Journal of Organometallic Chemistry, 353 (1988) 243–249
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The reactions of sulphur dioxide with the coordinatively unsaturated complexes $[MCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2]$ (M = Ru, Os), and the role of the adduct $[OsCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2(SO_2)]$

Max Herberhold * and Anthony F. Hill

Laboratorium für Anorganische Chemie der Universität Bayreuth, Postfach 10 12 51, D-8580 Bayreuth (F.R.G.)

(Received March 21st, 1988)

Abstract

The 16-electron *p*-tolyl complexes $[MCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2]$ (M = Os (**1a**), Ru (**1b**)) react with liquid sulphur dioxide, SO_2, to give the adduct $[OsCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2(SO_2)]$ (**2a**) and the *S*-sulphinate complex $[RuCl_2\{S(=O)_2C_6H_4Me\text{-}4)\}(CO)(PPh_3)_2]$ (**3b**) respectively. The adduct **2a** slowly undergoes conversion in solution into the *S*-sulphinate $[OsCl\{S(=O)_2C_6H_4Me\text{-}4)\}(CO)(PPh_3)_2]$ (**3a**), a process which is retarded by high concentrations of SO_2. The *S*-sulphinate complexes **3** react with carbon monoxide to give the *O*-sulphinates $[MCl\{OS(=O)C_6H_4Me\text{-}4)\}(CO)_2(PPh_3)_2]$ (M = Os (**5a**), Ru (**5b**)). It is suggested that the formation of **2a** represents a diversion rather than an intermediate in the insertion process leading to **3a**.

Introduction

One of the most systematically studied and perhaps the best understood reactions in organotransition-metal chemistry is the "insertion" of sulphur dioxide into the metal σ-organyl bond [1] (eq. 1). In fact, it has been shown that in the majority of

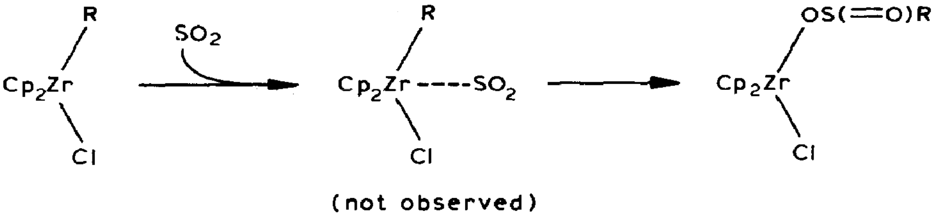
$$L_nMR + SO_2 \rightarrow L_nMSO_2R \qquad (1)$$

cases the reaction is not a true insertion, but rather an outer-sphere process involving electrophilic backside attack at C_α leading to an ion pair which subsequently collapses to a sulphinate complex [1]. This process, by necessity, results in configuration-inversion at C_α [1,2].

An interesting departure from this mode of reaction is provided by the reaction of $[Zr(R)Cl(\eta\text{-}C_5H_5)_2]$ with less than one equivalent of SO_2, in which the configuration is retained at C_α [3]. The organozirconium precursor is coordinatively un-

0022-328X/88/$03.50

saturated, a feature which is presumably fundamental to this result, and indeed the outcome of the reaction may be rationalised in terms of an intermediate SO_2 complex which enters into a true insertion step (eq. 2). Further reaction with SO_2 results in (formal) insertion into the η^5-cyclopentadienylmetal–carbon bonds [3]:



(2)

