyl acetylenedicarboxylate

reacts differently with the CpCp* species [Ru₂(CO)(μ -CO){ μ - η^1 : η^3 -C(O)C₂Ph₂}(η -C₅Me₅)(η -C₅H₅)] (2), to afford a μ -C=C(CO₂Me)₂ vinylidene ligand *via* an unprecedented 1,2-migration of a methylcarboxylate group, necessarily involving C–C bond cleavage.

Photolysis of a toluene solution of the CpCp* complex [Ru₂(CO)₂(μ -CO)₂(η -C₅Me₅)(η -C₅H₅)] (1)[†] and diphenylacetylene for 10 h affords 2,[†] which upon heating with an excess of dimethyl acetylenedicarboxylate undergoes rapid alkyne exchange to afford the corresponding dimetallacyclopentenone species [Ru₂(CO)(μ -CO){ μ - η^1 : η^3 -C(O)C₂(CO₂Me)₂}(η -C₅Me₅)(η -C₅H₅)] (3a)[†] (see Scheme 1). Unexpectedly, heating 3a for 45 min in toluene leads to formation of the μ -vinylidene species [Ru₂(CO)₂(μ -CO){ μ -C=C(CO₂Me)₂}(η -C₅Me₅)(η -C₅H₅)] (4),[†] isolated in 70% yield, and not the dimetallacyclobutene complex of the analogous Cp₂ system. Complex 4 exists as a mixture of *cis* and *trans* isomers, the structures of both of which were confirmed through X-ray diffraction studies. The results for the *cis* isomer are displayed in Fig. 1 and its caption.[‡]

In addition to establishing the presence of the μ -C=C(CO₂Me)₂ ligand, the structural determination on 4 reveals that the consequence of a Cp ligand on one ruthenium and a strongly



Scheme 1 Reagents and conditions: i, UV, 10 h, PhC \equiv CPh; ii, 110 °C, 10 min, RC \equiv CR; iii, toluene reflux, 45 min; iv, 110 °C, 1 h; v, 110 °C, 22 h.

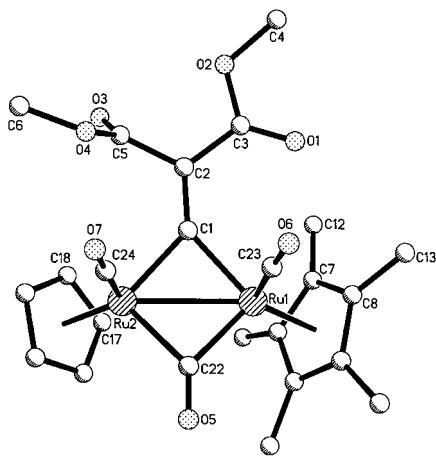


Fig. 1 Molecular geometry of *cis-4*; all hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)–Ru(2) 2.7197(5), Ru(2)–C(1) 2.018(2), Ru(1)–C(1) 2.025(4), Ru(1)–C(23) 1.853(4), Ru(2)–C(24) 1.858(5), Ru(2)–C(22) 2.037(4), Ru(1)–C(22) 2.044(4), C(1)–C(2) 1.342(6); Ru(1)–C(1)–Ru(2) 84.5(2).

