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The coordination chemistry of iminooxosulphuranes

VII*. Coordinative activation of tolyliminooxosulphurane towards electrophiles

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Abstract

The reactions of the *p*-tolyliminooxosulphurane complexes $[Ru(CO)(L)(PPh_3)_2(OSNR)]$ (L=CO, CNC_6H_3Me-2,6, CN^tBu; R=C_6H_4Me-4 (*p*-tolyl)) and $[OsCl(NO)(PPh_3)_2(OSNR)]$ with a range of electrophiles have been investigated: $[Ru(CO)(CNC_6H_3Me_2$-2,6$)(PPh_3)_2(OSNR)]$ reacts with hexafluoroantimonic acid to give the *N*-protonated salt $[Ru(OSNHR)(CO)(CNC_6H_3Me_2$-2,6$)(PPh_3)_2]SbF_6$, which in turn reacts with nucleophilic ligands CN^tBu and SCN^- to give the η^1-sulphinamido complexes $[Ru(OSNHR)(CO)(CN^tBu)(CNC_6H_3Me_2$-2,6$)(PPh_3)_2]^+$ and $[Ru(OSNHR)(SCN)(CO)(CNC_6H_3Me_2$-2,6$)(PPh_3)_2]$. Alkylation of $[Ru(CO)(L)(PPh_3)_2(OSNR)]$ with R'X occurs at oxygen, giving the complexes $[Ru(R'OSNR)(CO)(L)(PPh_3)_2]X$ (L=$CNC_6H_3Me_2$-2,6, R'=CH_3, X=CF_3SO_3; R'=C_2H_5, X=SO_3F; L=CO, R'=CH_3, X=CF_3SO_3). Silylation of $[Ru(CO)(CNC_6H_3Me_2$-2,6$)(PPh_3)_2(OSNR)]$ with $Me_3SiOSO_2CF_3$ occurs at oxygen, to give $[Ru(Me_3SiOSNR)(CO)(CNC_6H_3Me_2$-2,6$)(PPh_3)_2]O_3SCF_3$ whilst $[OsCl(NO)(PPh_3)_2(OSNR)]$ with BF_3OEt_2 gives $[OsCl(NO)(PPh_3)_2(F_3BOSNR)]$. The adducts formed by reactions of coordinated iminooxosulphuranes with $HSbF_6$, $Me_3SiOSO_2CF_3$ and BF_3OEt_2 reacted with KOH/MeOH, CsF and acetone, respectively to regenerate the zerovalent iminooxosulphurane complexes, but alkylation was found to be irreversible.

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* For Part VI see ref. 1.

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Introduction

The coordination of unsaturated molecules to transition metals often results in extensive rehybridisation and relocation of electron density. This may be manifest in two ways, both of which have been important in the development of transition metal coordination chemistry. Firstly exotic and independently unstable molecules may be observed within the protective environment of a coordination sphere. Secondly and in direct contrast, the reactivity of simple organic substrates may be greatly enhanced towards either electrophilic or nucleophilic attack. The application of the latter approach has been primarily the domain of organic chemists. We describe herein the activation of an inorganic functional group, the sulphinylamino cumulene, towards electrophilic modification via coordination to electron-rich metal centres.

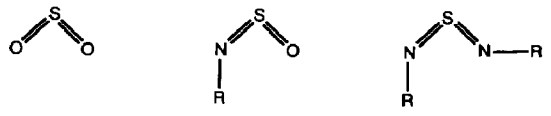
Iminooxosulphuranes, as imino derivatives of sulphur dioxide (Scheme 1), may coordinate to low-valent metal centres in three different ways; coordination may be through the sulphur atom such that the metal is contained in the plane of the cumulene, displaced from this plane or such that the nitrogen–sulphur double bond coordinates side-on in a manner reminiscent of olefin coordination and adequately described by the Dewar–Chatt–Duncanson model ([1] and refs. therein). It is the latter with which we are concerned in this report because it is this form of coordination which results in the greatest transfer of electron density from the metal to the cumulene. Coordinative activation of an unsaturated substrate towards electrophilic attack is based upon the transfer of electron density from a metal centre, out through the ligated substrate, to an external electrophile.

Results and discussion

We have recently described the synthesis of zerovalent iminooxosulphurane complexes of ruthenium [1,2] and osmium [1,3] which proceed in high yield. In particular the complexes $[Ru(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2(OSNR)]$ (R = C_6H_4Me-4, C_6H_4Me-2) may be easily prepared on a 1–8 g scale and have therefore facilitated a detailed study of their reactivity towards electrophiles.