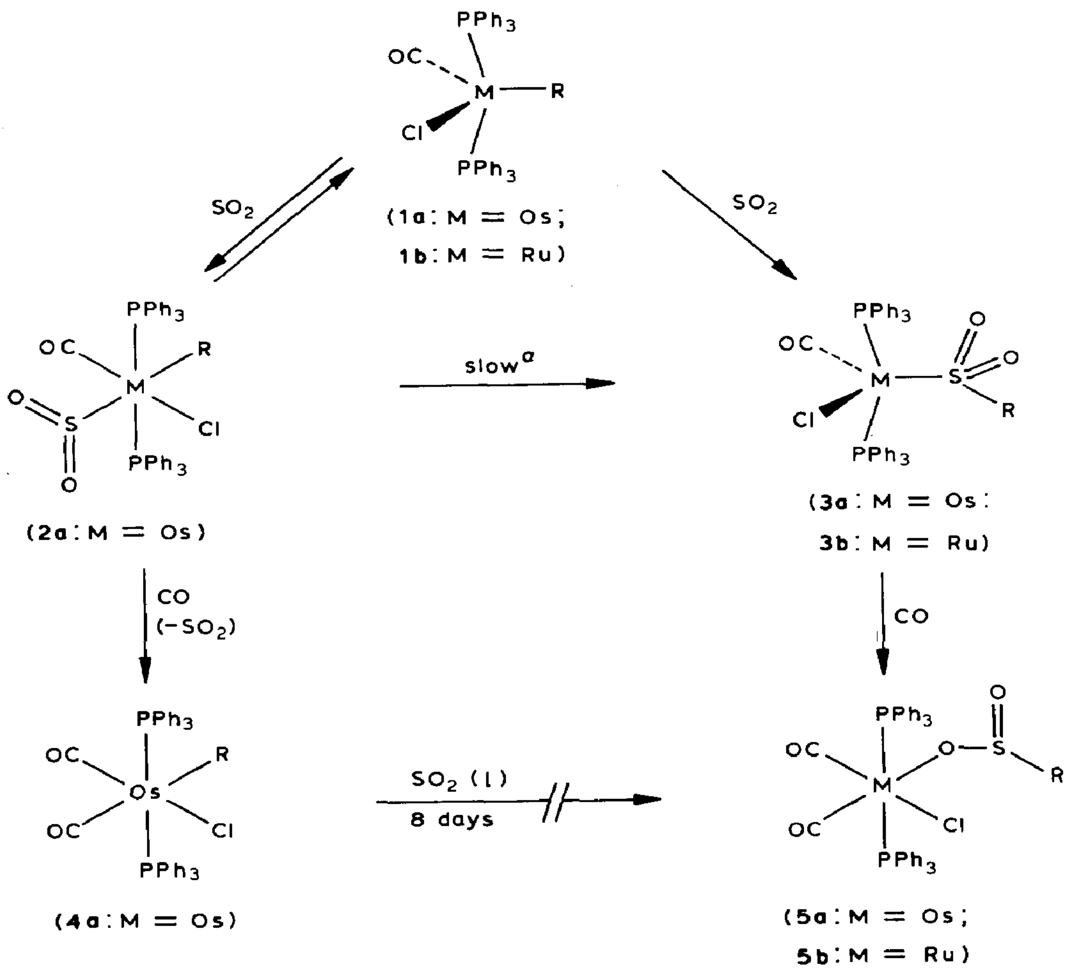
A similar formation of an intermediate SO_2 complex has been suggested for the reactions of the coordinatively unsaturated platinum(II) compounds *trans*-$[PtCl(R)L_2]$ (L = PEt_3, $AsEt_3$, $SeEt_2$, $TeEt_2$; R = alkyl, aryl) with sulphur dioxide, which lead to the η^1-*S*-sulphinate insertion products *trans*-$[PtCl\{S(=O)_2R\}L_2]$ [17]. However, the reactions of SO_2 with the η^1-allylplatinum(II) complexes *trans*-$[PtCl(CH_2CH{=}CH_2)(PR_3)_2]$ apparently proceed by electrophilic attack of SO_2 at the allylic double bond followed by rearrangement to the η^1-*S*-sulphinate complexes [18].

We were interested in the interaction of SO_2 with other coordinatively unsaturated organometallics which might lead to further deviations from the accepted SO_2 "insertion" mechanism. We report here an example where concomitant coordination of SO_2 and a σ-organyl group to a transition metal apparently represents a diversion in the insertion process rather than an intermediate as might have been expected.

Results and discussion

The red complexes $[MCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2]$ (M = Os (**1a**), Ru (**1b**)) [4] are coordinatively unsaturated and have provided interesting information about the insertion reactions of small molecules, e.g., methylene, CH_2 [5], carbon monoxide, CO [4], and isocyanides [6]. The 16-electron σ-aryl complexes adopt a square pyramidal geometry with the organyl ligand occupying the apical position (cf. [7]). Accordingly, the initial coordination of a ligand is expected to occur at the site *trans* to the tolyl group, as has been shown to be the case for the complexes $[MCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2(SNNMe_2)]$ [8,9].

A suspension of **1a** in liquid SO_2 (room temperature) rapidly becomes bright orange owing to the quantitative formation of an SO_2 adduct, **2a**. Infrared data for SO_2 complexes are particularly diagnostic for the purpose of assigning coordination modes [10], and it can be deduced from the infrared spectrum of **2a** that the SO_2 ligand is bound in a monodentate manner and coplanar with the osmium atom (η^1-*S*-coplanar). Two strong, sharp bands (Nujol 1309, 1121 cm^{-1}) are the only features not attributable to ligands present in the starting complex, whilst the absorption due to the carbonyl ligand is apparent at 1962 cm^{-1}. This value is considerably higher than in the starting complex **1a** (1906 cm^{-1}), and notwithstanding the change in coordination geometry upon SO_2 ligation (square pyramidal → octahedral) it appears that the SO_2 ligand is acting as a strong acceptor ligand.



