The Mechanism of Metal-promoted 1,3-Sulphur Shifts involving the Apparent Insertion of Carbon Monoxide into a Carbon–Sulphur Bond

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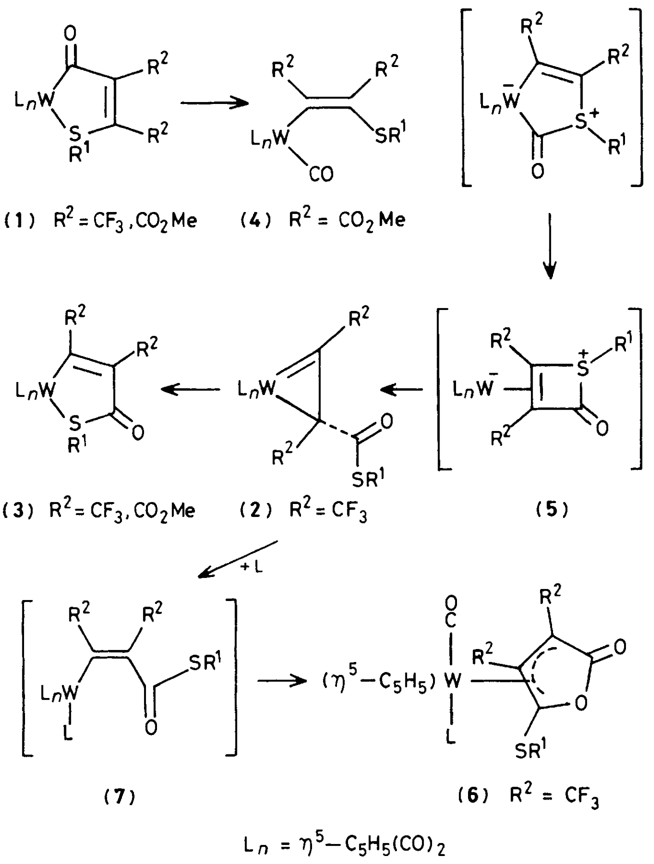
The isomerisation of the acyl chelate complex $[W\{C(O)C(CO_2Me):C(CO_2Me)SR\}(CO)_2(\eta\text{-}C_5H_5)]$ into $[W\{C(CO_2Me):C(CO_2Me)C(O)SR\}(CO)_2(\eta\text{-}C_5H_5)]$ (R = Me or Pr^i), which involves a 1,3 shift of the SR group, has been shown to proceed *via* the mercapto vinyl complex $[W\{\sigma\text{-}C(CO_2Me):C(CO_2Me)SR\}(CO)_3(\eta\text{-}C_5H_5)]$, illustrating that the mechanism involves deinsertion of the acyl carbon monoxide followed by apparent insertion of co-ordinated CO into the C–S bond of the vinyl ligand.

Previously[1] we have demonstrated that metallocyclic complexes (**1**), obtained from the reaction of $[WSR^1(CO)_3(\eta\text{-}C_5H_5)]$ (R^1 = Me or Et) with $R^2C{\equiv}CR^2$ ($R^2 = CF_3$ or CO_2Me), undergo an unusual 1,3 sulphur shift which, in the case R^1 = Me, $R^2 = CF_3$, proceeds *via* a novel η^2-vinyl intermediate (**2**) to give complexes (**3**). We now report that when $R^2 = CO_2Me$ the isomerisation proceeds *via* an σ-vinyl complex (**4**) thus providing evidence for an unusual 1,3 shift mechanism.†

Complexes (**1**; R^1 = Me or Pr^i; $R^2 = CO_2Me$) were obtained as before[1] from the reaction of $[WSR^1(CO)_3(\eta\text{-}C_5H_5)]$ with $MeO_2CC{\equiv}CCO_2Me$ in hexane at 20 °C. Thermolysis of (**1**) has been shown previously to give (**3**; R^1 = Me, $R^2 = CO_2Me$),[1] characterised by *X*-ray diffraction studies.[2] We have now established that with R^1 = Pr^i a similar reaction occurs but at 50 °C a yellow tricarbonyl intermediate is isolated in moderate yield which has structure (**4**) according to spectroscopic data: i.r. ($CHCl_3$) ν(CO) 2039s, 1958vs, and 1936s; ν(>C=O) 1710m cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 5.56 (s, 5H, C_5H_5), 3.70 (s, 3H), 3.69 (s, 3H, CO_2Me), 3.30 (septet, 1H), and 1.24 (d, 6H, $CHMe_2$); mass spectrum *m/z* 550, $[M]^+$ and ions $[M - CO]^+$, $[M - 2CO]^+$, and $[M - 3CO]^+$. The geometry of the vinyl ligand cannot be assigned from the data available but is presumably *cis* as in (**1**) and (**3**). Careful work established that traces of a similar species are formed on controlled thermolysis of (**1**; R^1 = Me, $R^2 = CO_2Me$) but conversion into (**3**) occurs more readily than with the isopropyl derivative.