Protonation

Beginning with the simplest of electrophiles, the proton, a solution of $[Ru(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2(OSN\text{-}C_6H_4Me\text{-}4)]$ was treated with hydrogen chloride gas. The product $[RuCl_2(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$, isolated in high yield, was devoid of any component derived from the iminooxosulphurane ligand. The dichloro complex is also obtained from solution of $[Ru(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_3]$ in chloroform. Thus whilst the iminooxosulphurane ligand in the



sulphur dioxide iminooxosulphurane diiminosulphurane

Scheme 1. Imino analogues of sulphur dioxide.

precursor is known to strongly bind to the ruthenium centre, it has become lost from the coordination sphere. In a study by Ashton and Manning [4] attempts to isolate products from the reactions of $[Fe(CO)(L)(PPh_3)_2(OSN\text{-}aryl)]$ (L=CO, CN^tBu) with a variety of electrophiles led in all cases to elimination of the iminooxosulphurane from the coordination sphere. It seems reasonable to assume that, in these and our own reactions, multiple protonations occur such that the metal becomes oxidised and the iminooxosulphurane reduced and lost from the divalent metal:

$$M^0[OSNR] + 2\ H^+ \rightarrow M^{2+} + RNH_2 + "SO"$$

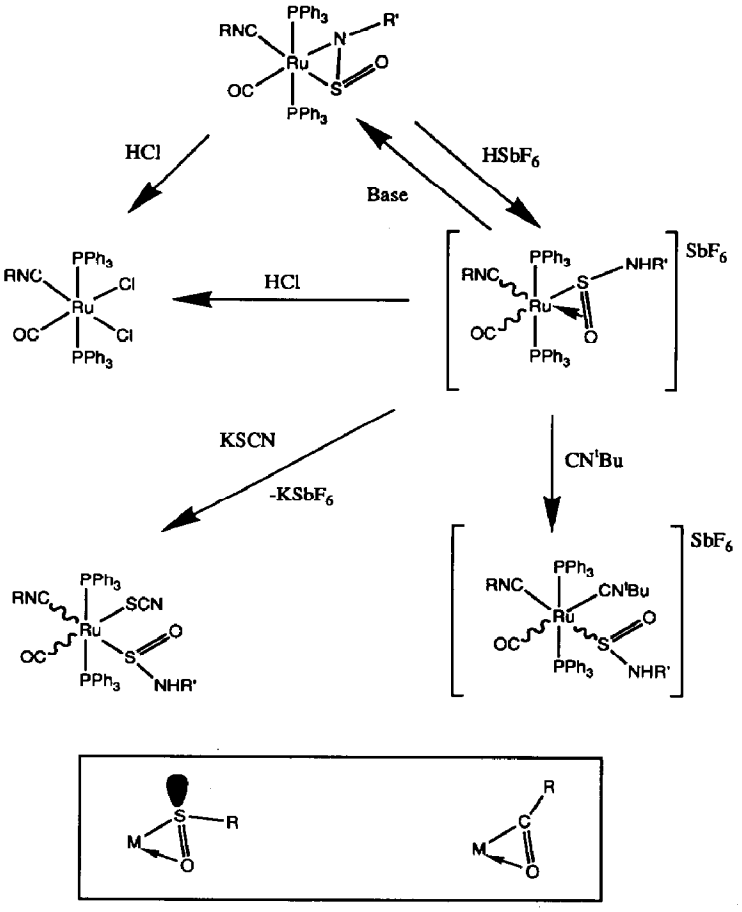
A key step in this process would be the second protonation and this would no doubt be facilitated by initial coordination of halide to reduce the complex charge to zero. Therefore use of an acid with a non-coordinating anion was expected to allow interception of the primary protonation product. Indeed this proved to be possible.

Treating solutions of $[Ru(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2(OSNR)]$ in dichloromethane with hexafluoroantimonic acid ($HSbF_6$) resulted in immediate decolourisation and formation of ionic 1 : 1 adducts $[Ru(OSNHR)(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]SbF_6$. Similar salts could be obtained using perchloric or tetrafluoroboric acid, however $HSbF_6$ was the acid of choice for the practical reasons of safety, product crystallinity and transparency in the regions of interest in the infrared spectrum of the complex cation. The cationic nature of the complex follows from its insolubility in aromatic hydrocarbons, the appearance of a strong band at 658 cm^{-1} characteristic of the SbF_6-anion and the high values for ν(CO) (1977) and ν(CN) (2161 cm^{-1}), both of which show increases of ca. 50 cm^{-1} from the corresponding values in the spectrum of the precursor complex (1927 and 2107 cm^{-1}, respectively).

The nature of the iminooxosulphurane-derived ligand may be surmised from spectroscopic data: The infrared spectrum features a peak at 3355 cm^{-1} ruling out protonation at sulphur, whilst the ^1H NMR spectrum shows a broad peak at 5.24 with no observed coupling to phosphorus, indicating the formation of an $NHC_6H_4Me\text{-}4$ group which is not directly bound to the metal. The ν(SO)-associated activity in the infrared spectrum of the salt at 898 cm^{-1} occurs at much lower energy than in the starting complex (1029 cm^{-1}) consistent with an η^2-(*S*, *O*) sulphinamide ligand (Scheme 2). Physical data for this and subsequent compounds are collected in Tables 1 and 2.

