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

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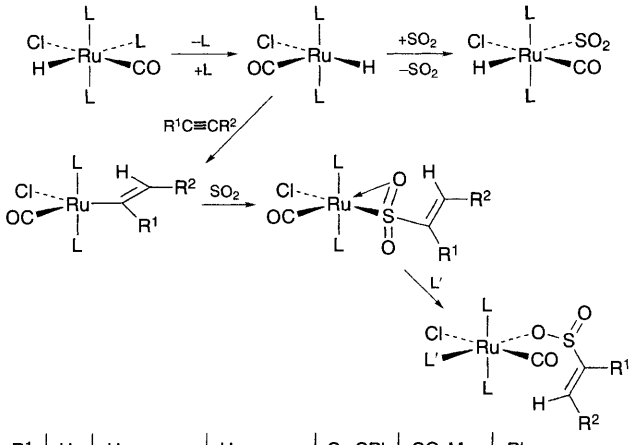
The reaction of $[RuClH(CO)(PPh_3)_3]$ with alkynes ($R^1C{\equiv}CR^2$) and SO_2 provides the vinylsulfinate-*S,O* complexes $[Ru(\eta^2\text{-}SO_2CR^1{=}CHR^2)Cl(CO)(PPh_3)_2]$ in a process reminiscent of hydroformylation.

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 SO_2 in catalytic processes has been illustrated very recently in the palladium catalysed hydrosulfination of olefins[2] and an early report of the palladium chloride mediated condensation of ethene and SO_2 to $EtSO_2CH_2CH{=}CHMe$ 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 $[RuClH(CO)(PPh_3)_3]$ with a range of alkynes, $R^1C{\equiv}CR^2$ (Scheme 1), in the presence of sulfur dioxide leads to the pale yellow or colourless vinyl sulfinate complexes $[Ru(SO_2CHR^1{=}CHR)Cl(CO)(PPh_3)_2]$ 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 $[M(SO_2C_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$ (M = Ru, Os)[5] remains, in the absence of crystallographic data, a matter for conjecture; however, infrared data for the $RuSO_2$ 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 $[Ru(OSOCR^1{=}CHR^2)Cl(CO)(L')(PPh_3)_2]$ (L′ = CO, $CNBu^t$, $CNC_6H_3Me_2\text{-}2,6$), accompanied by an apparent rearrangement of the sulfinate to the monodentate *O*-bound coordination mode 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.



R^1	H	H	H	C≡CPh	CO_2Me	Ph
R^2	Ph	$C_6H_4Me\text{-}4$	$CH_2PPh_3^+$	Ph	CO_2Me^*	Ph

Scheme 1 L = PPh_3, L′ = CO, $CNC_6H_3Me_2\text{-}2,6$, $CNBu^t$ (**trans* vinyl geometry)

Our view of the mechanism is based on the following observations: (i) The complex $[RuClH(CO)(PPh_3)_3]$ reacts reversibly with SO_2 to provide $[RuClH(CO)(SO_2)(PPh_3)_2]$. (ii) Reaction of $[RuClH(CO)(PPh_3)_3]$ with alkynes provides $[Ru(\sigma\text{-vinyl})Cl(CO)(PPh_3)_2]$.[4] (iii) Reaction of the related σ-aryl complex $[Ru(C_6H_4Me)Cl(CO)(PPh_3)_2]$ with SO_2 provides the sulfinate $[Ru(SO_2C_6H_4Me)Cl(CO)(PPh_3)_2]$.[5] (iv) The σ-vinyl complexes $[Ru(R^1CH{=}CHR^2)Cl(CO)(PPh_3)_2]$ may be prepared separately and converted to the corresponding sulfinates on treatment with SO_2. (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 $[Os(C_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$ with SO_2, 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 SO_2 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.

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† *Spectroscopic data* for $[Ru(O_2SCHCC_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$: (Pale yellow) IR/$cm^{-1}$ (Nujol): 1972 [ν(CO)], 1609 [ν(C=C)], 1174, 1039, 974 [$\nu(SO_2)$]; (CH_2Cl_2) 1973 [ν(CO)]. ^1H NMR ($CDCl_3$, 25 °C) 2.33 (s, 3H, C_6H_4Me), 6.29, 6.46 (AB, 2 H, RuSCH=CH, J_{AB} = 18 Hz), 6.90, 7.09 [$(AB)_2$, 4 H, C_6H_4Me, J_{AB} = 9 Hz], 7.40, 7.60 [m(br)x2, 30 H, PC_6H_5]. FABMS (nba matrix): *m/z* = 869 [9%, M^+], 655 [23%, M − $ClSO_2CHCHC_6H_4Me$]; 625 [20%, $Ru(PPh_3)_2^+$]. The product obtained for $MeOCOC{\equiv}CCO_2Me$ has the less common *trans* vinyl geometry, this being preferred in the intermediate κ²-vinyl complex due to chelation by one ester group.[4]

References

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