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The coordination chemistry of iminooxosulphuranes

III *. Synthesis of the ruthenium complexes $[Ru(CO)(PPh_3)_2(L)(OSNR)]$ ($L = CO, CN^tBu, CNC_6H_3Me_2$-2,6; $R = C_6H_4Me$-2, C_6H_4Me-4)

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Abstract

The tris(phosphine) complexes $[Ru(CO)(PPh_3)_3(L)]$ ($L = CO$, CN^tBu, $CNC_6H_3Me_2$-2,6) react with iminooxosulphuranes, RN=S=O, ($R = C_6H_4Me$-2, C_6H_4Me-4) by a displacement of one labile phosphine ligand to provide $[Ru(CO)(PPh_3)_2(L)(OSNR)]$. Spectroscopic data indicate that the heterocumulenes are bound to ruthenium through both nitrogen and sulphur. Sulphur dioxide coordinates in a similar bidentate mode, through sulphur and oxygen, in the complexes $[Ru(CO)(PPh_3)_2(L)(SO_2)]$ that are obtained upon treatment of the corresponding tris(phosphine) precursors with gaseous sulphur dioxide.

Introduction

The coordination of sulphur dioxide to a transition metal can involve a wide range of possible bonding geometries [2]. However, three modes of coordination predominate: coplanar $\{\eta^1\text{-(S)}\}$, monodentate pyramidal $\{\eta^1\text{-(S)}\}$, and bidentate pseudo-olefinic $\{\eta^2\text{-(S,O)}\}$ (Scheme 1).

Attempts to derive empirical rules to allow the prediction of bonding-mode preference for a given complex have been plagued by counter-examples [2]. Nevertheless, molecular orbital considerations have shed light on some of the factors

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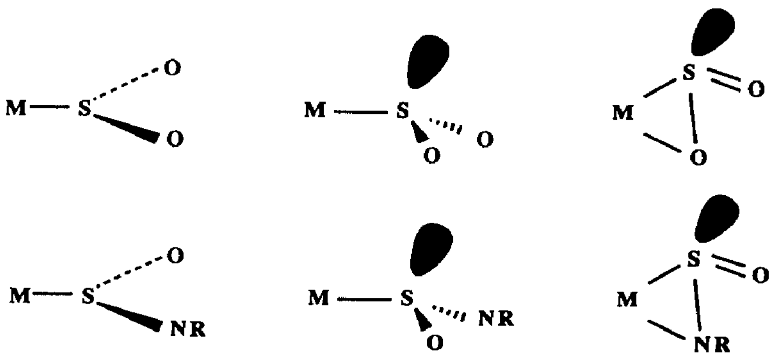
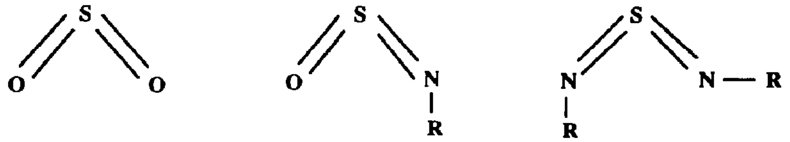
* For Part II see ref. 1.



Scheme 1. Bonding modes for SO_2 and iminooxosulphuranes.



Scheme 2. Imino derivatives of SO_2.

which may be important in determining coordination geometries for a given *d*-configuration [3].

Iminooxosulphuranes and diiminosulphuranes have heterocumulenic functional groups (Scheme 2) which are isoelectronic with SO_2 and are obtained (formally) by replacing one or both oxo substituents by imino groups. (For reviews on the chemistry of these compounds see refs. 4, 5).

As might therefore be expected these cumulenes have been observed to coordinate to low-valent metal centres in modes analogous to each of the above three geometries (Scheme 1) [6–11]. The bidentate mode of coordination has been observed to involve only the nitrogen–sulphur linkage [6–9]. This is perhaps not suprising when the molecular orbitals of the parent molecule HN=S=O are compared with those of SO_2 [12].

The paucity of examples of iminooxosulphurane complexes has precluded any detailed analysis of factors which may be important in discriminating between possible modes of coordination. Herein we describe a series of iminooxosulphurane complexes of zerovalent ruthenium which can be prepared in high yield. Their thermal stability and high degree of reactivity have facilitated an extensive investigation of ligand-based chemistry. The reactions of the coordinated "sulphinylamine" group will form the basis of a subsequent report [13].