Scheme 1. Reactions of $MClR(CO)(PPh_3)_2$ (R = 4-tolyl; M = Os (**1a**), Ru (**1b**)) with sulphur dioxide. [a] Presumably via **1a** by SO_2 dissociation.

By extension of the rules developed by Hoffmann et al. for the bending of coordinated nitrosyl ligands [11], it has been possible to derive similar rules for interpreting the pyramidalisation of coordinated SO_2 [12]. In the light of these rules, it is not suprising that the SO_2 ligand when coordinated to the d^6-ML_5 fragment **1a**, does so in the η^1-S-coplanar mode. What is, however, suprising about the adduct **2a** is that the SO_2 ligand is labile. The extensive compilation of data on substitution behaviour for coordinated SO_2, examined by Kubas and co-workers [10], suggests that SO_2 bound in a coplanar fashion should be inert towards substitution and dissociation, as well as oxidation. Accordingly, correlations between the mode of SO_2 coordination and the lability of the SO_2 ligand should be employed with caution (cf. [19]). We find that **2a** is decolourised immediately when its solutions are treated with carbon monoxide at atmospheric pressure. The product isolated in quantitative yield is $[OsCl(C_6H_4Me\text{-}4)(CO)_2(PPh_3)_2]$ (**4a**), previously prepared by carbonylation of **1a** [4] or oxidation of $[Os(\equiv CC_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$ [13]. The 18-electron complex **4a** shows no tendency towards ligand substitution reactions and may be recovered unchanged from liquid SO_2 after one week.

The lability of the SO_2 ligand in the adduct **2a** may possibly be associated with the presence of a strongly *trans*-directing ligand, i.e., $-C_6H_4Me-4$, coordinated *trans* to SO_2. In support of this, it should be noted that the only other examples of labile osmium-SO_2 complexes also contain SO_2 opposite to a strongly *trans*-directing ligand, namely the hydrido ligands in the complexes $[OsClH(CO)(PR_3)_2(SO_2)]$ (R = cylohexyl [14], phenyl [15]).

In contrast to the reaction in liquid SO_2, exposure of (**1a**) to SO_2 gas in an inert solvent, e.g., dichloromethane, tetrahydrofuran or toluene, leads to a completely different result: The yellow complex $[OsCl\{S(=O)_2C_6H_4Me-4\}(CO)(PPh_3)_2]$ (**3a**) is isolated as the only product. On the basis of infrared data (Table 1) it appears that the sulphinate ligand in **3a** is bound to osmium through sulphur (cf. [16]). The sulphinate complex **3a** is also obtained when solutions of the SO_2 complex **2a** are kept at room temperature, and while small amounts of SO_2 improve the overall yield, the transformation requires 2–3 days when the SO_2 complex is suspended in liquid SO_2. Furthermore, the sharp singlet in the $^{31}P\text{-}\{^1H\}$ NMR of **2a** (further confirmation of the mode of coordination) is broadened significantly by the addition of gaseous SO_2, indicating rapid exchange between free and coordinated SO_2.

It might be assumed that, given rapid exchange of SO_2, the concentration of the 16-electron, coordinatively unsaturated species **1a** is reduced significantly in the presence of high concentrations of SO_2. The reduction in reaction rate with increase in concentration of SO_2 is therefore consistent with a mechanism in which SO_2 directly attacks the metal carbon bond of the unsaturated species **1a**. It should be noted that in a coordinatively-unsaturated, square-pyramidal σ-organometallic complex, the vacant site would be expected to be *trans* to the σ-organyl ligand. Thus this type of mechanism in which an SO_2 complex is actually a diversion rather than an intermediate may be quite widespread in pentacoordinate chemistry, though not recognised as such.

Similar behaviour was observed for the ruthenium complex $[RuCl(C_6H_4\text{-}Me\text{-}4)(CO)(PPh_3)_2]$ (**1b**) on treatment with SO_2, except that no evidence was obtained for the formation, even for the fleeting, of the SO_2 adduct analogous to **2a**: A suspension of red **1b** in liquid SO_2 slowly dissolved to give the yellow η^1-sulphinate complex $[RuCl\{S(=O)_2C_6H_4Me-4\}(CO)(PPh_3)_2]$ (**3b**), spectroscopic data for which are listed in Table 1.

