The coordination chemistry of iminooxosulphuranes

V *. The osmium and iridium series [MLCl(PPh₃)₂(OSA)] (ML = OsNO, IrCO; A = O, CH₂, S, NR; R = *o*-tolyl, *p*-tolyl and *p*-tosyl)

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.)
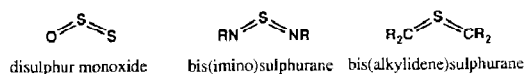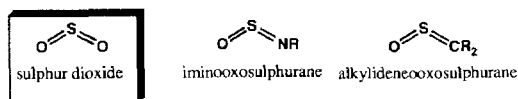
(Received November 17th, 1989)

Abstract

The preparation and characterisation of the two analogous series of compounds [OsCl(NO)(PPh₃)₂(OSA)] (A = O, CH₂, S, NR; R = C₆H₄Me-4, C₆H₄Me-2, SO₂C₆H₄Me-4) and [IrCl(CO)(PPh₃)₂(OSA)] (A = O, S, NSO₂C₆H₄Me-4) are described. A comparison of spectroscopic data for the complexes supports the isolobal relationship between the molecules OSA.
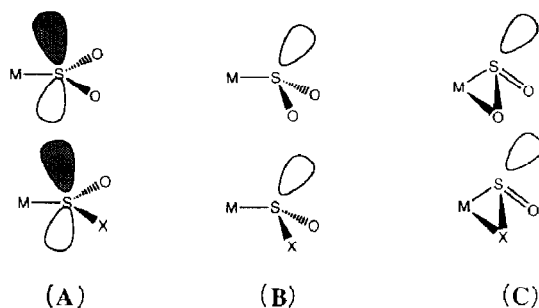
Introduction

In addition to sulphur dioxide, SO_2, the family of sulphur(IV) heterocumulenes includes a wide range of molecules obtained by formally replacing an oxo group by other suitable two-electron ligands, e.g., :NR, :CR₂, (R = hydrido, alkyl, aryl) or the heavier chalcogens, S, Se, and Te (Scheme 1). Whilst many substituted sulphines [2], iminooxosulphuranes and diiminosulphuranes [3] are stable isolable compounds, disulphur monoxide, S=S=O [4], sulphine CH₂=S=O [5], thionyl imine, HN=S=O [6] and sulphur diimine S(=NH)₂ [7] have only transient existence. Nevertheless these species have been observed spectroscopically [8–10] and been the subject of theoretical studies [10].

---

* For Part IV see ref. 1.

O=S=O	O=S=NR	O=S=CR₂
sulphur dioxide	iminooxosulphurane	alkylideneooxosulphurane
O=S=S	RN=S=NR	R₂C=S=CR₂
disulphur monoxide	bis(imino)sulphurane	bis(alkylidene)sulphurane

Scheme 1. Derivatives of sulphur dioxide.

(A)   (B)   (C)

(X = S, CR₂, NR; R = alkyl, aryl, sulphonyl.)

Scheme 2. Coordination modes for SO_2 and analogues.

Sulphur dioxide binds to transition metals in a wide range of modes (Scheme 2) depending primarily on the electron density at the metal and, to a lesser extent, on the frontier orbital symmetry of the metal ligand complex fragment involved [11]. The coordination chemistry of sulphurous heterocumulenes is less well established than that of the parent molecule sulphur dioxide. Examples of complexes of each class of compound in Scheme 1 have been reported but no complete series exists for one metal-ligand fragment which would allow a direct comparison of the bonding properties of these molecules. We report herein full details for the preparation of two such series, $[IrCl(CO)(PPh_3)_2(ASO)]$ (A = O, S, NSO₂C₆H₄Me-4) and $[OsCl(NO)(PPh_3)_2(ASO)]$ (A = O, S, CH₂, NR; R = C₆H₄Me-4, C₆H₄Me-2, SO₂C₆H₄Me-4). Preliminary accounts of some of the results have appeared [12,13].

