

**The Mechanism of Isomerisation of the C=C Bond in Ethenethiolato Ligands Co-ordinated to Molybdenum and Tungsten. The Molecular Structures of (*E*)-*exo*-[W{ $\eta^3$ -SC(CF<sub>3</sub>)=C(CF<sub>3</sub>)H}(CF<sub>3</sub>C $\equiv$ CCF<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] and (*Z*)-*endo*-[W{ $\eta^3$ -SC(CF<sub>3</sub>)=C(CF<sub>3</sub>)H}(CF<sub>3</sub>C $\equiv$ CCF<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)]**

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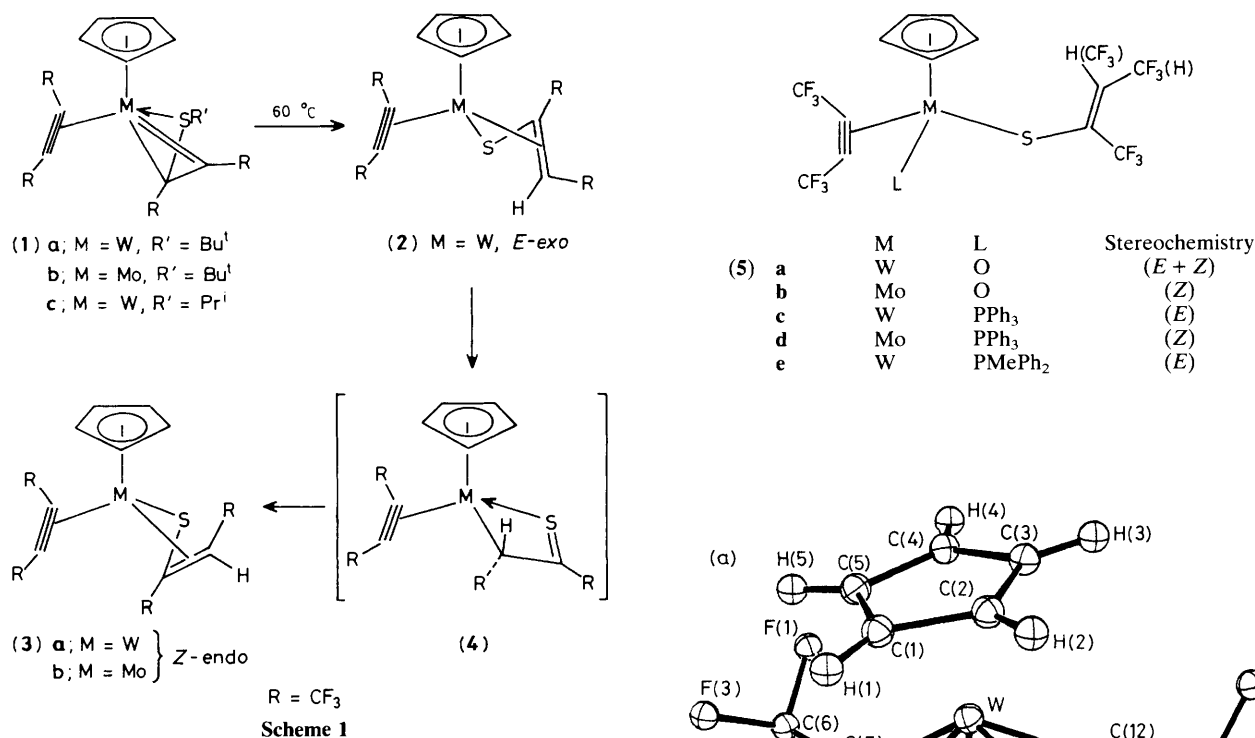
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Thermolysis of the  $\eta^2$ -vinyl complex [W{ $\eta^3$ -C(CF<sub>3</sub>)C(CF<sub>3</sub>)SBut}(CF<sub>3</sub>C $\equiv$ CCF<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] gives the  $\eta^3$ -ethenethiolato derivative (*E*)-*exo*-[W{ $\eta^3$ -SC(CF<sub>3</sub>)=C(CF<sub>3</sub>)H}(CF<sub>3</sub>C $\equiv$ CCF<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)], which undergoes concomitant *exo*  $\rightarrow$  *endo* and *E*  $\rightarrow$  *Z* isomerisation to give (*Z*)-*endo*-[W{ $\eta^3$ -SC(CF<sub>3</sub>)=C(CF<sub>3</sub>)H}(CF<sub>3</sub>C $\equiv$ CCF<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)], thus providing evidence for a ring-flip mechanism in metal-promoted alkene isomerisations.

