

Preliminary communication

COMPETITION BETWEEN INSERTION OF SULFUR DIOXIDE INTO THE METHYL— OR PHENYL—TRANSITION METAL BOND

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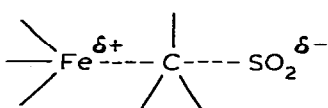
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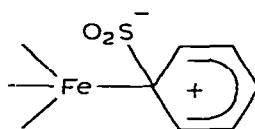
Summary

The first competition experiments between insertion of an unsaturated reagent into the methyl— or phenyl—transition metal bond are reported. For methyl(phenyl)-platinum(II) or -gold(III) derivatives insertion of SO₂ into the methyl—metal bond always occurs, usually with retention of stereochemistry at the metal, and this is the opposite of the trend found for alkyl(aryl) derivatives of main group metals.

The insertion of unsaturated reagents into alkyl—transition metal bonds is of great significance in catalysis and considerable effort has been made to understand the mechanisms involved. Sulfur dioxide insertions have been studied in great detail for coordinatively saturated complexes such as $[(\eta^5\text{-C}_5\text{H}_5)\text{LL}'\text{Fe-R}]$ (L, L' = PPh₃ or CO). When R = alkyl, the reactions occur primarily with inversion of stereochemistry at carbon but retention at the metal, and a mechanism involving electrophilic attack by SO₂ at the backside of R has been proposed (A), but when R = aryl, a Wheland-type intermediate (B) is proposed [1, 2].



(A)



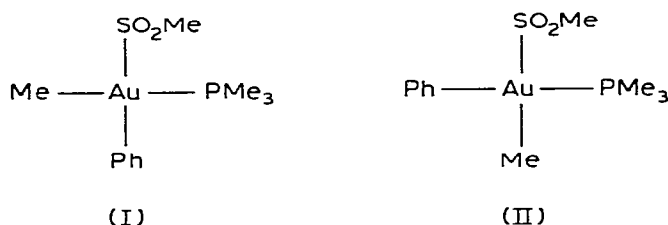
(B)

For coordinatively unsaturated metal complexes, an alternative mechanism is possible in which SO₂ coordinates to the metal followed by migration of the alkyl or aryl group to the coordinated SO₂ to give the insertion product [1, 3].

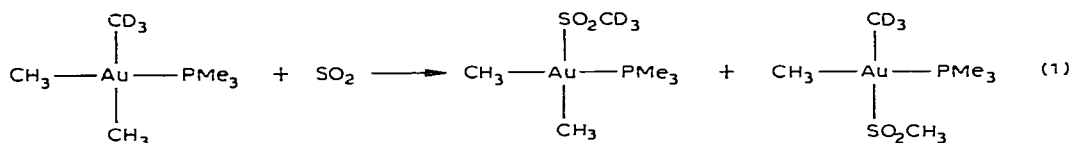
It has been argued that mechanistic information can be obtained by study of

the selectivity of attack by electrophiles on complexes of type $M \begin{smallmatrix} \text{Me} \\ \backslash \\ \text{Ph} \end{smallmatrix}$. Thus, if direct attack at carbon occurs, the phenyl group should be cleaved preferentially due to resonance stabilisation of the Wheland intermediate, whereas, if the electrophile first attacks the metal, the methyl group should be cleaved since the methyl-metal bond is almost certainly weaker than the phenyl-metal bond [4]. Thus HCl cleaves the phenyl-gold bond in *cis*-[AuMe₂Ph(Ph₃)] (attack at carbon predicted), but the methyl-platinum bond in *cis*-[PtMePh(PMePh₂)₂] (attack at platinum predicted). No competition reactions have been reported with unsaturated reagents and methyl(phenyl)-transition metal complexes, and our first studies are concerned with SO₂ insertion reactions. A solution of *cis*-[PtMePh(PMePh₂)₂] in CH₂Cl₂ was treated with an excess of SO₂ at room temperature and gave *cis*-[Pt(SO₂Me)Ph(PMePh₂)₂] which was characterised as the *cis*-*S*-sulfinate derivative by the NMR data (δ (MeS) 2.05s, 3J (PtH) 11 Hz; δ (MeP) 2.26d, 2J (PH) 9 Hz; 1.35d, 2J (PH) 10 Hz, 3J (PtH) 33 Hz; δ (P) 3.72(d), 1J (PtP) 1927 Hz (*trans* to Ph); δ (P) -8.78(d), 1J (PtP) 2652 (*trans* to SMeO₂), 2J (PP) 16 Hz). The presence of non-equivalent phosphine groups and the small value of 2J (PP) proves the *cis*-stereochemistry, while the magnitudes of 1J (PtP) indicate phosphine groups *trans* to carbon and sulfur donors [5] and this confirms the *S*-sulfinate structure indicated by the IR data [1] [ν (SO₂) 1180, 1045 cm⁻¹].