The type of bidentate coordination proposed for the sulphinamide ligand in the salt $[Ru(OSNHC_6H_4Me\text{-}4)(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]SbF_6$ would be expected to be weak. A similarly weak bidentate coordination has been observed in acyl complexes which would otherwise be coordinatively unsaturated, e.g., in the complex $[RuI(\eta^2\text{-}C(O)CH_3)(CO)(PPh_3)_2]$. We have suggested that the anomalous infrared activity associated with the sulphinato ligand in the complex $[RuCl(SO_2C_6H_4Me\text{-}4)(CO)(PPh_3)_2]$ may be due to weak coordination of the oxygen of the SO_2 group to satisfy the EAN rule requirements for ruthenium [5] and indeed this sulphoxide coordination is readily displaced by carbon monoxide or isonitrile ligands. Thus the cationic sulphinamide complex was treated with potential ligands to determine whether the metallacycle could be easily opened.

A solution of $[Ru(OSNHC_6H_4Me\text{-}4)(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]SbF_6$ treated with t-butyl isonitrile results in the rapid formation of the six-coordinate bis(isonitrile) compound $[Ru(OSNHC_6H_4Me\text{-}4)(CO)(CN^tBu)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$-



Scheme 2. Protonation of coordinated iminooxosulphuranes (R = $C_6H_3Me_2$-2,6, R' = C_6H_4Me-4).

SbF_6. The infrared spectrum of the new complex suggests that the isonitrile ligands are *cis* coordinated (ν(CN) 2191, 2176 cm^{-1}), however the possibility that the appearance of two ν(NC) bands arises from the effect of the two different imino substituents may not be disregarded. In the present context of RuSO metallacycle opening, the change in ν(SO) activity is particularly interesting with the band for the new complex occurring at 998 cm^{-1}, i.e., ca. 100 cm^{-1} to higher energy of that observed in the spectrum of the presumed bidentate sulphinamide complex, as expected. Furthermore, this value compares well with those obtained for monodenate sulphinamido tungsten complexes [6]. A neutral ruthenium monodenate sulphinamido complex, [Ru(OSNHC$_6$H$_4$Me-4)(SCN)(CO)(CNC$_6$H$_3$Me$_2$-2,6)-(PPh_3)$_2$] is obtained when the hexafluorantimonate salt is treated with potassium thiocyanate. As in the case of the bis(isonitrile) salt, the sulphinamide ligand gives rise to a strong absorption in the infrared at 1004 cm^{-1} In both monodentate sulphinamide complexes the ν(NH) frequency occurs at lower energy (3313 and 3309 cm^{-1}) and the δ(N*H*) resonances in the ^{1}H NMR to lower field (δ 5.51 and 5.34 ppm), than in the η^2-(*S*, *O*) sulphinamide cation.

The protonation of [Ru(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh_3)$_2$(OSNR)] is reversible: The non-nucleophilic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) rapidly regenerates

Table 1

Infrared data for the complexes [a] (cm^{-1})

Complex	ν(NO)/ ν(CO)	ν(CN)	ν(SO)/ ν(SN)	other
[(**Ru**)(OSNHC$_6$H$_4$Me-4)]SbF$_6$	1977	2161	898	3355(NH), 1273(C–N), 1219, 808, 658(SbF)
[(**Ru**)(OSNHC$_6$H$_4$Me-4)(CN^{t}Bu)]SbF$_6$	2025	2191, 2176	998	3313(NH) 1312(C–N), 846, 817, 658(SbF)
[(**Ru**)(OSNHC$_6$H$_4$Me-4)(SCN)]	1967	2090	1004	3309(NH), 2190(SCN), 1311(C–N), 1217, 849, 813, 790
[(**Ru**)(CH$_3$OSN-C$_6$H$_4$Me-4)]OTf	1966	2149	966	1266(C–N), 1152, 1031, 975, 801, 784
[(**Ru**)(CH$_3$CH$_2$OSN-C$_6$H$_4$Me-4)]O$_3$SF	1965	2143	972	1279(C–N), 1066, 999, 871, 806
[(**Ru′**)(CH$_3$OSN-C$_6$H$_4$Me-4)]SbF$_6$	2054, 2000	–	957	1269(C–N), 869, 808, 658(SbF)
[(**Ru**){(CH$_3$)$_3$SiOSN-C$_6$H$_4$Me-4}]OTf	1966	2147	889	1275(C–N), 1223, 1031, 853, 813
[(**Os**)(F$_3$BOSN-C$_6$H$_4$Me-20]	1817	–	916	1278(C–N), 1233, 1076vs(BF)