Finally, the reactions of the *S*-sulphinate complexes **3a** and **3b** with carbon monoxide are noteworthy. The complexes are formally unsaturated (though we do not exclude some stabilisation through weak η^2-(S=O) coordination of a sulphoxide group), and it was expected that the molecules would react with donor ligands. Incorporation of CO does, indeed, occur under mild conditions, but it is accompanied by isomerisation of the *S*-sulphinate ligands to *O*-sulphinates in $[MCl\{OS(=O)\text{-}C_6H_4Me\text{-}4\}(CO)_2(PPh_3)_2]$ (M = Os (**5a**), Ru (**5b**)). Isomerisation of coordinatively-unsaturated sulphinates of iridium(I) upon addition of ligands has been previously described [16], but increased coordination at the metal centre was found to result in isomerisation of an *O*-sulphinate to an *S*-sulphinate, whereas in the present example, the opposite is true. These observations may be rationalised by considering the coordination numbers involved. The iridium(I) case involves a transition from four to five ligands, and as such the coordination sphere is not particularly sterically encumbered. For the ruthenium(II) and osmium(II) cases, however, a five-coordi-

Table 1

Spectroscopic data ($R = C_6H_4Me$-4, $L = PPh_3$)

Compound	Infrared (Nujol) (cm^{-1})		NMR ($CDCl_3$) [a] (ppm)	
	ν(CO)	ν(SO)	^{31}P-$\{^1H\}$ [b]	^1H [c]
[OsCl(R)(CO)L_2(SO_2)] (orange) (**2a**)	1962	1309, 1121	12.4	2.23
[OsCl{S(=O)$_2$-R}(CO)L_2] (pale yellow) (**3a**)	1952	1159, 1119, 944, 909	28.2	2.33
[RuCl{S(=O)$_2$-R}(CO)L_2] (yellow) (**3b**)	1974	1189, 1159, 955	37.1	2.35
[OsCl{O-S(=O)-R}(CO)L_2] (colourless) (**5a**)	2037, 1973	1080, 968, 920	27.9	2.33
[RuCl{O-S(=O)-R}(CO)L_2] (colourless) (**5b**)	2057, 1989	1085, 1047, 970, 928	18.1	2.31

[a] Data were determined from saturated solutions of the complexes in $CDCl_3$ at 25 °C. [b] Reported relative to external $\delta(D_3PO_4) = 0.00$. [c] δ(tolyl-CH_3), Reported relative to internal $\delta(SiMe_4) = 0.00$.

nate complex must subsequently accomodate six ligands, three of which are comparatively bulky. Some of the steric strain may be relieved by isomerisation of the *S*-sulphinate ligand, and this may be the determining factor.

Conclusions

We have described the synthesis of **2a**, a d^6-$ML_5(SO_2)$ complex, which (i) contravenes previous empirical rules regarding the lability of the SO_2 ligand in such complexes, and (ii) represents a diversion rather than an intermediate in the insertion of SO_2 into the metal–carbon bond of **1a**.

Operation of steric factors has been noted in the isomerisation of coordinated sulphinates.

Experimental

General experimental procedures and instrumentation have been described previously [8]. The complexes [OsCl(C_6H_4Me-4)(CO)(PPh_3)$_2$] (**1a**) and [RuCl(C_6H_4-Me-4)(CO)(PPh_3)$_2$] (**1b**) were prepared by a published method [4]. Reactions involving liquid SO_2 were carried out in a pressure Schlenk tube behind a suitable safety shield in a fume cupboard.

[OsCl(C_6H_4Me-4)(CO)(PPh_3)$_2$(SO_2)] (2a)

[OsCl(C_6H_4Me-4)(CO)(PPh_3)$_2$] (**1a**) (0.25 g, 0.29 mmol) was suspended in liquid SO_2 (2 cm^3) in an open Schlenk tube and stirred until all the SO_2 had evaporated. The bright orange residue may be recrystallised quickly from liquid SO_2, while extended periods in solution lead to decomposition (vide infra). The residue is, however, spectroscopically pure (^{31}P-{^1H} NMR), typically highly crystalline, and may be used in subsequent reactions without further purification. Yield 0.27 g (98%). The complex loses SO_2 upon heating (atmospheric pressure, 50–60 ° C) to regenerate **1a**. The compound is indefinitely stable in the solid state at room temperature.

