Journal of Organometallic Chemistry, 395 (1990) 327–332
Elsevier Sequoia S.A., Lausanne

JOM 20731

The coordination chemistry of iminooxosulphuranes

IX *. The insertion reactions of tosyliminooxosulphurane with coordinatively unsaturated ruthenium and osmium aryl complexes

Max Herberhold *

Laboratorium für Anorganische Chemie der Universität Bayreuth, Universitätsstrasse 30, D-8580 Bayreuth (F.R.G.)

and Anthony F. Hill

Department of Chemistry, University of Warwick, Coventry CV4 7AL (U.K.)

(Received December 15th, 1989)

Abstract

The 16-electron compounds [MRCl(CO)$(PPh_3)_2$] (M = Ru, Os; R = C_6H_4Me-4) react with toluene sulphonyliminooxo-λ^4-sulphurane (RSO_2NSO, tosyl-NSO) to give the *N*-(tosyl)toluenesulphinimidato-*S* complexes [MCl{SR(NSO_2R)O}(CO)-$(PPh_3)_2$] (which are presumably stabilised by weak coordination of a sulphimide group). No reaction is observed between the complexes [MRCl(CO)$(PPh_3)_2$] and the less electrophilic iminooxo-λ^4-sulphuranes R′NSO (R′ = R, C_6H_4Me-2, ferrocenyl). In keeping with its coordinative unsaturation, the complex [OsCl{SR(NSO_2R)O}(CO)$(PPh_3)_2$] reacts with xylyl isonitrile to give [OsCl{SR (NSO_2R)O}($CNC_6H_3Me_2$-2,6)(CO)$(PPh_3)_2$]. No insertion reactions were observed between tosyl-NSO and the 18-electron complexes [Ir(CH_3)I(NO)$(PPh_3)_2$], [OsRCl-$(CO)_2(PPh_3)_2$], [RuBr(CF_3)$(CO)_2(PPh_3)_2$] and [Ru(C_6H_5)Cl(CO)($CNC_6H_3Me_2$-2,6)$(PPh_3)_2$].

The insertion of sulphur dioxide into the metal–carbon bond of coordinatively saturated transition metal alkyls and aryls is one of the most systematically studied and best understood reactions in organotransition-metal chemistry [2,3]. An important distinction arises, however, when the metal centre involved is coordinatively unsaturated and prior coordination of the SO_2 molecule may occur so that the

---

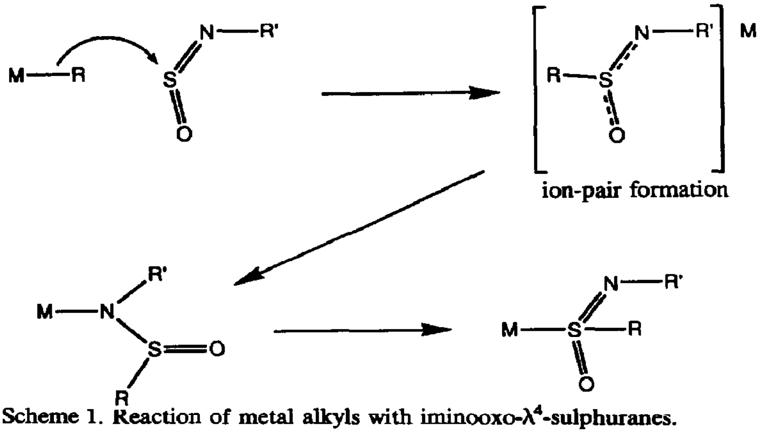
* For Part VIII see ref. 1.

stereochemistry at C_α of the alkyl ligand is reversed [4]. We have described the reaction of the 16-electron complexes $[MRCl(CO)(PPh_3)_2]$ (M = Ru, Os; R = C_6H_4Me-4 [5]) with sulphur dioxide [6] and imines of divalent sulphur [7]. We report here the reaction of these complexes with iminooxo-λ^4-sulphuranes.