[a] Infrared data were obtained from Nujol mulls between KBr discs in the range 400–4000 cm^{-1} and from CsI pellets for the range 200–400 cm^{-1}. (**Ru**) = Ru(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$; (**Ru′**) = Ru(CO)$_2$(PPh$_3$)$_2$; (**Os**) = Cl(NO)(PPh$_3$)$_2$, OTf = O$_3$SCF$_3$.

the zerovalent iminooxosulphurane complex from [Ru(OSNHC$_6$H$_4$Me-4)(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$]SbF$_6$. The protonation/deprotonation sequence is sufficiently clean that is may be used to purify aged samples of the iminooxosulphurane complexes. Conversion to the sulphinamide salt is virtually quantitative and a suspension of the latter in ethanol, to which has been added a small amount of potassium hydroxide, smoothly converts to the zerovalent precursor.

In keeping with the original proposal that multiple protonation was responsible for the displacement of the iminooxosulphurane from the metal centre, we find that the cationic sulphinamide complex [Ru(OSNHC$_6$H$_4$Me-4)(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$]SbF$_6$ is rapidly converted to [RuCl$_2$(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$] by gaseous hydrogen chloride. The use of non-coordinating anions to intercept intermediates is a recurring feature of the chemistry described in the remainder of this paper.

Table 2

NMR data for the complexes [a]

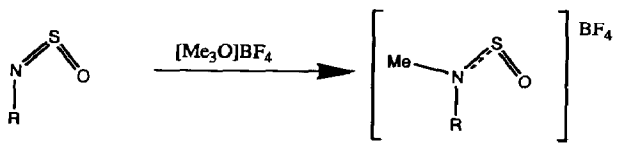
Complex	$^{31}P-\{^1H\}$ [b]	^1H
	δ (ppm)	δ (ppm)
[(**Ru**)(OSNHC$_6$H$_4$Me-4)]SbF$_6$	29.0	1.94 (s, 6H, C$_6$H$_3$*Me*$_2$) 2.16 (s, 3H, C$_6$H$_4$*Me*) 5.24 (s,(br), 1H, *NH*)
[(**Ru**)(OSNHC$_6$H$_4$Me-4)(CN^{t}Bu)]SbF$_6$	28.8	1.16 (s, 9H, ^{t}Bu) 1.82 (s, 6H, C$_6$H$_3$*Me*$_2$) 2.14 (s, 3H, C$_6$H$_4$*Me*) 5.51 (s,(br), 1H, N*H*)
[(**Ru**)(OSNHC$_6$H$_4$Me-4(SCN)]	29.7	1.86 (s, 6H, C$_6$H$_3$*Me*$_2$) 2.15 (s, 3H, C$_6$H$_4$*Me*) 5.34 (s(br), 1H, N*H*)
[(**Ru**)(CH$_3$OSNC$_6$H$_4$Me-4)]OTf	32.1	2.10 (s, 6H, C$_6$H$_3$*Me*$_2$) 2.32 (s, 3H, C$_6$H$_4$*Me*$_2$) 2.73 (s, 3H, OC*H*$_3$)
[(**Ru**)(CH$_3$CH$_2$OSNC$_6$H$_4$Me-4)]O$_3$SF	31.5	2.08 (s, 6H, C$_6$H$_3$*Me*$_2$) 2.32 (s, 3H, C$_6$H$_4$*Me*) 2.79, 3.57 (m×2, 5H, OC*H*$_2$C*H*$_3$)
[(**Ru'**)(CH$_3$OSNC$_6$H$_4$Me-4)]SbF$_6$	30.6	2.28 (s, 3H, C$_6$H$_4$*Me*) 2.84 (s, 3H, OC*H*$_3$)
[(**Ru**){(CH$_3$)$_3$SiOSNC$_6$H$_4$Me-4}]OTf	28.7	1.90 (s, 9H, Si*CH*$_3$) 2.13 (s, 6H, C$_6$H$_3$*Me*$_2$) 2.31 (s, 3H, C$_6$H$_4$*Me*)
[(**Os**)(F$_3$BOSNC$_6$H$_4$Me-2)]	2.7	1.90 (s, 3H, C$_6$H$_4$*Me*)

[a] NMR data for the compounds were obtained from saturated solutions of the complex in $CDCl_3$ at room temperature, in general, aromatic proton resonances due to xylyl and tolyl groups obscured by PPh_3 signals. [b] Measured at 89.56 MHz and given in ppm relative to internal $SiMe_4$ (0.00 ∂). (**Ru**) = Ru(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$; (**Ru'**) = Ru(CO)$_2$(PPh$_3$)$_2$; (**Os**) = Cl(NO)(PPh$_3$)$_2$, OTf = O$_3$SCF$_3$.