The ability of transition metals to promote changes in the stereochemistry of carbon-carbon double bonds is well known, and a variety of mechanisms have been put forward to account for the transformation. In the case of isomerisations involving  $\sigma$ -vinyl ligands  $\eta^1$ -ionic<sup>1</sup> or  $\eta^2$ -bonded intermediates<sup>2</sup> have been proposed, whereas isomerisation of buta-

dienyl complexes of palladium,<sup>3</sup> and recently rhodium,<sup>4</sup> has been explained in terms of a 'ring-flip' process. Our recent studies of  $\eta^2$ -vinyl complexes (**1**) now provide clear evidence for the participation of a 'ring-flip' process in the isomerisation of C=C bonds.

Thermolysis of the  $\eta^2$ -vinyl complex (**1a**)<sup>5</sup> in hexane at



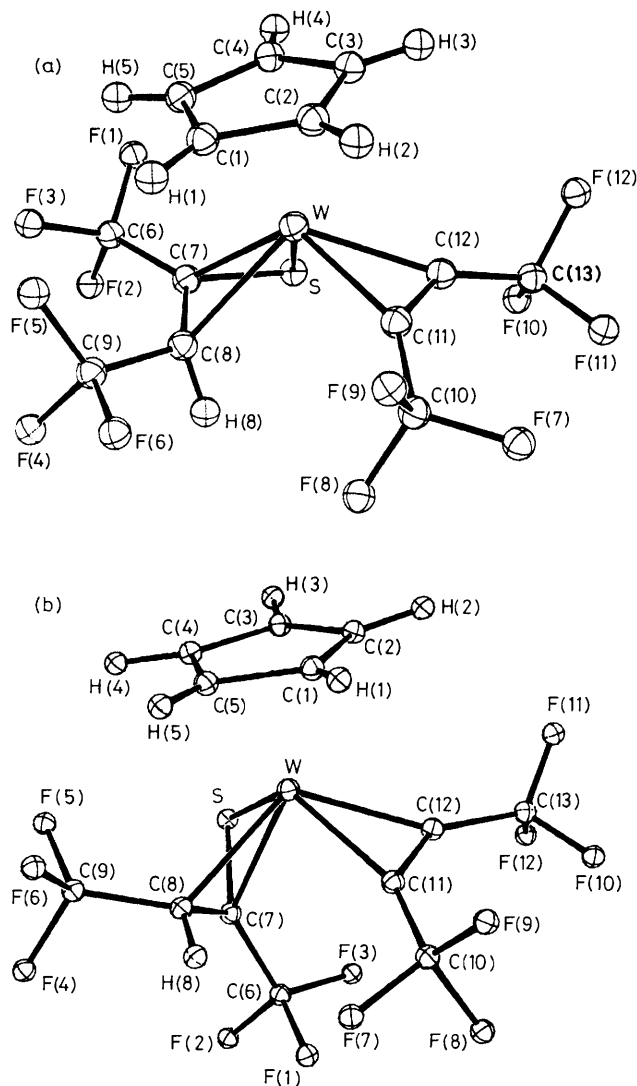
60°C, gives the ethenethiolato derivative (2) which subsequently isomerises under these conditions to give the thermodynamically favoured complex (3a) in ca. 80% yield (Scheme 1). The complex (1b) similarly gives (3b), but the molybdenum equivalent of (2) was not detected in this reaction. N.m.r. spectroscopy (<sup>1</sup>H and <sup>19</sup>F) provided evidence for a *cis*-SC(CF<sub>3</sub>)=C(CF<sub>3</sub>)H moiety in (2),  $J_{FF} = 10.2$  Hz, but a *trans*-arrangement in (3a),  $J_{FF} = 0$  Hz. This was subsequently confirmed by X-ray diffraction studies of (2) and (3a) (see Figure 1),<sup>†</sup> which revealed that loss of the Bu<sup>t</sup>S substituent from (1a) results in transfer of a hydrogen atom to C(8), to yield (2) which contains an ethenethiolato CH(CF<sub>3</sub>)=C(CF<sub>3</sub>)S ligand with the expected *cis*-arrangement of CF<sub>3</sub> groups [C(6)–C(7)–C(8)–C(9) –8(1)°]. Isomerisation to a *trans* configuration across C(7)–C(8) produces (3a) in which the C(6)–C(7)–C(8)–C(9) torsion angle is –119(1)°.