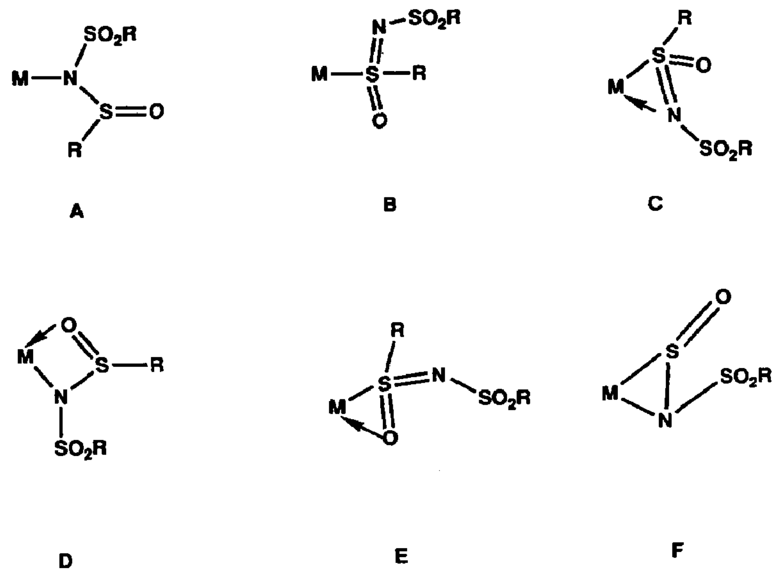
Results and discussion

The complexes $[MRCl(CO)(PPh_3)_2]$ (M = Ru, Os; R = C_6H_4Me-4), prepared by Roper and Wright [5] by the reaction of $[RuClH(CO)(PPh_3)_3]$ and ditolylmercury, react readily with unsaturated organic and inorganic species [5–8]. These complexes are ideal models for investigating reactions involving aryl ligands in which coordinative saturation may be important, since the corresponding 18-electron complexes $[MRCl(CO)_2(PPh_3)_2]$ are easily accessible via carbonylation under very mild conditions [5]. We find that a slow reaction takes place in toluene between $[MRCl(CO)(PPh_3)_2]$ and the sulphur(IV) heterocumulene tosyl-NSO. The red organometallic precursors dissolve with formation of pale yellow solutions, from which compounds of composition $[MCl\{SR(NSO_2R)O\}(CO)(PPh_3)_2]$ are obtained by removal of solvent and crystallisation from dichloromethane/light petroleum. The white (M = Os) or pale yellow (M = Ru) complexes show peaks in the ^1H NMR spectrum indicating the presence two different tolyl methyl groups, the integrals for which indicate an insertion adduct of 1/1 stoichiometry. The shift in the carbonyl band from 1906 cm^{-1} for the osmium precursor [5] to 1953 cm^{-1} for the adduct $[OsCl\{SR(NSO_2R)O\}(CO)(PPh_3)_2]$ indicates the formation of a ligand less electron-releasing than the strong σ-donor tolyl group. A similar shift was observed upon SO_2 insertion and formation of $[OsCl(SO_2R)(CO)(PPh_3)_2]$ (ν(CO) 1952 cm^{-1}) [6].

The reactions of activated iminooxo-λ^4-sulphuranes with coordinatively saturated metal alkyls have been extensively investigated by Wojcicki and co workers and found to proceed via electrophilic attack at the metal–carbon bond by the sulphur(IV) centre (Scheme 1) [9] in a manner completely analogous to that observed for reaction of sulphur dioxide [2,3]. The *N*-(alkylsulphinyl)alkanesulphonamidato-*N* complexes thus formed (Scheme 2, A) may be isolated in some cases, but thermally rearrange to the more sterically congested *N*-(al-



Scheme 1. Reaction of metal alkyls with iminooxo-λ^4-sulphuranes.



Scheme 2. Ligand coordination geometries.

kylsulphonyl)alkanesulphinimidato-*S* tautomers (Scheme 2, **B**). In the case in question, the structure of the ligand formed is complicated by the possibility of bidentate coordination to the metal centre. Three plausible bidentate modes of coordination for (alkylsulphonyl)alkanesulphinimidato-*S* ligands are suggested in Scheme 2 (**C**–**E**). The possibility of monodenate coordination of either an *N*-(alkylsulphinyl)-alkanesulphonamidato-*N* or *N*-(alkylsulphonyl)alkanesulphinimidato-*S* ligand cannot be ruled out, but these types of ligands typically give infrared bands at ca. 1080, 1020, and 1000 cm^{-1} [9], whilst the complexes derived from RSO_2NSO and $[MRCl(CO)(PPh_3)_2]$ have such bands at 1027 and 1002 (M = Ru) or 1038 and 933 cm^{-1} (M = Os). The fact that the metal involved has a strong effect upon the frequency of one of the bands suggests that it is intimately associated with the vibration, and thus the formation of a metallacycle such as **C** is probable. We have observed bands in this region for related 3-membered MNS metallacycles of type **F** (Scheme 2) [10].