Results and discussion

The parent sulphur dioxide complexes $[MLCl(PPh_3)_2(SO_2)]$ (ML = OsNO, IrCO)

Vaska's complex, $[IrCl(CO)(PPh_3)_2]$ [14], has been shown to coordinate sulphur dioxide reversibly to form the adduct $[IrCl(CO)(PPh_3)_2(SO_2)]$ in which the sulphur dioxide ligand binds through a pyramidally-coordinated sulphur atom [15], this having been established crystallographically [16] (A, Scheme 2). The 16-electron metal ligand fragment OsCl(NO)(PPh₃)₂ is isolobal with Vaska's complex but not readily isolable. However, suitable precursors exist which essentially react as the desired species by virtue of the presence of weakly coordinated ligands. These include $[OsCl(NO)(PPh_3)_2L]$ (L = CH₂CH₂[17], PPh₃[18]), and both compounds react readily with gaseous SO_2 to provide the 18-electron complex [OsCl(NO)-(PPh₃)₂(SO₂)]. Spectroscopic data for this and subsequent complexes are listed in Tables 1 and 2.

Table 1

Infrared data [cm⁻¹] for the complexes [a]

Complex (L$_n$Os = Cl(NO)(PPh$_3$)$_2$Os; L$_m$Ir = Cl(CO)(PPh$_3$)$_2$Ir)	ν(NO)/ν(CO)	ν(SO)	ν(AS)	ν(MCl)
L$_m$Ir(OSNC$_6$H$_4$NO$_2$-4) [22]	2000	1080	1110	270
L$_m$Ir(OSNSO$_2$C$_6$H$_4$Me-4) (orange)	2034	1023, 1014	1118	
L$_m$Ir(S$_2$O) (yellow)	2038	1040		
L$_n$Os(SO$_2$) (yellow)	1737	1133	846	278
L$_n$Os(OSNSO$_2$C$_6$H$_4$Me-4) (yellow)	1768	1088	920	279
L$_n$Os(OSNC$_6$H$_4$Me-2) (red)	1742	1078	946	284
L$_n$Os(OSNC$_6$H$_4$Me-4) (red)	1739	1079	946	280
L$_n$Os(S$_2$O) (orange)	1744	1063	–	293
L$_n$Os(CH$_2$SO) (orange)	1719	1035	–	282

[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.

The complex may also be prepared by keeping solutions of the corresponding carbonyl complex [OsCl(NO)(PPh$_3$)$_2$(CO)] [18] in liquid sulphur dioxide for prolonged periods (ca. 1 week). This reaction is very slow and presumably proceeds via electrophilic attack by sulphur dioxide at the 18-electron carbonyl complex (linear → bent nitrosyl?) followed by loss of carbon monoxide, the complex being inert towards simple dissociative substitution by nucleophilic ligands, e.g., phosphines. Spectroscopic data for the complex indicate that the sulphur dioxide ligand coordinates in a pseudo-olefinic manner, through one sulphur oxygen multiple bond (C, Scheme 2). Thus an IR band attributable to sulphur–oxygen stretching is observed at 1133 and 846 cm⁻¹ and may be compared directly with the corresponding bands of the ruthenium complex, [RuCl(NO)(PPh$_3$)$_2$(SO$_2$)] [19] which occur at slightly higher frequencies, viz. 1150 and 895 cm⁻¹. The latter complex has been shown to contain the sulphur dioxide ligand coordinated in a pseudo-olefinic (C) manner [19b].

Whilst the two metal-ligand fragments [MLCl(PPh$_3$)$_2$] (ML = OsNO, IrCO) are formally isolobal, their chemistries apparently diverge. According to the spectroscopic data for the adducts (see below), the iridium centre (formally monovalent) is less electron-rich than the osmium centre (formally zerovalent, NO considered to be bound as NO⁺). The pseudo-olefinic (or metallaoxathiirane) mode of coordination (C) is more efficient for removing the excess of electron density from an electron-rich metal centre than the pyramidal mode. The sulphur dioxide ligand in the iridium complex is weakly held and readily dissociates, whilst that of the osmium complex is irreversibly bound. This must be due in part to the relative energies of the 16-electron complexes formed upon dissociation, and has been observed for other

Table 2

NMR data for the complexes [a]