The geometries of the W(η<sup>2</sup>-CF<sub>3</sub>C≡CCF<sub>3</sub>)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) moieties in (2) and (3a) are nearly identical. Each complex also contains a WSC(7)C(8) 'butterfly' in which the W–S bonds are short and the W atom is almost equidistant from C(7) and

<sup>†</sup> Standard experimental and computational techniques were employed for both structure analyses. All measurements were made with Mo-K<sub>α</sub> radiation on an Enraf-Nonius CAD-4F diffractometer.

**Crystal data:** C<sub>13</sub>H<sub>6</sub>F<sub>12</sub>SW,  $M_r = 606.1$ . (a) *cis*-Isomer (2), monoclinic,  $a = 35.551(5)$ ,  $b = 7.072(1)$ ,  $c = 13.548(2)$  Å,  $\beta = 107.00(1)^\circ$ ,  $U = 3282(1)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 2.453$  g cm<sup>-3</sup>,  $F(000) = 2256$ ,  $\mu(\text{Mo-K}\alpha) = 74.3$  cm<sup>-1</sup>, space group C2/c. Full-matrix least-squares refinement of 244 parameters gave  $R = 0.025$ ,  $R_w = 0.031$  for 2610 unique reflections. (b) *trans*-Isomer (3a), monoclinic,  $a = 7.353(3)$ ,  $b = 15.764(12)$ ,  $c = 14.205(5)$  Å,  $\beta = 94.81(3)^\circ$ ,  $U = 1641(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.454$  g cm<sup>-3</sup>,  $F(000) = 1128$ ,  $\mu(\text{Mo-K}\alpha) = 74.3$  cm<sup>-1</sup>, space group P2<sub>1</sub>/n. Full-matrix least-squares refinement of 268 parameters gave  $R = 0.027$ ,  $R_w = 0.034$  for 2167 unique reflections. For (2), H-atoms were constrained to ride on the C-atoms to which they were bonded (C–H 0.96 Å) whereas for (3a) H-atom parameters were refined.

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.



**Figure 1.** The molecular structures of (a) the *cis*-isomer (2) and (b) the *trans*-isomer (3a) of [W{CH(CF<sub>3</sub>)=C(CF<sub>3</sub>)S}(η<sup>2</sup>-CF<sub>3</sub>C<sub>2</sub>CF<sub>3</sub>)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)]. Corresponding atoms are numbered identically. Respective selected bond lengths in (2) and (3a) are: W–S 2.303(2) and 2.275(3), W–C(7) 2.166(6) and 2.174(8), W–C(8) 2.211(6) and 2.210(8), W–C(11) 2.074(6) and 2.082(8), W–C(12) 2.079(7) and 2.058(8), S–C(7) 1.757(7) and 1.744(9), C(7)–C(8) 1.448(8) and 1.440(12), C(11)–C(12) 1.266(9) and 1.292(11) Å.