electron-donating Cp* on the other is an equal spread of electron density over the diruthenium centre, *i.e.* there is extensive delocalisation. Thus, the bridging carbons C(1) and C(22) are approximately equidistant from Ru(1) and Ru(2), and the terminal carbonyls are the same distance from their respective metal centres. The vinylidene unit in **4** shows a significant 'lean' away from the Cp* end of the molecule [Ru(1)–C(1)–C(2) 141.0(3)°, Ru(2)–C(1)–C(2) 134.1(2)°], presumably due to unfavourable steric interactions between the bulky CO₂Me and Cp* groups. The formation of **4** is proposed (see Scheme 1) to involve initial rearrangement of **3a** to give a dimetallacyclobutene complex **5** followed by the generation of a zwitterionic μ -cyclopropenyl intermediate **6** in which a methylcarboxylate group has adopted a position bridging the α - and β -carbons of a μ -vinyl ligand, a common species in organo-diruthenium chemistry. We suggest that the driving force for this transformation is the stabilisation of the metal-centred positive charge by the electron-donating Cp* ligand. Subsequent ring opening of **6** leads directly to the μ -vinylidene complex **4**. Attempts to trap intermediate **6** as a μ -vinyl cation through addition of methyl triflate to the reaction mixture were unsuccessful. However, indirect evidence for the proposed mechanism comes from heating **2** in the presence of hexafluorobut-2-yne, which also has strongly electron-withdrawing substituents. This leads initially to formation of the corresponding dimetallacyclopentenone complex **3b** which then rearranges to [Ru₂(CO)₂(μ -CO){ μ - η^1 : η^1 -(F₃C)C=C(CF₃)};(η -C₅Me₅)(η -C₅H₅)] (**7**),[†] isolated in 80% yield as a mixture of *cis* and *trans* isomers, and firmly established as a dimetallacyclobutene complex through an X-ray crystallographic study on the *cis* isomer, the results of which are displayed in Fig. 2 and its caption.[‡] Upon prolonged heating, complex **7** decarbonylates to afford the dimetallatetrahedrane species [Ru₂(μ -CO){ μ - η^2 : η^2 -(F₃C)CC(CF₃)};(η -C₅Me₅)(η -C₅H₅)] (**8**),[†] the Cp₂ analogue of which is known,⁵ with no evidence for substituent migration being observed. This is attributed to the inability of the CF₃ group to participate in a charge-separated intermediate of type **6**.

In conclusion, the reactivity of the CpCp* complex **2** towards alkynes RC≡CR mirrors that of the analogous Cp₂ system when R = CF₃ but when R = CO₂Me a previously unseen methylcarboxylate migration occurs to yield a μ -C=C(CO₂Me)₂ vinylidene complex, attributed to the stabilisation of a zwitterionic μ -cyclopropenyl intermediate by the electron-donating Cp* ligand.

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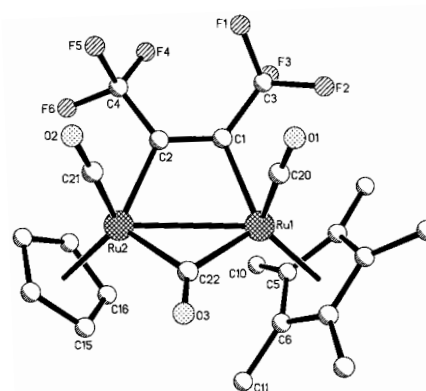


Fig. 2 Molecular geometry of *cis-7*; all hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)–Ru(2) 2.861(1), Ru(1)–C(1) 2.112(2), Ru(2)–C(2) 2.105(2), Ru(1)–C(20) 1.863(3), Ru(2)–C(21) 1.862(3), Ru(1)–C(22) 2.025(2), Ru(2)–C(22) 2.070(2), C(1)–C(2) 1.313(3); Ru(1)–C(1)–C(2) 111.3(2), Ru(2)–C(2)–C(1) 111.7(2).

Notes and references

[†] Complex **1** was synthesised in 82% yield through addition of [RuI(CO)₂(η -C₅Me₅)] (13.00 mmol) to a freshly prepared THF solution of Na[Ru(CO)₂(η -C₅H₅)] (18.00 mmol) and the mixture stirred for 2 h. Isopropyl alcohol (10 cm³) was added and the mixture stirred for 10 min. Chromatography on alumina gave the orange-red complex **1**, purified by recrystallisation from the minimum of hot heptane. Complex **4** was prepared by heating a toluene solution of **3a** (0.06 mmol) at reflux for 45 min. Chromatography on alumina yields a yellow band containing the *cis* and *trans* isomers in 70% yield.