*[OsCl{S(=O)$_2$C$_6$H$_4$Me-4}(CO)(PPh$_3$)$_2$] (**3a**)*

A solution of **1a** (1.00 g, 1.15 mmol) in toluene (20 cm^3) or dichloromethane (20 cm^3) was treated with a stream of SO_2 gas for 20 s. The Schlenk tube was sealed and the suspension stirred for 4 h. The solvent volume was then decreased under reduced pressure to ca. 10 cm^3, and hexane was added slowly to precipitate the crude product, which was recrystallised from dichloromethane/pentane at − 30 ° C as pale yellow micorcrystals. Yield 0.98 g (91%). M.p. 179 ° C (decomp.).

*[RuCl{S(=O)$_2$C$_6$H$_4$Me-4}(CO)(PPh$_3$)$_2$] (**3b**)*

A stream of SO_2 gas was passed through a suspension of **1b** (0.50 g, 0.64 mmol) in dichloromethane (30 cm^3) 20 s. The Schlenk tube was sealed and the mixture stirred until all the red starting complex had dissolved to give a bright yellow solution. The solvent volume was reduced in vacuo to ca. 10 cm^3, and pentane was added dropwise to induce crystallisation of the crude yellow product, which was recrystallised from dichloromethane/pentane at − 30 ° C. Yield 0.46 g (86%). M.p. 164 ° C.

*[OsCl{OS(=O)C$_6$H$_4$Me-4}(CO)$_2$(PPh$_3$)$_2$] (**5a**)*

A solution of **3a** (0.20 g, 0.23 mmol) in tetrahydrofuran was kept at 60 ° C under CO pressure (5 atm) for 3 h in an autoclave. Addition of ethanol to the cooled solution and subsequent removal of the bulk of the solvent under reduced pressure (rotary evaporator) gave the product as white crystals. Yield 0.14 g (69%). M.p. 211 ° C.

Characteristic spectroscopic data for the new complexes are listed in Table 1.

Acknowledgements

We gratefully acknowledge the financial support of the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We also thank the Deutsche Akademische Austauschdienst for a fellowship (to A.F.H.).

References

1 A. Wojcicki, Adv. Organomet. Chem., 12 (1974) 31.
2 G.M. Whitesides and D.J. Boschetto, J. Am. Chem. Soc., 93 (1971) 1529.
3 J.A. Labinger, D.W. Hart, W.E. Seibert III and J. Schwartz, J. Am. Chem. Soc., 97 (1975) 3851.
4 W.R. Roper and L.J. Wright, J. Organomet. Chem., 142 (1977) C1.
5 D.S. Bohle, G.R. Clark, C.E.F. Rickard, W.E.B. Shepard and L.J. Wright, J. Chem. Soc., Chem. Commun., (1987) 563.
6 W.R. Roper, G.E. Taylor, J.M. Waters and L.J. Wright, J. Organomet. Chem., 157 (1978) C27.
7 W.R. Roper, G.E. Taylor, J.M. Waters and L.J. Wright, J. Organomet. Chem., 182 (1979) C46.
8 M. Herberhold and A.F. Hill, J. Organomet. Chem., 315 (1986) 105.

9 A. Gieren, C. Ruiz-Pérez, T. Hübner, M. Herberhold and A.F. Hill, J. Chem. Soc. Dalton Trans., (1988) 1693.

10 R.R. Ryan, G.J. Kubas, D.C. Moody and P.G. Eller, Struct. Bonding, 46 (1981) 47.

11 R. Hoffmann, M.M.L. Chen, M. Elian, A.R. Rossi and D.M.P. Mingos, Inorg. Chem., 13 (1974) 2666.

12 R.R. Ryan and P.G. Eller, Inorg. Chem., 15 (1976) 494.

13 G.R. Clark, K. Marsden, W.R. Roper and L.J. Wright, J. Am. Chem. Soc., 102 (1980) 6570.

14 F.G. Moers, R.W.M. ten Hoedt and J.P. Langhout, J. Inorg. Nucl. Chem., 36 (1974) 2279.

15 M. Herberhold and A.F. Hill, unpublished results.

16 C.A. Reed and W.R. Roper, Chem. Comm., (1969) 155.

17 F. Faraone, L. Silvestro, S. Sergi and R. Pietropaolo, J. Organomet. Chem., 34 (1972) C55; cf. ibid., 46 (1972) 379.

18 Y.-R. Hu, A. Wojcicki, M. Calligaris and G. Nardin, Organometallics, 6 (1987) 1561.

19 W.A. Schenk, Angew. Chem., 99 (1987) 101; Angew. Chem., Int. Ed. Engl., 26 (1987) 98.