Results and discussion

The zerovalent ruthenium complex $[Ru(CO)_3(PPh_3)_2]$ has been reported to react with sulphur dioxide to provide the substituted derivative $[Ru(CO)_2(PPh_3)_2(SO_2)]$ [14]. Further study of this reaction led to the isolation of the Lewis-acid adduct $[Ru(CO)_2(PPh_3)_2(SO_2 \cdot SO_2)]$ [15]. The first coordination sphere of this complex contains a bidentate (S,O) sulphur dioxide molecule to which a second molecule of SO_2 is bound such that the *exo* oxo substituent of the first molecule acts as a Lewis-base to the sulphur of the second. From this it is possible to infer that the coordination mode of SO_2 in the parent complex $[Ru(CO)_2(PPh_3)_2(SO_2)]$ is also bidentate [15].

This result is of special interest because it provides an indication of the type of bonding situation which might lead to activation of the sulphur(IV) cumulene; electron density is transferred from the electron-rich metal centre, through the cumulene, to an external electrophilic reagent. In embarking upon a study of the coordinative activation of iminooxosulphuranes, we sought a suitable "support" complex fragment upon which to carry out ligand modification and, accordingly, sources of the 16-electron metal-ligand fragments $Ru(CO)(PPh_3)_2(L)$ ($L = CO$, CN^tBu, $CNC_6H_3Me_2$-2,6) were investigated.

Ruthenium dicarbonyl complexes

In our studies on the complexes $[OsCl(NO)(PPh_3)_2(OSA)]$ ($A = O$, $NSO_2C_6H_4Me$-4) we have found the labile complexes $[OsCl(NO)(PPh_3)_2(L)]$ ($L = CH_2CH_2$, PPh_3) to be more convenient substrates than the corresponding carbonyl complex ($L = CO$) [9,16]. Accordingly, treatment of the tris(phosphine) complex $[Ru(CO)_2(PPh_3)_3]$ [17] with SO_2 gas rapidly provides the known complex $[Ru(CO)_2(PPh_3)_2(SO_2)]$ [15] in high yield. With *p*-tolyliminooxosulphurane, $OSNC_6H_4Me$-4, the analogous complex $[Ru(CO)_2(PPh_3)_2(OSNC_6H_4Me\text{-}4)]$ is obtained exclusively. Extended reaction times are to be avoided owing to the occurrence of complex secondary reactions between the product and liberated triphenylphosphine. Spectroscopic data for the complex suggest that the heterocumulene is bound to ruthenium in a bidentate manner through nitrogen and sulphur; two absorptions in the carbonyl region of the infrared spectrum (2015 and 1941 cm^{-1}) indicate a *cis* disposition for the two carbonyl ligands.

The appearance of one signal in the $^{31}P\text{-}\{^1H\}$ NMR spectrum suggests that the two phosphines are in chemically equivalent environments on the NMR timescale. This contrasts with the observed inequivalence of the phosphine environments apparent in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of $[OsCl(NO)(PPh_3)_2(OSNSO_2C_6H_4Me\text{-}4)]$, for which an [AB] quartet is observed, consistent with the presence of a rigid pyramidal sulphur contained in the equatorial coordination plane. The infrared spectrum of $[Ru(CO)_2(PPh_3)_2(OSNC_6H_4Me\text{-}4)]$ in the region 1300–800 cm^{-1} is particularly informative: two strong bands at 1040 and 938 cm^{-1} are consistent with a pseudo-olefinic coordination of the iminooxosulphurane cumulene. This mode of coordination is also suggested by the high values for $\nu(CO)$, which, upon comparison with other π-acid (L) complexes of the type $[Ru(CO)_2(PPh_3)_2(L)]$ ($L = PhCCPh$ 1950, 1895; C_2H_4 1955, 1900 [17]; CF_2 1983, 1910 [18]; CS_2 2010, 1945 cm^{-1} [19]), suggest a considerable drift of electron density from the metal to the cumulene. The two alternative monodenate bonding modes (Scheme 1) do not allow for efficient removal of electron density from the metal.