Complex (L$_n$Os = Cl(NO)(PPh$_3$)$_2$Os; L$_m$Ir = Cl(CO)(PPh$_3$)$_2$Ir)	^{31}P{^{1}H} [b]		^{1}H [c]
	∂ (ppm)	J(PP') (Hz)	∂ (ppm)
L$_m$Ir(OSNSO$_2$C$_6$H$_4$Me-4) (orange)	7.0	–	2.36
L$_m$Ir(S$_2$O) (yellow)	−11.6, 11.6	397	
L$_n$Os(SO$_2$) (yellow)	3.6	–	
L$_n$Os(OSNSO$_2$C$_6$H$_4$Me-4) (yellow)	−15.5, 9.1	350	2.38 (s, 3 H, CH_3)
L$_n$Os(OSNC$_6$H$_4$Me-2) (red)	−2.2, −2.8	[d]	1.86 (s, 3 H, CH_3)
L$_n$Os(OSNC$_6$H$_4$Me-4) (red)	−5.5, −2.8	[d]	2.15 (s, 3 H, CH_3)
L$_n$Os(S$_2$O) (orange)	−12.5, 4.7	372	
L$_n$Os(CH$_2$SO) (orange)	−1.0, 1.9	297	2.11 (d×d×d, 1 H, SCH ^{a}, J(PH) 9.3, 13.1; J(H ^{a}H ^{b}) 7.9 Hz), 2.67 (d×d×d, 1H, SCH ^{b}, J(PH) 10.5, 14.9, J(H ^{a}H ^{b}) 7.9 Hz)

[a] NMR data for the compounds were obtained from saturated solutions of the complex in CDCl$_3$ at room temperature. [b] Measured at 36.20 MHz and given in ppm relative to external D$_3$PO$_4$/D$_2$O (0.00 ∂), values reported are corrected for roof effects. [c] Measured at 89.56 MHz and given in ppm relative to internal SiMe$_4$ (0.00 ∂). [d] ∂-values given are for central pair of peaks of AB system, outer peaks not observed.

unsaturated molecules, e.g., carbon disulphide [20], formaldehyde, ethylene and alkynes [17].

The iminooxosulphurane complexes

The formal replacement of the oxo atoms in sulphur dioxide by an imino moiety leads to the iminooxosulphurane and diiminosulphurane classes of compounds (Scheme 1). The changes in the energy of the cumulene molecular orbitals which accompany this change will be discussed in more detail elsewhere [21]. It suffices to point out here that whilst the energies of the three potential donor orbitals for transition metal ligation [σ''(O/N), σ''(S) and π^b(OS/NS)] all increase in energy, it is the one associated with the N=S π-bonding that shows the greatest relative increase [10]. We therefore expect that iminooxosulphuranes should show a stronger tendency towards π-coordination than sulphur dioxide. This is also born out by Mülliken charge analysis, which shows that whilst (negative) charge on oxygen is essentially identical for the molecules SO$_2$ and HNSO, the positive charge on sulphur becomes delocalised out to the NH group, and this relocation should be
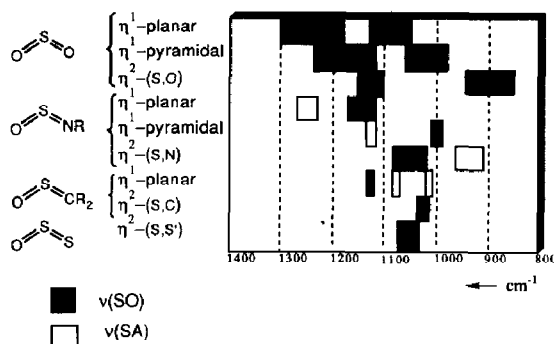
Fig. 1. Diagnostic infrared regions for O=S=A bound to a transition metal, A = O, NR, CR_2, and S.

important for directing retrodative interactions. These differences are not large, and cases where this distinction may be observed in coordination compounds will presumably be rare, but one example is provided by the rhodium complex [RhCl(PPh$_3$)$_2$(OSNSO$_2$C$_6$H$_4$Me-4)], in which the iminooxosulphurane cumulene is bound through the N=S double bond [21]. The analogous sulphur dioxide complex involves a planar coordination of the SO_2 molecule (**B**, Scheme 2).