In the absence of a crystallographic study it was not possible to unequivocally distinguish between the possible modes of coordination shown in Scheme 2, but evidence to suggest that the ligands are indeed bound to the metal in a bidentate manner comes from the reaction of the osmium complex $[OsCl\{SR(NSO_2R)O\}(CO)(PPh_3)_2]$ with xylyl isonitrile. The addition of xylyl isonitrile is rapid and the colourless complex $[OsCl\{SR(NSO_2R)O\}(CNC_6H_3Me_2\text{-}2,6)(CO)(PPh_3)_2]$ is formed in high yield. There is virtually no change in the position of the ν(CO) band, which appears at 1956 cm^{-1}, but a strong band at 2135 cm^{-1} indicates coordination of the isonitrile. On the basis of the EAN rule, the *N*-(alkylsulphonyl) alkanesulphinimidato-*S* ligand must be a 1-electron monodentate ligand in this complex. The band which was attributed to the OsNS metallacycle in the precursor (933 cm^{-1}) is now observed at 996 cm^{-1}, shifted to higher energy, in keeping with the opening of a bidentate S=N coordination. The infrared data for the monodenate ligand are similar to those for the *S*-coordinated ligand in $[Fe\{SCH_3(NSO_2CH_3)O\}$-

$(CO)_2(\eta\text{-}C_5H_5)]$ [9]. We have observed a similar magnitude of shift for the $\nu(SO)$-associated band in the complex $[Ru(OSNHC_6H_4Me\text{-}4)(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]^+$ on treatment with t-butyl isonitrile to give $[Ru(OSNHC_6H_4Me\text{-}4)(CO)(CN^tBu)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]SbF_6$[11]; the starting former complex in this case presumably contains a RuSO metallacycle, which is opened by coordination of the isonitrile.

The extension of these reactions to other iminooxosulphuranes was briefly investigated. It was found that in the absence of strongly electron-withdrawing groups to activate the sulphur-λ^4-heterocumulene no reaction occurred. Thus treatment of $[MRCl(CO)(PPh_3)_2]$ with either tolyl (*ortho* or *para*) or ferrocenyl substituted iminooxo-λ^4-sulphuranes in refluxing toluene simply resulted in quantitative recovery of the organometallic starting material. Similar results were obtained previously by Wojcicki using coordinatively saturated metal alkyls [9], but we had hoped that prior coordination might circumvent the electrophilicity requirements of the "backside-attack" mechanism.

We were similarly unsuccessful in extending the reaction to other coordinatively saturated alkyls of metals from groups 8 and 9: The complexes $[Ir(CH_3)I(NO)(PPh_3)_2]$, $RuBr(CF_3)(CO)_2(PPh_3)_2]$, $[Ru(C_6H_5)Cl(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$ and $[OsRCl(CO)_2(PPh_3)_2]$ all failed to react with tosyl-NSO. The failure of $[OsRCl(CO)_2(PPh_3)_2]$ to undergo insertion of SO_2, even when the latter is used as solvent, has been noted [6].

The possibility of prior coordination of the very electrophilic iminooxosulphurane tosyl-NSO remains an intriguing possible alternative to the accepted route to insertion, and the results presented here would appear to imply its operation. We have so far failed to prepare 18-electron iminooxosulphurane complexes of divalent ruthenium or osmium, which might be intermediates in this process, but the complexes $[MCl_2(OSNSO_2R)(PPh_3)_2]$ (M = Ru, Os) [10c] are stable examples of coordinatively unsaturated metal(II) complexes and are currently under investigation.

Experimental

General experimental procedures and instrumentation [7a] and the compounds $[MRCl(CO)(PPh_3)_2]$ (M = Ru, Os; $R = C_6H_4Me\text{-}4$) and RSO_2NSO [12] have been described elsewhere. Light petroleum refers to that fraction of b.p. 40–60 °C. Physical data for the complexes are listed in Table 1. Compounds gave satisfactory elemental microanalyses.

$[MCl\{SR(NSO_2R)O\}(CO)(PPh_3)_2]$

A suspension of $[MRCl(CO)(PPh_3)_2]$ (1.00 mmol) in toluene (30 cm^3) was treated with a solution of *p*-tosyliminooxo-λ^4-sulphurane in toluene (0.10 mol/l, 10.5 cm^3, 1.05 mmol) and the mixture stirred until all the organometallic reagent had dissolved. The solvent was removed under reduced pressure and the residue washed with light petroleum (2×20 cm^3) then recrystallised from dichloromethane/light petroleum at −30 °C. $[RuCl\{SR(NSO_2R)O\}(CO)(PPh_3)_2]$: Yield 76%, M.p. 188 °C. $[OsCl\{SR(NSO_2R)O\}(CO)(PPh_3)_2]$: Yield 83%, M.p. 162 °C.