C(8). However, the orientations of the WSC(7)C(8) units are markedly different in the two complexes: the Cp–W–C(7)–C(6) torsion angles, where Cp is the cyclopentadienyl ring centroid, are respectively 22 and 180°. The differing orientations of the ethenethiolato ligands in (2) and (3a) are reminiscent of the *endo/exo* rotamers which have been postulated to explain the fluxionality of (C<sub>5</sub>H<sub>5</sub>)M(allyl) complexes (M = Mo or W)<sup>6</sup> and it is convenient to view the W–ethenethiolato interactions in (2) and (3a) as quasi- $\pi$ -allylic in character. The W–S bonds are on average 0.17 Å shorter than the corresponding bond in (1c), whereas the mean W–C(alkyne) distances, respectively 2.08, 2.08 and 2.07 Å in (1c), (2) and (3a), are nearly identical in the three complexes. This suggests that the W–SC<sub>2</sub> allylic bonding in (2) and (3a) is supported by S→W  $\pi$ -donation and that the  $\eta^2$ -CF<sub>3</sub>C≡CCF<sub>3</sub> ligands behave as two-electron donors as in (1) rather than as the four-electron donors suggested by formal electron counting and by analogy with [Mo(SC<sub>6</sub>F<sub>5</sub>)(CO)(CF<sub>3</sub>C≡CCF<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)].<sup>7</sup>

Despite these differences in metal–alkyne bonding, (2) and (3) exhibit reactivity similar to that of the complexes [MSC<sub>6</sub>F<sub>5</sub>(CO)(CF<sub>3</sub>C≡CCF<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] (M = Mo or W)<sup>7</sup> in forming 1:1 addition products (5) on reaction with dioxygen (hexane; 20–40°C) or tertiary phosphines (hexane; 70°C). The complexes (5) apparently contain an  $\eta^1$ -SC(CF<sub>3</sub>)=C(CF<sub>3</sub>)H ligand resulting from de-co-ordination of the alkene C=C bond: spectroscopic data (5d): i.r.(CDCl<sub>3</sub>)  $\nu_{C=C}$  1672w and  $\nu_{C-C}$  1635w cm<sup>-1</sup>; n.m.r. <sup>1</sup>H(CDCl<sub>3</sub>)  $\delta$  7.1–7.8 (br, m, 15H) 6.29 (q,  $J_{HF}$  7.5 Hz, 1H), and 4.96 (d,  $J_{HP}$  0.5 Hz, 5H); <sup>19</sup>F [(CD<sub>3</sub>)<sub>2</sub>CO; –50°C]  $\delta$  –51.97 (m, 3F, CF<sub>3</sub>C≡C), –55.35 (m, 3F, CF<sub>3</sub>C≡C), –58.78 [dq,  $J_{FH}$  7.5,  $J_{FF}$  1.5 Hz, 3F, C=C(CF<sub>3</sub>)H], and –61.31 [br, s, 3F, SC(CF<sub>3</sub>)=C]. The reactions of (2a) with PPh<sub>3</sub> and dioxygen, which were followed by <sup>19</sup>F n.m.r. spectroscopy, gave (5c) and the *E*-isomer of (5a) exclusively, demonstrating that de-co-ordination occurs with retention of stereochemistry at the C=C bond. This result indicates that isomerisation of the C=C

bond, (2) → (3a) is probably not influenced by external reagents, in contrast with some cases where rearrangement is promoted by nucleophilic attack at an alkene carbon atom.<sup>1</sup>

The fact that the reaction (2) → (3a) involves concomitant *exo* → *endo* and *E* → *Z* isomerisations strongly suggests a common pathway for the two processes, and in particular an intermediate of type (4). The  $\eta^3 \rightarrow \eta^2 \rightarrow \eta^3$  changes in bonding which occur in the process (2) → (4) → (3) simultaneously achieve *exo* → *endo* and *E* → *Z* isomerisation. We also note that related 'ring-flip' mechanisms have been independently proposed on previous occasions to explain *E* → *Z* isomerisation in butadienyl complexes<sup>3,4</sup> and *exo* → *endo* isomerisation in 1,3-diene derivatives.<sup>8</sup>

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