As reported by Blake and Reynolds [22], simple aryliminooxosulphuranes do not form stable adducts with Vaska's complex. Thus [IrCl(SO$_4$)(CO)(PPh$_3$)$_2$] is the only product isolated from the reaction of [IrCl(CO)(PPh$_3$)$_2$] with O=S=NC$_6$H$_5$. In the case of an aryliminooxosulphurane bearing the strongly electron-withdrawing substituent O=S=NC$_6$H$_4$NO$_2$-4, a moderately stable complex was obtained, but washing solid samples of the complex with benzene or diethyl ether led to elimination of the cumulene. We find that treating Vaska's complex with the exceptionally electrophilic iminooxosulphurane O=S=NSO$_2$C$_6$H$_4$Me-4 (tosyl-NSO) provides a thermally stable 1 : 1 adduct.

The bright-orange compound shows a carbonyl band in the IR at 2034 cm^{-1}, an increase of ca. 70 cm^{-1} over that for the precursor complex and of ca. 35 cm^{-1} relative to that for the p-nitrophenyl-NSO complex [IrCl(CO)(PPh$_3$)$_2$(OSNC$_6$H$_4$-NO$_2$-4)] (ν(CO) 2000 cm^{-1}), indicating substantial transfer of electron density from the metal to the cumulene. Bands arising from the N=S=O group appear at 1118, 1023 and 1014 cm^{-1} (Nujol), and correspond to those observed for [IrCl(CO)(PPh$_3$)$_2$(OSNC$_6$H$_4$NO$_2$-4)] at 1110 and 1080 cm^{-1} [22]. Figure 1 displays published infrared data for complexes of sulphur dioxide analogues organised in terms of the coordination modes, and it appears that the infrared data for [IrCl(CO)(PPh$_3$)$_2$(OSN-tosyl)] fall into neither of the regions typical of coordination modes **A** or **C**. We therefore suggest that the cumulene in this complex is bound in a pyramidal manner through sulphur, analogous to the bonding adopted by SO_2 in the related sulphur dioxide complex. All manipulations of [IrCl(CO)(PPh$_3$)$_2$(OSN-tosyl)] must be carried out with strict exclusion of moisture, since adventitious water rapidly hydrolyses the complex to [IrCl(CO)(PPh$_3$)$_2$(SO$_2$)] and toluene sulphonamide.

Similar chemistry is observed for the rhodium based system: [RhCl(CO)(PPh$_3$)$_2$] reacts rapidly with tosyl-NSO to form a 1 : 1 adduct [RhCl(CO)(PPh$_3$)$_2$(OSN-tosyl)]. The cumulene-associated bands at 1126 and 1007 cm^{-1} (Nujol) indicate that again

the iminooxosulphurane is coordinated in a pyramidal manner, as is SO_2 in $[RhCl(CO)(PPh_3)_2(SO_2)]$ [11]. The hydrolysis of the former to the latter is more rapid than in the iridium case, in keeping with a decrease in metal basicity on going from Ir to Rh. An alternative route to $[RhCl(CO)(PPh_3)_2(OSN\text{-}tosyl)]$ involves the carbonylation of $[RhCl(PPh_3)_2(OSN\text{-}tosyl)]$ at atmospheric pressure, a reaction accompanied by a change in the cumulene coordination mode [21].

The osmium ethylene complex $[OsCl(NO)(PPh_3)_2(CH_2CH_2)]$ reacts under high dilution with tosyl-NSO by displacement of the labile ethylene ligand to provide the yellow complex $[OsCl(NO)(PPh_3)_2(OSN\text{-}tosyl)]$. If the reaction is carried out in high concentration, a novel coupling reaction of C=C and O=S multiple bonds occurs [23].