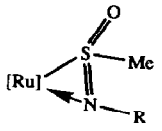
Alkylation

Perez and Kresze have shown that the dienophilic reactivity of iminooxosulphuranes may be enhanced by a comparatively facile alkylation with trialkyloxonium salts [7] (Scheme 3). It is therefore somewhat surprising that the iron complexes [Fe(CO)$_2$(PPh$_3$)$_2$(OSN-Aryl)] are unreactive towards potent alkylating agents [4], more so when the reactivity of these complexes is compared to that of the related compound [Fe(CO)$_2$(PPh$_3$)$_2$(CS$_2$)] [8].

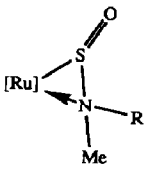
In contrast, the iminooxosulphurane ligand is rapidly cleaved from the ruthenium complexes [Ru(CO)(L)(PPh$_3$)$_2$(OSNC$_6$H$_4$Me)] (L = CO, CNC$_6$H$_3$Me$_2$-2,6) upon treatment with methyl iodide, a comparatively mild alkylating agent. The use of a



Scheme 3. Alkylation of free iminooxosulphuranes.



A



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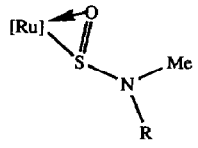

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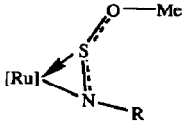


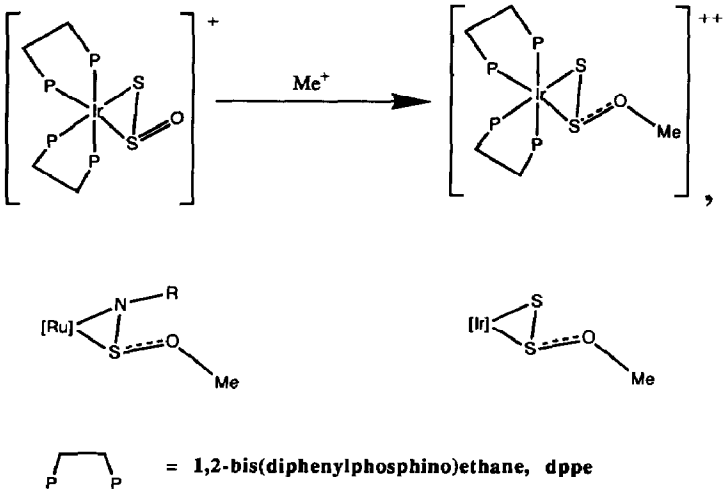
D

Scheme 4. Isomers for methylation of coordinated iminooxosulphuranes ([Ru] = [Ru(CO)(CNC$_6$H$_3$Me$_2$)(PPh$_3$)$_2$]$^+$, R = C$_6$H$_4$Me-4).

nonnucleophilic counter anion allowed the isolation of intermediates in the protonation studies and so a similar strategy was employed here. Methyl trifluoromethylsulphonate (MeOTf, methyl triflate) reacts immediately with the complexes [Ru(CO)(L)(PPh$_3$)$_2$(OSNC$_6$H$_4$Me)] in dichloromethane or tetrahydrofuran (THF) to form ionic 1 : 1 adducts. The infrared spectra are not altered by anion exchange indicating the absence of any association between the complex cation and the OTf$^-$ counter-anion. This anion exchange may be accomplished quickly in ethanol/dichloromethane solutions with NaSbF$_6$, NH$_4$PF$_6$ and NaBF$_4$, however, the complexes are slowly hydrolysed by prolonged contact with ethanol. The products of this hydrolysis have not been identified.

A number of possible structures may be considered (Scheme 4, however on the basis of spectroscopic data, structure **D** would appear to be most reasonable: Structures **A** and **B**, whilst chemically reasonable, should give rise to AB-systems in the ^{31}P-{^{1}H} NMR spectra due to the asymmetry of the phosphorus environments. Structures **C** and **D**, through the availability of dynamic fluxional processes allow for an averaging of the phosphines. The discrimination between **C** and **D** is difficult and rests, somewhat tenuously, upon spectroscopic data, and contrast in reactivity with the protonation products described above. The products display methyl resonances at ca. 2.8 ppm which, allowing for the net monopositive charge on the complexes, compare well with the value observed for the related dicationic S=S=OCH$_3^+$ complex of iridium prepared by alkylation of the disulphur monoxide complex cation [Ir(dppe)$_2$(S$_2$O)]$^+$ (dppe = 1,2-bis(diphenylphosphino)ethane) (Scheme 5) [9]. Both alkylation reactions are therefore consistent with the transfer of electron density from the metal centre out, through the cumulene, to the exocyclic oxygen atom.