Ruthenium monocarbonyl-isonitrile complexes

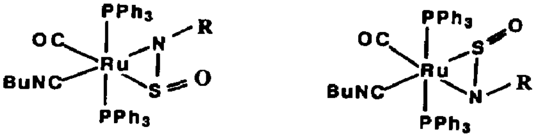
The strong acceptor function of an iminooxosulphurane ligated to a zerovalent ruthenium centre should be further enhanced by increasing the electron density at ruthenium. This is achieved by replacing one of the carbonyl ligands by a more weakly π-acidic isonitrile ligand. Manning did this by treating the complexes

[Fe(CO)$_2$(PPh$_3$)$_2$(OSN-aryl)] with t-butyl isonitrile [8] to produce [Fe(CO)(CN^{t}Bu)(PPh$_3$)$_2$(OSN-aryl)]. A similar strategy failed with the ruthenium dicarbonyl complex owing to reactions between the isonitrile and coordinated iminooxosulphurane which led to decomposition of the complex.

The complex [Ru(CO)(CNC$_6$H$_4$Me-4)(PPh$_3$)$_3$] is accessible via a multistep procedure from [RuClH(CO)(PPh$_3$)$_3$] [20] or by dehydrohalogenation of [RuClH(CO)(CNC$_6$H$_4$Me-4)(PPh$_3$)$_2$] in the presence of an excess of triphenylphosphine [21]. During the course of these studies, a "one-pot" synthesis of the related complex [Ru(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_3$] was developed [13] employing the commercially available xylyl isonitrile CNC$_6$H$_3$Me$_2$-2,6 (Fluka, Aldrich). Alternatively, the two step dehydrohalogenation method [21] is applicable to the synthesis of the complex [Ru(CO)(CN^{t}Bu)(PPh$_3$)$_3$].

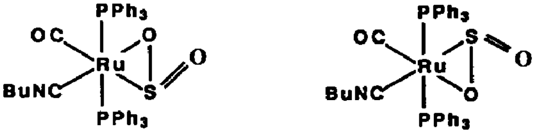
Solutions of the orange/red complex [Ru(CO)(CN^{t}Bu)(PPh$_3$)$_3$] in tetrahydrofuran (thf) or toluene when treated with *p*-tolyliminooxosulphurane give the complex [Ru(CO)(CN^{t}Bu)(PPh$_3$)$_2$(OSNC$_6$H$_4$Me-4)] in high yield (87%). The orange complex gives bands in the infrared spectrum at 2155 [ν(CN)] and 1920 cm^{-1} [ν(CO)] as well as absorptions indicative of the π-bound –N=S=O moiety (1029 and 928 cm^{-1}). The ν(NS)- and ν(SO)-associated absorptions are both observed at lower energies than those for the corresponding dicarbonyl complex.This suggests that the more electron-rich centre is more able to weaken both the N=S and S=O double bonds. Coordination of the cumulene in a bidentate manner involves retrodative bonding from filled metal-based *d*-orbitals to an anti-bonding orbital. This orbital, whilst being predominantly of S and N character, also extends significantly out into the exocyclic S=O bond. It is this interaction which is primarily responsible for the facility with which Lewis-acids coordinate to the exocyclic oxygen of π-bound SO$_2$ complexes.

Upon (formal) replacement of one of the two carbonyls in [Ru(CO)$_2$(PPh$_3$)$_2$(OSNC$_6$H$_4$Me-4)] by an isonitrile ligand, the question of geometrical isomers arises. In π-bound SO$_2$ complexes where the SO$_2$ molecule may coordinate in such a way that the sulphur and oxygen atoms bound to the metal are *trans* to different ligands, the sulphur atom typically coordinates *trans* to the poorer acceptor ligand [2]. A theoretical interpretation of this phenomenon has been offered [3]. On the basis of purely spectroscopic data it is not possible to determine which of the possible isomers of [Ru(CO)(CN^{t}Bu)(PPh$_3$)$_2$(OSNC$_6$H$_4$-4) is formed, i.e., S *trans* to the carbonyl (**A**) or isonitrile (**B**) ligand (Scheme 3). The spectroscopic data for the corresponding SO$_2$ complex are, however, instructive.



A **B**

Scheme 3. R = C$_6$H$_4$Me-*p*.



C D

Scheme 4

Complex [Ru(CO)(CN^{t}Bu)(PPh$_3$)$_3$] reacts rapidly with sulphur dioxide gas in tetrahydrofuran (thf) to provide the adduct [Ru(CO)(CN^{t}Bu)(PPh$_3$)$_2$(SO$_2$)] as orange air-sensitive crystals (from thf/pentane mixtures). The ν(SO)-associated infrared activity confirms π-coordination (1051 and 857 cm^{-1}), and bands at 2150 and 1902 cm^{-1} are assigned ν(CN) and ν(CO), respectively.

