The Unusual Stevens Type Rearrangements of Some Dialkyl Sulfides on a Rh–Rh Bond

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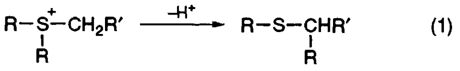
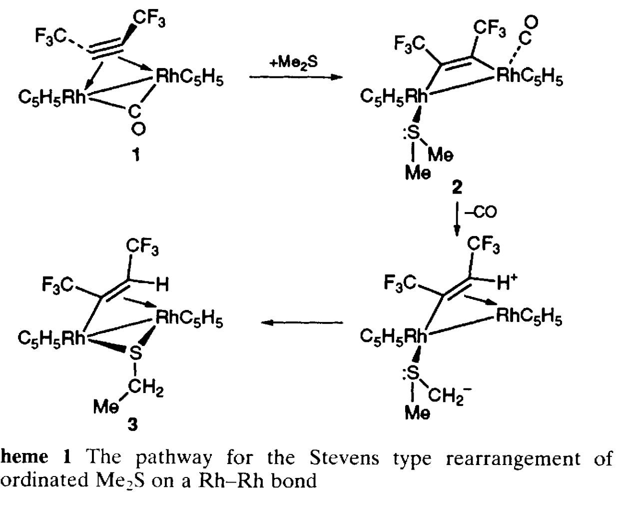
The coordinative addition of dimethyl sulfide to $(C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ is followed by an intramolecular transformation to give $(C_5H_5)_2Rh_2(\mu\text{-}SCH_2Me)\{\mu\text{-}C(CF_3)CH(CF_3)\}$, and the corresponding reaction with Et_2S gives a related complex with a chiral bridging sulfido group SCHMeEt.

The range of organic transformations induced by metal complexes has been expanded through use of polynuclear metal–metal bonded complexes.[1] One reason for this is that metal–metal bonds extend the variety of possible bonding modes for organic ligands, and this may lead to novel synthetic pathways and ultimately to new organic syntheses. Our previous studies[2] with the dirhodium complex $(C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ **1** have revealed an incredible array of reaction types in which bridging groups are implicated. Here we report the reactions of **1** with some dialkyl sulfides that involve unexpected rearrangements, including the conversion of a terminally coordinated dimethyl sulfide ligand to a bridging ethylsulfido group.

When **1** is treated with excess Me_2S (hexane, room temperature), there is an immediate colour change from green to red corresponding to formation of the coordinative addition product $(C_5H_5)_2Rh_2(CO)(SMe_2)(\mu\text{-}CF_3C_2CF_3)$ **2**. This product has been fully characterized in solution, but attempts to isolate it by removal of volatiles results in loss of Me_2S and reformation of **1**. Distinctive spectroscopic features for **2** are a terminal carbonyl stretching frequency at 1988 cm^{-1} in the IR spectrum, and two singlet resonances at δ 5.42 and 5.21 for the inequivalent cyclopentadienyl groups in the ^1H NMR spectrum; the resonance for the coordinated dimethyl sulfide is obscured by that for the free ligand. If **2** is left in solution in the presence of excess Me_2S, there is a further colour change over several hours to purple. Chromatographic workup gives purple crystals of $(C_5H_5)_2Rh_2(\mu\text{-}SCH_2Me)\{\mu\text{-}C(CF_3)CH(CF_3)\}$ **3** in 63% yield. Analytical and spectroscopic data† are consistent with this formula, but the apparent conversion of Me_2S to SCH_2Me was so unexpected that we decided to determine the structure of **3** by an X-ray crystal structure determination.‡ This revealed the molecular structure shown in Fig. 1 and confirmed the formation of bridging alkenyl and sulfido groups. We view the formation of **3** from **2** as a metal mediated Stevens rearrangement. In the conventional Stevens rearrangement of sulfur compounds,[3] a sulfonium ion is treated with base leading to migration of a group from sulfur to an adjacent carbon atom as depicted in eqn. (1). In our situation, the coordination of sulfur to rhodium creates a sulfonium ion equivalent, and the coordinated hexafluorobut-2-yne serves as the proton acceptor. A suggested pathway for the rearrangement is shown in Scheme 1. The intermediate in the conversion of **2** to **3** has not been identified. An alternative representation **4** is possible, but we favour the zwitterion form shown in Scheme 1 because it would be more likely than **4** to rearrange. Regardless of the nature of the intermediate, activation of a methyl C–H bond has occurred under remarkably mild conditions. The complex **3** is more readily formed by treatment of **1** with the thiol EtSH.

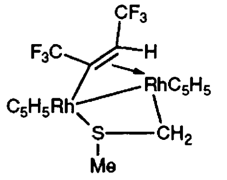


$$R\text{-}\overset{+}{\underset{R}{S}}\text{-}CH_2R' \xrightarrow{-H^+} R\text{-}S\text{-}\underset{R}{C}HR' \quad (1)$$



Scheme 1 The pathway for the Stevens type rearrangement of coordinated Me_2S on a Rh–Rh bond

To test the generality of the rearrangement shown in Scheme 1, we examined reactions with other dialkyl sulfides. The corresponding reaction with diethyl sulfide yields an addition product $(C_5H_5)_2Rh_2(CO)(SEt_2)(\mu\text{-}CF_3C_2CF_3)$ **5** [IR ν/cm^{-1} 1990] which converts in solution to three products which can be separated by chromatography. One is the known[4] dicarbonyl complex $(C_5H_5)_2Rh_2(CO)_2(\mu\text{-}CF_3C_2CF_3)$ (37% yield) which is formed from **1** and CO that is released in the production of the other products. There are two μ-sulfido species, one of which is **3**; this is isolated in 31% yield. We propose that **3** is generated from **4** by the elimination of ethene from one ethyl group in the coordinated diethyl sulfide and proton transfer of the remaining H to the alkyne. The order of these events has not been established. The other product was isolated in 10% yield and characterized from spectroscopic results§ as $(C_5H_5)_2Rh_2(\mu\text{-}SCHMeEt)\{\mu\text{-}C(CF_3)CH(CF_3)\}$ **6**. The formation of **6** presumably involves a Stevens rearrangement in which transfer of a methylene proton preceeds the