The structural assignment **D** is also consistent with the observation that the methylated complexes fail to react with either of the nucleophilic ligands SCN$^-$ or



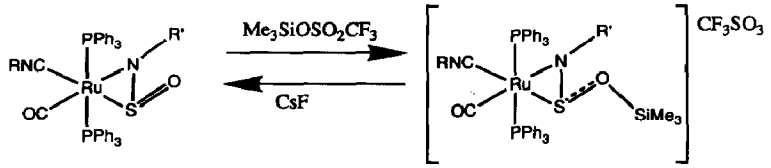
Scheme 5. Alkylation of coordinated disulphur monoxide.

CN^tBu whilst the protonated complexes react rapidly (1–2 min), providing monodentate iminooxosulphurane-derived ligands.

The generality of the reaction was investigated briefly. Methyl iodide reacts slowly to provide $[Ph_3PCH_3]I$ as the only isolated product. As with hydrogen chloride, the ability of the counter anion to coordinate to the cationic complex may be responsible for subsequent alkylation and degradation of the compound. Coordination would presumably by only transient in view of the inability of the thiocyanate anion to coordinate strongly. Ethyl fluorosulphonate provides the ethyl analogues of the methylation reaction.

Silylation

The reaction of $[Ru(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2(OSNC_6H_4Me\text{-}4)]$ with Me_3SiCl leads to rapid cleavage of the iminooxosulphurane ligand and formation of the dichloro complex $[RuCl_2(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$. Clearly the problem of multiple attack is once again apparent. When the potent silylating agent trimethylsilyl trifluoromethysulphonate, Me_3SiOTf, is used, however, this problem is avoided and a simple 1 : 1 adduct may be isolated of composition $[Ru(Me_3SiOSNC_6H_4Me\text{-}4)(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2][O_3SCF_3]$ (Scheme 6). The infrared activity associated with ν(SO) apparent in the starting material disappears upon silylation and whilst a band presumably due to ν(NS) appears at 889 cm^{-1}. The trimethylsilyl group is evident at in the ^1H NMR at δ 1.90 ppm with signals due to the methyl



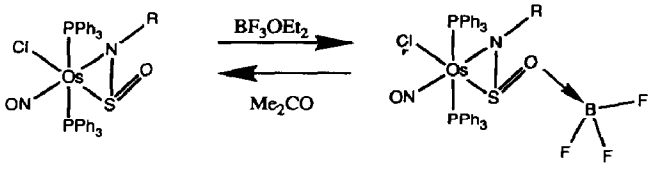
Scheme 6. Silylation of coordinated iminooxosulphuranes R = $C_6H_3Me_2$-2,6, R′ = C_6H_4Me-4).

substituents of the iminooxosulphurane and isonitrile occurring at δ 2.31 and 2.13 ppm, respectively.

The alkylation products described above were hydrolysed by ethanol to unidentified products. The silylated compound $[Ru(Me_3SiOSNC_6H_4Me\text{-}4)(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2][O_3SCF_3]$, however, is cleanly converted to the precursor iminooxosulphurane complex by caesium fluoride in thf solution. This appears to be a reflection of the increased facility of nucleophilic attack at silicon as opposed to carbon.

Lewis-acid adduct formation

The preceding results indicate a large build-up of negative charge on the exocyclic oxygen atom of the iminooxosulphurane as a result of coordination to an electron-rich metal centre. The reactions of η^2-(S, N) iminooxosulphurane complexes with the Lewis-acid boron trifluoride (as the diethyl etherate) were therefore investigated, bearing in mind the exceptionally hard nature of the acid. The zerovalent osmium complex $[OsCl(NO)(PPh_3)_2(OSNC_6H_4Me\text{-}2)]$ (prepared quantitatively in situ from $[OsCl(NO)(PPh_3)_2(CH_2CH_2)]$ [13] and OSN-C_6H_4Me-2) showed no detectable change when treated with $BF_3 \cdot OEt_2$ (10 fold excess) in tetrahydrofuran (monitored by solution infrared spectroscopy of the ν(NO) absorption). When the solvent was removed and replaced by the less nucleophilic solvent dichloromethane, the red colour of the precursor was replaced by a bright orange solution which showed ν(NO) activity at 1813 cm^{-1}, approximately 85 cm^{-1} to higher energy than in the precursor iminooxosulphurane complex. A thermally stable complex may be isolated by crystallisation from dichloromethane/pentane mixtures which corresponds to the adduct $[OsCl(NO)(PPh_3)_2(F_3BOSNC_6H_4Me\text{-}2)]$ (Scheme 7). In this case the ν(SO) region of the infrared spectrum is obscured by strong absorptions associated with the O-BF_3 group however a band at 916 cm^{-1} may be tentatively assigned to ν(NS) activity. Similar results were obtained for the ruthenium complexes when treated with $BF_3 \cdot OEt_2$. As in the silylation case, adduct formation is reversible and addition of a hard, potentially coordinating solvent (tetrahydrofuran or acetone), the BF_3 is rapidly liberated with regeneration of the iminooxosulphurane precursor. The complexation/decomplexation sequence may be cycled repeatedly with no deterioration of the sample, so long as moisture is strictly eliminated from the reaction vessel. It is noteworthy that only very basic, aliphatic iminooxosulphuranes form (very weak) adducts with BF_3 in the free state, as determined by tensimetric titrations for a range of iminooxosulphuranes [10]. Clearly the π-component of the coordination to a transition metal is very important.