Scheme 1

The transformations (**1**) → (**4**) → (**3**) involve expulsion of CO from the heterocyclic ring and W–S bond fission followed apparently by insertion of a carbonyl ligand into a C–S bond of the vinyl ligand. This and other known features of the 1,3 shift reaction can be accommodated by the mechanism in Scheme 1 in which nucleophilic attack on co-ordinated CO in (**4**) is followed by ring closure to give (**5**) and subsequent ring opening to give the η^2-vinyl complex (**2**). Previously[3] we have isolated zwitterionic heterocyclic complexes related to (**5**) and demonstrated their formation *via* a ring closure analogous to the transformation (**1**) → (**5**). Heterocyclic analogues of (**5**) are also implicated in the protonation reactions of $[Fe\{C(CH_2OH){=}C{=}CH_2\}(CO)_2(\eta\text{-}C_5H_5)]$[4] while acyl nitrogen chelate complexes related to (**1**) undergo oxidation to produce β-lactams.[5]

Recent interest in the chemistry of η^2-vinyl complexes, in particular the possibility that they may act as precursors to σ-vinyl derivatives,[6] suggested that reactions of (**2**) with nucleophiles might be informative. Reactions with nucleophiles L = CNBu^t, PMe_2Ph, or $P(OMe)_3$ (20 °C, diethyl ether) gave monocarbonyl complexes (**6**) for which a lactone structure is proposed: spectroscopic data, (**6**; R^1 = Pr^i, L = CNBu^t): i.r. (CH_2Cl_2) ν(C≡N), 2172, ν(CO) 1990s, ν(>C=O) 1742 cm^{-1}; n.m.r. ($CDCl_3$) ^{1}H, δ 5.28 (s, 5H, C_5H_5), 3.26 (septet, 1H, C*H*Me$_2$, *J* 6.9 Hz), 1.48 (s, 9H, Bu^{t}NC), 1.32 (d, 3H CH*Me*$_2$, *J* 6.8 Hz), and 1.21 (d, 3H, CH*Me*$_2$, *J* 6.9 Hz); ^{19}F, δ −55.4 (3F, q, J_{FF} 8.2 Hz) and −56.7 (3F, q, J_{FF} 8.2 Hz); mass spectrum *m/z* 652, $[M]^+$ and ions $[M - CO]^+$ and $[M - Pr^i]^+$. This proposal is supported by our observation that (**2**; R^1 = Me or Pr^i) reacts similarly with carbon monoxide (8 atm, 20 °C) to give (**6**; L = CO) characterised previously by *X*-ray diffraction studies when R^1 = Me.[7] This complex was originally obtained[7] from the photochemical reaction of $CF_3C{\equiv}CCF_3$ with $[WSMe(CO)_3(\eta\text{-}C_5H_5)]$ in a sealed tube, presumably *via* the reaction of (**2**; R^1 = Me) with CO generated during the reaction. Related lactone complexes have been isolated from the reaction of vinyl ketone derivatives $[Mo\{CMe{=}CMe(COR)\}(CO)_2(\eta\text{-}C_5H_5)]$ with CO, CNBu^t, or PPh_3 and it was proposed that ring formation proceeds *via* the σ-vinyl intermediate (**7**).[8] The reaction (**2**) → (**6**) could clearly involve a similar intermediate

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† Satisfactory elemental analyses have been obtained for all complexes.

as a result of a co-ordination-promoted $\eta^2 \rightarrow \sigma$ vinyl transformation, *i.e.* (**2**) → (**7**) → (**6**).

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