The iminooxosulphurane complex, whilst containing formally zerovalent osmium, has undergone substantial electron relocalisation from the electron-rich metal centre to the very electrophilic iminooxosulphurane cumulene. This is directly evident in the high $\nu(NO)$ frequency for the complex (1768 cm^{-1}) compared with that for the precursor, and is indirectly manifest in the increase in stability of the complex towards hydrolysis (deactivation of the hydrolytically reactive OSN-tosyl). As with the iridium complex, $[OsCl(NO)(PPh_3)_2(OSN\text{-}tosyl)]$ may be hydrolysed to the corresponding sulphur dioxide complex, but harsher conditions are required, viz. heating to 60°C in moist dimethylformamide, as indicated by monitoring by $^{31}P\{^1H\}$ NMR spectroscopy. The infrared absorptions due to the NSO cumulene are observed at 1088 and 920 cm^{-1}, indicating that in the case of the more electron-rich osmium centre the iminooxosulphurane coordinates through the nitrogen and sulphur atoms of the heterocumulene. This type of coordination has been proposed in the compounds $[Pt(PPh_3)_2(OSN\text{-}tosyl)]$ [22], $[Fe(CO)_2(PPh_3)_2\text{-}(OSN\text{-}aryl)]$ [24] and $[Ru(CO)(PPh_3)_2(L)(OSN\text{-}aryl)]$ (L = CO, CN^{t}Bu, $CNC_6H_3\text{-}Me_2\text{-}2,6$) [25] and crystallographically established for the complex $[Pt(PPh_3)_2(OSN\text{-}C_6H_2Me_3\text{-}2,4,6)]$ [26].

The pyramidal nature of the sulphur atom removes the *meso* plane of symmetry, and accordingly the phosphine ligands should experience different chemical environments in the osmium complexes $[OsCl(NO)(PPh_3)_2(OSA)]$. In the case of the sulphur dioxide complex the phosphine ligands give rise to only one signal in the $^{31}P\{^1H\}$ NMR and it must be assumed that the ^{31}P nuclei are in time-averaged symmetrical environments due to fluxional processes involving the sulphur dioxide ligand. These may involve rotation, inversion, or swiveling of the SO_2 ligand, all processes which are expected to require little energy. In the case of the tosyl-iminooxosulphurane complex $[OsCl(NO)(PPh_3)_2(OSN\text{-}tosyl)]$, the three-membered metallacycle is apparently rigid, and so the phosphine ligands are distinct on the $^{31}P\{^1H\}$ NMR timescale and an AB-quartet is observed (9.1, −15.5 ppm, $J(AB)$ 350 Hz). Attempts to determine the barrier to rotation/inversion indicated complex decomposition prior to signal coalescence.

It is noteworthy that the osmium tosyliminooxosulphurane complex may also be prepared from the tris(phosphine) complex $[OsCl(NO)(PPh_3)_3]$, and also, more surprisingly, from the substitution-inert complexes $[OsCl(NO)(PPh_3)_2(L)]$ (L = CO, SO_2), albeit slowly. It would appear that again an electrophilic substitution mechanism is operating with attack at either the metal or the sulphur dioxide ligand. We have observed electrophilic attack by tosyl-NSO at allene, acetylene, nitroso-benzene [21], and ethylene [23] coordinated to the '$OsCl(NO)(PPh_3)_2$' fragment,

and there is a precedent for electrophilic attack by sulphur dioxide upon coordinated sulphur dioxide [27].

In contrast to the results obtained with Vaska's compounds, we found that the more basic osmium analogue forms stable adducts with simple unactivated aryliminooxosulphuranes. Thus $[OsCl(NO)(PPh_3)_2(L)]$ $(L = C_2H_4, PPh_3)$ reacts rapidly with $OSN-C_6H_4Me-4$ to give the red complex $[OsCl(NO)(PPh_3)_2(OSNC_6-H_4Me-4)]$ in quantitative yield. The complex is essentially stable towards moisture but rapidly decomposed by air. In keeping with the presence of a less electron-withdrawing substituent on the nitrogen of the cumulene, we find that the infrared data for the complex indicate less efficient retrodative bonding from the metal to the cumulene. Thus the nitrosyl ligand gives rise to bands at 1739 cm^{-1}, at ca. 30 cm^{-1} lower frequency than the band for the tosyl derivative. Bands at 1079 and 946 cm^{-1} attest to π-coordination of the cumulene through nitrogen and sulphur, and the frequencies are comparable to those observed for the tosyl derivative.

It was of interest to determine whether *ortho*-substitution of the aryliminooxosulphurane ligand destabilised coordination. Accordingly, the complex $[OsCl(NO)-(PPh_3)_2(OSNC_6H_4Me-2)]$ was prepared in a manner analogous to that described for the *p*-tolyl derivative. However, other than an increase in air sensitivity, no significant differences in reactivity were observed.