The stereochemistry of [Ru(CO)(CN^{t}Bu)(PPh$_3$)$_2$(OSNC$_6$H$_4$Me-4)] follows from a consideration of ν(CO) and ν(CN)-associated infrared data for the adducts of Ru(CO)(CN^{t}Bu)(PPh$_3$)$_2$ with SO$_2$ and OSNC$_6$H$_4$Me-4. Reasoning that the greatest electronic perturbation upon replacing an "oxo" group with an "imino" group will be suffered by the ligand *trans* to the site of exchange, it is apparent that the replacement occurs *trans* to the carbonyl ligand [$\Delta\nu$(CO) 18 vs. 5 cm^{-1} for $\Delta\nu$(CN)]. This result is also consistent with expectations based on the relative acceptor strengths of isonitrile and carbonyl ligands. Thus, in both the SO$_2$ and iminooxosulphurane complexes the sulphur atom is apparently coordinated *trans* to the isonitrile ligand, so that the π-acid orbital based primarily on sulphur competes with the poorest acceptor ligand for metal-based $d\pi$-electron density (isomers **B** and **D**, Schemes 3 and 4).

The complex [Ru(CO)(CNC$_6$H$_3$Me-2,6)(PPh$_3$)$_3$] reacts with the iminooxosulphuranes RNSO (R = C$_6$H$_4$Me-2, C$_6$H$_4$Me-4) in a manner completely analogous to that observed for the t-butyl isonitrile complex. The convenient synthesis of the tris(phosphine) precursor allows large scale preparations of the complexes [Ru(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$(OSNR)] (1–8 g), and this has greatly facilitated an investigation of the ligand-based chemistry of iminooxosulphuranes to be described later [13].

Experimental

General experimental procedures and instrumentation [9] and the synthesis of the compounds [Ru(CO)$_2$(PPh$_3$)$_3$] [17], [Ru(CO)(CN^{t}Bu)(PPh$_3$)$_3$], [Ru(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_3$] [13] and RNSO (R = C$_6$H$_4$Me-2, C$_6$H$_4$Me-4) [22] are described elsewhere.

The syntheses of the compounds [Ru(CO)(PPh$_3$)$_2$(L)(OSNR)] (L = CO, R = C$_6$H$_4$Me-4; L = CN^{t}Bu, R = C$_6$H$_4$Me-4; L = CNC$_6$H$_3$Me$_2$-2,6, R = C$_6$H$_4$Me-2, C$_6$H$_4$Me-4) and [Ru(CO)(PPh$_3$)$_2$(L)(SO$_2$)] are completely analogous. Accordingly, only exemplary preparative details for [Ru(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$(OSNC$_6$H$_4$Me-2)] and [Ru(CO)(CN^{t}Bu)(PPh$_3$)$_2$(SO$_2$)] are given in full. Physical data for the complexes are listed in Tables 1 and 2. Selected representative complexes gave satisfactory elemental microanalytical data.

Table 1

Infrared data for the complexes

Complex ($\mathrm{L = PPh_3}$)	ν(NO/CO)	ν(C≡N)	ν(SO)	ν(NS)	ν(C–N)
$[\mathrm{Ru(CO)_2L_2(SO_2)}]$ cf. [14]	2000		1096		
(yellow)	1932		847		
$[\mathrm{Ru(CO)(CN^tBu)L_2(SO_2)}]$	1902	2150	1051		
(orange)			857		
$[\mathrm{Ru(CO)(CNC_6H_3Me_2\text{-}2,6)L_2(OSNC_6H_4Me\text{-}2)}]$	1927	2106	1029	939	1300
(orange)					1285
$[\mathrm{Ru(CO)_2L_2(OSNC_6H_4Me\text{-}4)}$	2015		1040	938	1310
(orange)	1941				1283
$[\mathrm{Ru(CO)(CN^tBu)L_2(OSNC_6H_4Me\text{-}4)}]$	1920	2155	1029	928	1310
(orange)					1295
$[\mathrm{Ru(CO)(CNC_6H_3Me_2\text{-}2,6)L_2(OSNC_6H_4Me\text{-}4)}]$	1927	2107	1029	932	1306
(orange)					
$[\mathrm{PtL_2(OSNC_6H_4Me\text{-}4)}]$ cf. [6]			1056	922	1250
(pale yellow)					

[a] Infrared data were obtained from Nujol mulls between KBr discs in the range 400–4000 cm^{-1}.