Scheme 7. Reaction of a coordinated iminooxosulphurane with boron trifluoride (R = C_6H_4Me-2).

Conclusions

Coordination of iminooxosulphuranes to electron rich metal centres activates them towards electrophilic attack. To identify the initial product of electrophilic addition it is essential (in the cases studied here) to eliminate the possibility of multiple attack. In the case of positively charged electrophiles, this may be facilitated by the presence of a nucleophilic counter-anion which may coordinate and reduce the positive charge of the complex. Appreciating this problem allows the controlled electrophilic attack at a coordinated iminooxosulphurane cumulene by CH_3^+, $C_2H_5^+$, H^+ and Me_3Si^+, the latter two processes being easily reversed by a suitable base or nucleophile. Furthermore, neutral electrophiles, such as BF_3, may be employed.

Experimental

General experimental procedures and instrumentation [11] and the compounds [Ru(CO)(L)$(PPh_3)_2$(OSNR)] (L=CO, $CNC_6H_3Me_2$-2,6; R=C_6H_4Me-2, C_6H_4Me-4) [2] and [OsCl(NO)$(PPh_3)_2$(OSNR)] [12] are described elsewhere. Physical data for the complexes are listed in Tables 1 and 2.

[Ru(OSNHC$_6$H$_4$Me-4)(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$]SbF$_6$

A solution of [Ru(CO)($CNC_6H_3Me_2$-2,6)$(PPh_3)_2$(OSNC$_6$H$_4$Me-4)] (0.20 g, 0.21 mmol) in dichloromethane (20 cm^3) and ethanol (0.2 cm^3) was titrated with hexafluoroantimonic acid by monitoring the disappearance of the isonitrile and carbonyl absorptions in the infrared at 2107 and 1926 cm^{-1}, respectively, these being replaced by bands at 2149 and 1984 cm^{-1}. The mixture was freed of solvent under reduced pressure and the residue crystallised from a mixture of thf and pentane at −30 °C. Yield 0.19 g (77%) M.p. 206 °C decomp. Anal. Found: C, 53.7; H, 3.9; N, 2.0. $C_{53}H_{47}F_6N_2O_2P_2RuSSb$ calc.: C, 54.2; H, 4.0; N, 2.4%.

A convenient method of purification of the iminooxosulphurane complex [Ru(CO)($CNC_6H_3Me_2$-2,6)$(PPh_3)_2$(OSNC$_6$H$_4$Me-4)] is via the protonation procedure described above, followed by suspension of the salt in methanol containing a small amount of potassium hydroxide. The neutral iminooxosulphurane complex precipitates from this mixture in high purity.

[Ru(SCN)(OSNHC$_6$H$_4$Me-4)(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$]

Potassium thiocyanate (0.05 g, 0.50 mmol) and [Ru(OSNHC$_6$H$_4$Me-4)(CO)($CNC_6H_3Me_2$-2,6)$(PPh_3)_2$]SbF_6 (0.20 g, 0.17 mmol) were suspended in ethanol and stirred for 15 min. The yellow solid was isolated by filtration, washed with cold ethanol and pentane and dried in vacuo. Yield 0.14 g (83%). Decomposes without melting at 151 °C. Anal. Found: C, 65.1; H, 4.7; N, 4.0. $C_{54}H_{47}N_3O_2P_2RuS_2$ calc.: C, 65.0; H, 4.8; N, 4.2%.

[Ru(OSNHC$_6$H$_4$Me-4)(CO)(CNC$_6$H$_3$Me$_2$-2,6)(CN^{t}Bu)(PPh$_3$)$_2$]SbF$_6$

A solution of [Ru(OSNHC$_6$H$_4$Me-4)(CO)($CNC_6H_3Me_2$-2,6)$(PPh_3)_2$]SbF_6 (0.20 g, 0.17 mmol) in dichloromethane (20 cm^3) was treated with t-butyl isonitrile (ca. 0.02 cm^3) and stirred for 15 min. The solvent volume was reduced to ca. 5 cm^3 and toluene added to effect crystallisation of the colourless product which was isolated

by filtration and washed with pentane and dried in vacuo. Addition of pentane was occasionally necessary to induce crystallisation. Yield 0.16 g (75%). M.p. 102°C decomp. Anal. Found: C, 55.6; H, 4.7; N, 3.5. $C_{58}H_{56}F_6N_3O_2P_2RuSSb$ calc.: C, 55.4; H, 4.5; N, 3.3%.

