Hydrosulfination of Alkynes: Synthesis of Vinyl Sulfinato Complexes of Ruthenium(II)

Anthony F. Hill

Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY, E-mail: a.hill@ic.ac.uk

The reaction of [RuClH(CO)(PPh₃)₃] with alkynes (R¹C=CR²) and SO₂ provides the vinylsulfinate-*S*,*O* complexes [Ru(η^2 -SO₂CR¹=CHR²)Cl(CO)(PPh₃)₂] in a process reminiscent of hydroformylation.

The insertion of sulfur dioxide into transition metal σ -alkyl and σ -aryl bonds has been extensively studied and is now one of the best understood reactions in organotransition metal chemistry.¹ Surprisingly, however, very few useful applications of this reaction have been developed in dramatic contrast to carbonyl insertion. A potentially close analogy between CO and SO₂ in catalytic processes has been illustrated very recently in the palladium catalysed hydrosulfination of olefins² and an early report of the palladium chloride mediated condensation of ethene and SO₂ to EtSO₂CH₂CH=CHMe almost certainly also involves related processes.³ This report describes one such situation, namely the hydrosulfination of alkynes which may be viewed as a model process for the sulfur dioxide analogue of alkyne hydroformylation.

Treating a suspension of [RuClH(CO)(PPh₃)₃] with a range of alkynes, R¹C=CR² (Scheme 1), in the presence of sulfur dioxide leads to the pale yellow or colourless vinyl sulfinate complexes [Ru(SO₂CHR¹=CHR)Cl(CO)(PPh₃)₂] in spectroscopically† quantitative yield and isolated yields of 63-89% depending on the alkyne employed. The coordination of the sulfinate group to the 15 electron ruthenium centre in these and the related toluene sulfinates $[M(SO_2C_6H_4Me-4)Cl(CO) (PPh_3)_2$] (M = Ru, Os)⁵ remains, in the absence of crystallographic data, a matter for conjecture; however, infrared data for the RuSO₂ group are consistent with neither monodentate S nor O coordination. It therefore appears most likely that a weak or hemilabile dative interaction of one sulfoxide of an S-sulfinate operates (Scheme 1). This is supported by the rapid reaction with π -acid ligands to provide the complexes [Ru-(OSOCR¹=CHR²)Cl(CO)(L')(PPh₃)₂] (L' = CO, CNBu^t, CNC₆H₃Me₂-2,6), accompanied by an apparent rearrangement of the sulfinate to the monodentate O-bound coordination mode



Scheme 1 L = PPh₃, L' = CO, $CNC_6H_3Me_2-2.6$, $CNBu^t$ (**trans* vinyl geometry)

as indicated by IR data and supported by precedent for the related toluene sulfinate complex.⁵ In the absence of such ligands, the dihapto-S,O complexes are stable towards linkage isomerism.

Our view of the mechanism is based on the following observations: (i) The complex [RuClH(CO)(PPh₃)₃] reacts reversibly with SO₂ to provide [RuClH(CO)(SO₂)(PPh₃)₂]. (ii) Reaction of $[RuClH(CO)(PPh_3)_3]$ with alkynes provides $[Ru(\sigma$ vinyl)Cl(CO)(PPh₃)₂].⁴ (iii) Reaction of the related σ -aryl complex $[Ru(C_6H_4Me)Cl(CO)(PPh_3)_2]$ with SO₂ provides the sulfinate [Ru(SO₂C₆H₄Me)Cl(CO)(PPh₃)₂].⁵ (iv) The σ-vinyl complexes [Ru(R1CH=CHR2)Cl(CO)(PPh3)2] may be prepared separately and converted to the corresponding sulfinates on treatment with SO₂. (v) The sulfination of the preformed σ vinyl complexes is essentially instantaneous at room temperature; however, the temperature required for alkyne insertion varies according to the nature of the alkyne. (vi) In the reaction of $[Os(C_6H_4Me-4)Cl(CO)(PPh_3)_2]$ with SO₂, the insertion reaction was retarded by high concentrations of SO_2 (e.g. as a solvent) and this is due to the competitive though reversible formation of an isolable SO2 adduct with this ligand trans to the σ -aryl group and therefore unavailable for an intramolecular migratory insertion. In the case of the ruthenium analogue, the product of such a reaction could not be isolated due to the increased reaction rates, and such a compound may also reversibly divert the reaction sequence for the alkyne hydrosulfination process described here. These points lead us to the mechanism depicted in Scheme 1.

I wish to thank Johnson Matthey Ltd for the generous loan of ruthenium salts.

Received, 26th September 1994; Com. 4/05876C

Footnote

† *Spectroscopic data* for [Ru(O₂SCHCHC₆H₄Me-4)Cl(CO)(PPh₃)₂]: (Pale yellow) IR/cm⁻¹ (Nujol): 1972 [ν(CO)], 1609 [ν(C=C)], 1174, 1039, 974 [ν(SO₂)]; (CH₂Cl₂) 1973 [ν(CO)]. ¹H NMR (CDCl₃, 25 °C) 2.33 (s, 3H, C₆H₄Me), 6.29, 6.46 (AB, 2 H, RuSCH=CH, $J_{AB} = 18$ Hz), 6.90, 7.09 [(AB)₂, 4 H, C₆H₄Me, $J_{AB} = 9$ Hz], 7.40, 7.60 [m(br)x2, 30 H, PC₆H₅]. FABMS (nba matrix): m/z = 869 [9%, M⁺], 655 [23%, M – ClSO₂CHCHC₆H₄Me]; 625 [20%, Ru(PPh₃)₂+]. The product obtained for MeOCOC=CCO₂Me has the less common *trans* vinyl geometry, this being preferred in the intermediate κ^2 -vinyl complex due to chelation by one ester group.⁴

References

- 1 A. Wojcicki, Adv. Organomet. Chem., 1974, 12, 31.
- 2 W. Keim and J. Herwig, J. Chem. Soc., Chem. Commun., 1993, 1592.
- 3 H. S. Klein, J. Chem. Soc., Chem. Commun., 1968, 377.
- 4 M. R. Torres, A. Vegas, A. Santos and J. Ros, J. Organomet. Chem., 1986, 309, 169.
- 5 M. Herberhold and A. F. Hill, J. Organomet. Chem., 1988, 353, 243.
- 6 A. F. Hill, Adv. Organomet. Chem., 1994, 36, 159.