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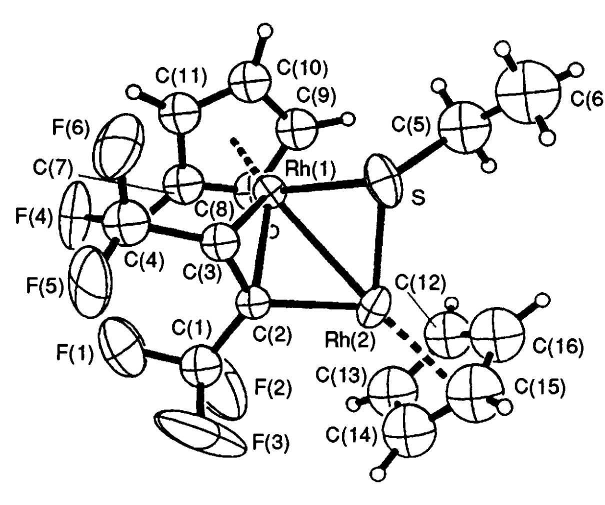

rearrangement. Two stereoisomers of **6** are possible, and NMR data indicate that a racemic mixture has been formed. It is possible to form **6** in high yield from **1** and the thiol EtMeHSH.

The reaction between **1** and Pr_2S yields the initial addition product, but there is no evidence of rearrangement when this complex is left in solution for several hours. No reaction occurs when Pr^i_2S is added to **1** in solution. Thus the size of the R groups is important in controlling the course of these reactions.

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Footnotes

† *Selected spectroscopic data* for **3**; IR, no ν(CO) peaks observed; ^1H NMR ($CDCl_3$) δ 5.49 (s, 5H, Cp), 5.31 (s, 5H, Cp), 2.64 (m, 2H, CHH′), 1.44 [q, 1H, ^3J(H–CF_3) 10.0 Hz, C(CF_3)H], 1.37 [t, 3H, ^3J(H–H) 7.5 Hz, Me]; ^{19}F NMR ($CDCl_3$) δ −50.3 [q, 3F, ^5J(F–F) 12.7 Hz, CF_3] and −53.8 [m, 3F, ^3J(F–H) 10.0 Hz and ^5J(F–F) 12.7 Hz, CF_3]; MS, *m/z* (relative intensity) 560 (20, M^+), 531 (10, $[M - Et]^+$), 368 (30, $C_{10}H_{10}Rh_2S^+$), 303 (15, $C_5H_5Rh_2S)^+$, 233 (100, $C_{10}H_{10}Rh^+$).

‡ *Crystal data* for **3**: $C_{16}H_{16}F_6Rh_2S$, M = 560.2, orthorhombic, space group *Pbca*, a = 16.061(2), b = 18.165(2), c = 12.344(3) Å, U = 3601(1) Å^3, Z = 8, D_c = 2.07, D_m = 2.06(1), Mo-Kα radiation, R = 0.066 for 2080 unique reflections with $I > 3\sigma I$ collected in the range $6° < 2\theta < 60°$. We thank Dr G. Fallon of this department for providing and refining the crystal data. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre. See Information for Authors, Issue No. 1.

§ *Selected spectroscopic data* for **6**: IR, no ν(CO) peaks observed; ^1H NMR ($CDCl_3$) δ 5.50 and 5.48 (2 × s, 5H, C_5H_5), 5.33 and 5.31 (2 × s, 5H, C_5H_5), 2.50 (m, 1H, CH), 1.9–1.6 (m, 2H, CH_2), 1.49 [q, 1H, ^3J(H–CF_3) 10.0 Hz, C(CF_3)H], 1.35 and 1.32 [2 × d, 3H, ^3J(H–H) 6.7 Hz, Me], 1.00 [td, 3H, ^3J(H–H) 7.5 Hz and ^4J(H–H) 1.5 Hz, Me]; ^{19}F NMR ($CDCl_3$) δ −49.9 (overlapping q with 0.02 ppm separation, 3F, CF_3) and −53.9 (m, 3F, CF_3); ^{13}C NMR ($CDCl_3$) δ 86.1 and 86.0 (2 × s, Cp), 83.7 and 83.6 (2 × s, Cp), 55.7 and 55.6 (2 × s, CH), 33.4 and 32.3 (2 × s, CH_2), 23.2 and 22.1 (2 × s, S–CH–Me), 11.4 (s, CH_3 of ethyl); MS, *m/z* (relative intensity) 588 (6, M^+).

References

1 See, for example, R. D. Adams, Z. Li, P. Swepston, W. Wu and J. Yamamoto, *J. Am. Chem. Soc.*, 1992, **114**, 10657.

2 R. S. Dickson, Polyhedron Special Report No. 39, *Polyhedron*, 1991, **10**, 1995.

3 See, for example, R. K. Olson and J. O. Currie, Jr., in *The Chemistry of the Thiol Group, Part 2*, ed. S. Patai, Wiley 1974, ch. 12, p. 56.

4 R. S. Dickson, G. N. Pain and S. H. Johnson, *Organomet. Synth.*, 1988, **4**, 283; R. S. Dickson and S. H. Johnson, *Aust. J. Chem.*, 1978, **31**, 661.