[Ru(CH$_3$OSNC$_6$H$_4$Me-4)(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$]O$_3$SCF$_3$

A solution of [Ru(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$(OSNC$_6$H$_4$Me-4)] (0.50 g, 0.53 mmol) in dichloromethane (50 cm^3) was treated with methyl trifluoromethylsulphonate (0.065 cm^3, 1.1 equivalents). Toluene was added and the solution concentrated slowly under reduced pressure to ca. 10 cm^3. The suspension was then cooled to −30°C overnight to complete crystallisation. Yield 0.56 g (96%). M.p. 124°C. Anal. Found: C, 59.6; H, 4.4; N, 2.7. $C_{55}H_{49}F_3N_2O_5P_2RuS_2$ calc.: C, 59.9; H, 4.5; N, 2.5%.

[Ru(CH$_3$OSNC$_6$H$_4$Me-4)(CO)$_2$(PPh$_3$)$_2$]SbF$_6$

The complex was prepared in the same manner as [Ru(CH$_3$OSNC$_6$H$_4$Me-4)(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$]O$_3$SCF$_3$ and recrystallised from a mixture of dichloromethane, ethanol and water containing an excess (2–3 equivalents) of sodium hexafluoroantimonate. Yield 0.36 g (67%) M.p. 133°C.

[Ru(CH$_3$CH$_2$OSNC$_6$H$_4$Me-4)(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$]O$_3$SF

A solution of [Ru(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$(OSNC$_6$H$_4$Me-4)] (0.50 g, 0.53 mmol) in dichloromethane (25 cm^3) was treated with a solution of ethyl fluorosulphonate in dichloromethane (10% vol/vol) in a dropwise manner until the reaction was complete as determined by solution infrared spectroscopy. Toluene (20 cm^3) was added and the solvent volume reduced in vacuo to ca. 15 cm^3. Further toluene (20 cm^3) was added and the suspension cooled to −30°C overnight to complete crystallisation of the yellow product. This was isolated by filtration and recrystallised from dichloromethane/toluene. Yield 0.39 g (69%). M.p. 124°C decomp. Anal. Found: C, 60.3; H, 4.7; N, 2.7. $C_{55}H_{50}F_3N_2O_5P_2RuS_2$ calc.: C, 59.9; H, 4.6; N, 2.5%.

[Ru(Me$_3$SiOSNC$_6$H$_4$Me-4)(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$]O$_3$SCF$_3$

A solution of [Ru(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$(OSNC$_6$H$_4$Me-4)] (0.50 g, 0.53 mmol) in dichloromethane (50 cm^3) and treated with trimethylsilyl trifluoromethylsulphonate in a dropwise manner until the infrared activity due to the starting complex had disappeared. The solvent volume was reduced to 10 cm^3 in vacuo and pentane (100 cm^3) added slowly to precipitate the ionic product. The colourless precipitate was isolated by decantation and washed twice with pentane (50 cm^3) and recrystallised from dichloromethane/pentane at −30°C. Yield 0.44 g (72%). M.p. 143°C decomp. Anal. Found: C, 58.5; H, 4.6; N, 2.3. $C_{57}H_{56}F_3N_2O_5P_2RuS_2Si$ calc.: C, 59.0; H, 4.8; N, 2.4%.

[OsCl(NO)(PPh$_3$)$_2$(F$_3$BOSNC$_6$H$_4$Me-2)]

A solution of [OsCl(NO)(PPh$_3$)$_2$(OSNC$_6$H$_4$Me-2)] in THF was prepared by adding two drops of OSNC$_6$H$_4$Me-2 to a solution of [OsCl(NO)(PPh$_3$)$_2$(CH$_2$CH$_2$)] (0.20 g, 0.25 mmol) in THF (20 cm^3). An excess of boron trifluoride diethyletherate (0.05 cm^3) was added and the solvent removed under reduced pressure. The orange

residue was crystallised from dichloromethane/pentane at −30 °C to provide the desired product as orange microcrystals. Yield 0.24 g (94%). Decomposes at 68 °C without melting to provide a dark red solid which melts at 122 °C and is presumably $[OsCl(NO)(PPh_3)_2(OSNC_6H_4Me\text{-}2)]$. Recrystallisation of $[OsCl(NO)(PPh_3)_2(F_3BO\text{-}SNC_6H_4Me\text{-}2)]$ from THF/pentane regenerates the starting complex $[OsCl(NO)(PPh_3)_2(OSNC_6H_4Me\text{-}2)]$. Satisfactory elemental microanalytical data were not obtained, presumably due to the lability of the BF_3 group.

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