The new complexes were characterised by elemental analyses and mass, IR (CH₂Cl₂ solution) and NMR (¹H, ¹³C-{¹H} and ¹⁹F, CDCl₃ solution) spectroscopy. Selected data: **1**, red crystals, ν (CO) 1989m, 1943s and 1759m, ¹³C-{¹H} NMR δ 225.0 (s, br, CO's), 101.5 (s, C₅Me₅), 90.4 (s, C₅H₅) and 9.3 (s, C₅Me₅). **2**, red crystals, ν (CO) 1968s, 1793m, 1742w and 1724w. **3a**, red crystals, ν (CO) 1984vs, 1808s, 1752w and 1709m. **3b**, orange powder, ν (CO) 1990s, 1810m and 1685w. *trans-4*, yellow crystals, ν (CO) 1963s, 1800m and 1704m, ¹³C-{¹H} NMR δ 293.1 (s, μ -C), 244.9 (s, μ -CO), 199.6 (s, CO), 198.9 (s, CO) and 135.7 (s, μ -C=C). *cis-4*, yellow crystals, ν (CO) 2002s, 1965w, 1796m and 1707w, ¹³C-{¹H} NMR δ 245.5 (s, μ -CO), 199.2 (s, CO), 197.5 (s, CO) and 135.1 (s, μ -C=C). *trans-7*, yellow crystals, ν (CO) 1961s and 1790m, ¹³C-{¹H} NMR δ 241.6 (s, μ -CO), 199.8 (s, CO), 199.3 (s, CO), 133.3 (qq, *J* 36, 8 Hz, CCF₃), 122.6 (q, *J* 276 Hz, CF₃), 122.2 (q, *J* 276 Hz, CF₃) and 122.2 (qq, *J* 36, 8 Hz, CCF₃), ¹⁹F NMR δ -50.0 (q, *J* 11 Hz, CF₃) and -55.1 (q, *J* 11 Hz, CF₃). *cis-7*, yellow crystals, ν (CO) 2006vs, 1973m and 1783m, ¹³C-{¹H} NMR δ 239.2 (s, μ -CO), 198.9 (s, CO), 196.7 (s, CO), 127.0 (qq, *J* 36, 7 Hz, CCF₃), 123.3 (q, *J* 274 Hz, CF₃), 123.2 (q, *J* 274 Hz, CF₃) and 120.4 (qq, *J* 36, 9 Hz, CCF₃), ¹⁹F NMR δ -52.3 (q, *J* 13 Hz, CF₃) and -59.8 (q, *J* 13 Hz, CF₃). **8**, green crystals, ν (CO) 1777s cm⁻¹, ¹³C-{¹H} NMR δ 248.3 (s, μ -CO), 127.7 (qq, *J* 48, 3 Hz, 2 CCF₃) and 127.0 (q, *J* 271 Hz, 2 CF₃). ¹⁹F NMR δ -59.0 (s, 2 CF₃).

[‡] Crystal data. For *cis-4*: C₂₄H₂₆O₇Ru₂, *M* = 628.6, orthorhombic, *P*2₁2₁ (no. 19), *a* = 8.500(2), *b* = 14.877(2), *c* = 18.743(3) Å, *V* = 2370.1(8) Å³, *T* = 173 K, *Z* = 4, μ = 1.32 mm⁻¹, 15275 reflections were collected of which 5395 remained after merging of equivalent data, *wR*₃ = 0.057 (for all 5395 data), *R*₁ = 0.034 [for 4374 data with *I* > 2 σ (*I*)]. For *cis-7*: C₂₂H₂₀F₆O₃Ru₂, *M* = 1096.9, triclinic, *P* $\bar{1}$ (no. 2), *a* = 8.784(2), *b* = 8.853(2), *c* = 16.052(3) Å, *a* = 77.99(2), β = 83.95(2), γ = 63.96(2)°, *V* = 1096.9(4) Å³, *T* = 173 K, *Z* = 2, μ = 1.45 mm⁻¹, 11237 reflections were collected of which 4949 remained after merging of equivalent data, *wR*₂ = 0.045 (for all 4949 data), *R*₁ = 0.021 [for 3947 data with *I* > 2 σ (*I*)]. CCDC reference number 186/1918. See <http://www.rsc.org/suppdata/dt/b0/b001666g/> for crystallographic files in .cif format.

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