Table 1

Spectroscopic data for the new complexes

Complex R = C_6H_4Me-4, R′ = $C_6H_3Me_2$-2,6	Infrared (Nujol)(cm^{-1})			NMR (ppm) $\delta(^1H)$ [a]
	ν(CO) (vs)	$\nu(SO_2)$	other	
[RuCl{SR(NSO_2R)O}(CO)(PPh_3)$_2$] (pale yellow)	1976	1261, 1156 1106, 1027	1007 (NSRu)	2.37 (s, 3H, CH_3-4) 2.41 (s, 3H, CH_3-4)
[OsCl{SR(NSO_2R)O}(CO)(PPh_3)$_2$] (colourless)	1953	1262, 1158, 1107, 1038	933m (NSOs)	2.35 (s, 3H, CH_3-4) 2.40 (s, 3H, CH_3-4)
[OsCl{SR(NSO_2R)O}(CNR′)-(CO)(PPh_3)$_2$] (colourless)	1956	1263, 1138, 1028	2135vs (CN) 996m (NS) 914w	2.32 (s(br), 6H, CH_3-4) 2.10 (s, 6H, CH_3-2,6)

[a] ^1H NMR data determined from saturated solutions in $CDCl_3$ at 35 °C (90 MHz) relative to internal $SiMe_4$.

[OsCl{SR(NSO_2R)O}($CNC_6H_3Me_2$-2,6)(CO)(PPh_3)$_2$]

A solution of [OsCl{SR(NSO_2R)O}(CO)(PPh_3)$_2$] (0.15 g, 0.14 mmol) in tetrahydrofuran (15 cm^3) was treated with one equivalent of xylyl isonitrile ($CNC_6H_3Me_2$-2,6, 0.020 g, 0.15 mmol) then stirred for 40 min. Light petroleum (60 cm^3) was added and the mixture concentrated under reduced pressure. The resulting precipitate was filtered off, washed with light petroleum, and recrystallised from dichloromethane/light petroleum at −30 °C. Yield 0.12 g (68%). M.p. 144 °C.

Acknowledgements

We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We also thank the Deutsche Akademische Austauschdienst for a fellowship to A.F.H., and Dr L. Haumaier for a sample of [Fe(η-C_5H_4NSO)(η-C_5H_5)].

References

1 M. Herberhold and A.F. Hill, J. Organomet. Chem., 395 (1990) 315.

2 A. Wojcicki, Adv. Organomet. Chem., 12 (1974) 31.

3 G.M. Whitesides and D.J. Boschetto, J. Am. Chem. Soc., 93 (1971) 1529.

4 J.A. Labinger, D.W. Hart, W.E. Seibert III and J. Schwartz, J. Am. Chem. Soc., 97 (1975) 3851.

5 W.R. Roper and L.J. Wright, J. Organomet. Chem., 142 (1977) C1.

6 M. Herberhold and A.F. Hill, J. Organomet. Chem., 353 (1988) 243.

7 (a) M. Herberhold and A.F. Hill, J. Organomet. Chem., 315 (1986) 105; (b) A. Gieren, C. Ruiz-Perez, T. Hübner, M. Herberhold and A.F. Hill, J. Chem. Soc., Dalton Trans., (1988) 1693.

8 D.S. Bohle, G.R. Clark, C.E.F. Rickard, W.R. Roper, W.E.B. Shepard and L.J. Wright, J. Chem. Soc., Chem. Commun., (1987) 563; W.R. Roper, G.E. Taylor, J.M. Waters and L.J. Wright, J. Organomet. Chem., 157 (1978) C27; 182 (1979) C46.

9 R.G. Severson and A. Wojcicki, J. Organomet. Chem., 149 (1978) C66; R.G. Severson, T.W. Leung, and A. Wojcicki, Inorg. Chem., 19 (1980) 915; T.W. Leung, G.G. Christoph, J. Gallucci and A. Wojcicki, Organometallics, 5 (1986) 366; T.W. Leung, G.G. Christoph and A. Wojcicki, Inorg. Chim. Acta, 76 (1983) L281; Y.-R. Hu, T.W. Leung, S.-C.H. Su, A. Wojcicki, M. Calligaris and G. Nardin, Organometallics, 4 (1985) 1001; T.W. Leung, G.G. Christoph, J. Gallucci and A. Wojcicki, Organometallics, 5 (1986) 846.

10 (a) M. Herberhold and A.F. Hill, J. Chem. Soc., Dalton Trans., (1988) 2027; (b) M. Herberhold and A.F. Hill, J. Organomet. Chem., 368 (1989) 111; (c) M. Herberhold and A.F. Hill, J. Organomet. Chem., 395 (1990) 195.

11 M. Herberhold and A.F. Hill, J. Organomet. Chem., 395 (1990) 207.

12 G. Kresze and W. Wucherpfennig, Angew. Chem., 79 (1967) 109; Angew. Chem., Int. Ed. Engl., 6 (1967) 149.