Similar reaction of *cis*-[AuMe₂Ph(PMe₃)] with SO₂ gave [AuMe(SO₂Me)Ph(PMe₃)] again characterised by elemental analysis and by the NMR and IR spectra (δ (MeS) 2.85s; δ (MeP) 1.52d, 2J (PH) 12 Hz; δ (MeAu) 1.22d, 3J (PH) 8.0 Hz; δ (³¹P) 3.08s from TMP reference, ν (SO₂) 1180, 1050 cm⁻¹). The product probably has structure I but minor peaks in the ¹H NMR spectrum were tentatively assigned to the isomeric complex (II).



In order to investigate whether insertion occurs with retention of stereochemistry at gold, reaction of SO₂ with *cis*-[AuMe₂(CD₃)(PMe₃)] was carried out, giving the products of equation 1 in effectively equal proportions.



Integration of the ¹H NMR spectrum gave the ratio MeS/MeAu (*trans* to PMe₃)/MeAu (*cis* to PMe₃) = 1/2/1, showing that the stereochemistry at gold is retained during the insertion. Any scrambling of methyl and methyl-d₃ groups during or after the SO₂ insertion would bring this ratio closer to 1/1.5/1.5.

More complex reactions were observed between SO_2 and gold(III) complexes with triphenylphosphine as ligand. Thus at room temperature *cis*-[AuMe₂Ph(PPh₃)] with SO_2 gave toluene and [Au(SO₂Me)(PPh₃)] as the major products, and intermediate gold(III) species were detected by low temperature ¹H and ³¹P NMR studies. Details of these reaction will be reported later, but it is clear that SO_2 inserts into the methyl-gold bond and that the initial products undergo reductive elimination of toluene.

The observation that retention of stereochemistry at the metal is generally observed during SO_2 insertion is most readily interpreted in terms of the mechanism involving coordination of SO_2 followed by migration of the methyl group but, since 14-electron d^8 complexes are expected to be T-shaped [6], it is also possible that intermediate ion pairs such as [PtPh(PMePh₂)₂]⁺ MeSO₂⁻ could be formed and then combine before stereochemical change at the metal can occur. Of greatest interest is the observation that SO_2 reacts with *cis*-[AuMe₂PhL] (L = PMe₃ or PPh₃) at the methyl-gold bond, whereas simple electrophiles such as HCl or HgCl₂ react by cleaving the phenyl-gold bond [4]. In reactions of SO_2 with main group metal derivatives, Me_nPh_{4-n}Sn, where electrophilic attack by SO_2 at carbon is strongly indicated, the phenyl-tin bond is always cleaved preferentially [7]. We conclude that in insertion of SO_2 into methyl-platinum(II) or methyl-gold(III) bonds, the SO_2 is not acting as a simple electrophilic reagent.

Acknowledgments

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References

- 1 A. Wojcicki, *Advan. Organometal. Chem.*, **12** (1974) 31.
- 2 S.L. Miles, D.L. Miles, R. Bau and T.C. Flood, *J. Amer. Chem. Soc.*, **100** (1978) 7278; M.C. Baird, D. Dong and D.A. Slack, *J. Organometal. Chem.*, **153** (1978) 219.
- 3 F. Faraone, L. Silvestro, S. Sergi and R. Pietropaolo, *J. Organometal. Chem.*, **46** (1972) 379. A. Johnson and R.J. Puddephatt, *J. Chem. Soc. Dalton*, (1977) 1384.
- 4 J.K. Jawad and R.J. Puddephatt, *J. Chem. Soc. Chem. Commun.*, (1977) 892; R.J. Puddephatt and M. Stalteri, unpublished work.
- 5 F.R. Hartley, *The Chemistry of Platinum and Palladium*, Applied Science Publ., London, 1973.
- 6 S. Komiya, T.A. Albright, R. Hoffman and J.K. Kochi, *J. Amer. Chem. Soc.*, **98** (1976) 7255.
- 7 U. Kunze and J.D. Koola, *J. Organometal. Chem.*, **80** (1974) 281.