$[\mathit{Ru(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2(OSNC_6H_4Me\text{-}4)}]$

A suspension of $[\mathrm{Ru(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_3}]$ (6.00 g, 5.73 mmol) in toluene (20 cm^3) was treated with $\mathrm{OSNC_6H_4Me\text{-}2}$ (1.00 g, 1.15 equivalents) and the bright yellow suspension stirred for 1 h. Pentane (60 cm^3) was then added, stirring was continued for a further 10 min, and the yellow product was isolated by filtration. Recrystallisation from a mixture of thf/pentane gave the product as the thf mono solvate (evident by ^{1}H NMR integration). Yield 5.17 g (91%). M.p. 148°C (decomp.). Anal.Found: C, 67.51; H, 4.72; N, 3.08. $\mathrm{C_{53}H_{46}O_2N_2P_2RuS}$ calc.: C, 67.86; H, 4.94; N, 2.99%.

Table 2

NMR data for the complexes

Complex ($\mathrm{L = PPh_3}$) [a]	^{31}P-{^{1}H}	^{1}H
$[\mathrm{Ru(CO)_2L_2(SO_2)}]$ cf. [14]		
(yellow)	37.7	–
$[\mathrm{Ru(CO)(CN^tBu)L_2(SO_2)}]$		
(orange)	38.5	0.80 [s, 9H, $\mathrm{C(C\mathit{H}_3)_3}$]
$[\mathrm{Ru(CO)(CNC_6H_3Me_2\text{-}2,6)L_2(OSNC_6H_4Me\text{-}2)}]$	37.5	1.96 [s, 3H, $\mathrm{C_6H_4C\mathit{H}_3}$]
(orange)		2.05 [s, 6H, $\mathrm{C_6H_3(C\mathit{H}_3)_2}$]
$[\mathrm{Ru(CO)_2L_2(OSNC_6H_4Me\text{-}4)}]$	35.6	2.16 [s, 3H, $\mathrm{C_6H_4C\mathit{H}_3}$]
(orange)		
$[\mathrm{Ru(CO)(CN^tBu)L_2(OSNC_6H_4Me\text{-}4)}]$	38.3	1.01 [s, 9H, $\mathrm{C(C\mathit{H}_3)_3}$]
(orange)		2.15 [s, 3H, $\mathrm{C_6H_4C\mathit{H}_3}$]
$[\mathrm{Ru(COL)(CNC_6H_3Me_2\text{-}2,6)L_2(OSNC_6H_4Me\text{-}4)}]$	36.8	2.05 [s, 6H, $\mathrm{C_6H_3(C\mathit{H}_3)_2}$]
(orange)		2.16 [s, 3H, $\mathrm{C_6H_4C\mathit{H}_3}$]
$[\mathrm{PtL_2(OSNC_6H_4Me\text{-}4)}]$ cf. [6]	20.0	2.05 [s, 3H, $\mathrm{C_6H_4C\mathit{H}_3}$]
(pale yellow)	16.6	

[a] NMR data were obtained from saturated solutions of the complexes in $\mathrm{CDCl_3}$ at room temperature. ^{31}P-{^{1}H}: Measured at 36.20 MHz and given in ppm to high frequency of external $\mathrm{D_3PO_4/D_2O}$ (0.00 δ). ^{1}H: Measured at 89.56 MHz and given in ppm relative to internal $\mathrm{SiMe_4}$ (0.00 δ). Activity due to the xylyl and tolyl ring protons was, in general, obscured by that due to the triphenylphosphine ligands.

[Ru(CO)(CN^{t}Bu)(PPh$_3$)$_2$(SO$_2$)]

Sulphur dioxide gas was passed over the surface of a suspension of [Ru(CO)(CN^{t}Bu)(PPh$_3$)$_3$] (0.25 g, 0.25 mmol) in toluene (5 cm^3) for 10 s. The Schlenk tube then sealed and the mixture stirred for 5 min. Pentane (5 cm^3) was then added dropwise to complete precipitation of the product, which was recrystallised from thf/pentane at −30 °C. Yield 0.16 g (83%). Decomposes without melting at 172°C. Anal. Found: C, 62.55; H, 4.62; N, 1.93. $C_{42}H_{39}O_3NP_2RuS$ calc: C, 62.99; H, 4.91%.

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