The disulphur monoxide complexes

Disulphur monoxide, S_2O, is not independently stable but has been identified in high dilution in the gas phase and characterised spectroscopically [4]. As it is an analogue of SO_2 the question of its coordination chemistry arises (cf. [41]), and indeed complexes of S_2O have been successfully prepared [28–32] and structurally characterised [29,32]. The S_2O ligands in these complexes can be generated by oxidation of the corresponding disulphur compounds with suitable oxygen atom transfer reagents, e.g., 3-chloro perbenzoic acid. The generality of this method is of course limited by the poor understanding of the reactions which lead to the disulphur precursors.

We sought a route to complexes of disulphur monoxide which might be of wider applicability, and were intrigued by the reaction discussed above whereby coordinated iminooxosulphuranes were hydrolysed to coordinated sulphur dioxide. We reasoned that if water was replaced as the diprotic nucleophile by hydrogen sulphide in these reactions, then the ligand produced would be the desired disulphur monoxide molecule. Treatment of the iridium complex $[IrCl(CO)(PPh_3)_2(OSN-tosyl)]$ with gaseous hydrogen sulphide did, indeed, give the yellow complex $[IrCl(CO)(PPh_3)_2(S_2O)]$ in good yield [12]. The infrared spectrum shows a band at 1040 which may be attributed to sulphur–oxygen stretching, and its frequency may be compared with that, viz. 1038 cm^{-1}, observed for the complex $[Re(CO)_2(S_2O)(\eta-C_5H_5)]$ [30]. The $\nu(CO)$ band at 2038 cm^{-1} is at higher frequency than that for the corresponding tosyl-NSO complex, indicating that the S_2O ligand in this complex is a stronger acceptor than pyramidally bound tosyl-NSO. The $^{31}P\{^1H\}$ NMR spectrum of $[IrCl(CO)(PPh_3)_2(S_2O)]$ consists of an AB-quartet pattern consistent with inequivalent phosphine environments. Thus it would appear that the S_2O molecule binds in a psuedo-olefinic manner to Vaska's complex, i.e., in a mode different from that for SO_2, and has a high barrier to rotation.

The complex $[Re(CO)_2(S_2O)(\eta\text{-}C_5H_5)]$ contains S_2O coordinated through its sulphur-sulphur π-bond, whilst the corresponding sulphur dioxide complex has the rhenium atom coplanar with the SO_2 cumulene, to which it is bound through sulphur (A, Scheme 2). These observations suggest that S_2O has a stronger tendency towards π-coordination than SO_2 or even tosyl-NSO. The need for a situation permitting comparisons, with S_2O, R-NSO and SO_2 each bound to a metal-ligand fragment in the same coordination mode, prompted the synthesis of the osmium complex $[OsCl(NO)(PPh_3)_2(S_2O)]$. It would be expected that the S_2O ligand would be π-coordinated, and it has already been shown that the iminooxosulphurane and sulphur dioxide complexes show this bonding preference.

There was no apparent change upon treatment of a tetrahydrofuran solution of $[OsCl(NO)(PPh_3)_2(OSN\text{-}tosyl)]$ with hydrogen sulphide at room temperature. However, addition of a non-nucleophilic base, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), to generate the hydrosulphide ion led to a slow darkening of the reaction mixture and the formation of a green compound, which was isolated by column chromatography on silica gel with dichloromethane as eluent. The complex showed no band in the region $1600-600$ cm^{-1} other than those attributable to the phosphine ligand. The position of the band due to the nitrosyl ligand, at 1746 cm^{-1}, is typical of a zerovalent osmium species ligated by a strong π-acid and may be compared with that observed for other π-adducts $[OsCl(NO)(PPh_3)_2(L)](L = O_2$, 1740 [17]; CH_2S, 1728 [18]; Ph–NO, 1729 [33]; and SO_2, 1737 cm^{-1}). The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet, i.e., the molecule has a *meso* plane and accordingly no pyramidal sulphur atoms in the equatorial plane. The identity of the green complex was finally established by unequivocal synthesis.

The complexes $[Os(CO)_2(PPh_3)_2(E_2)]$ have been prepared via the reaction of the tris(phosphine) complex $[Os(CO)_2(PPh_3)_3]$ with elemental sulphur or selenium [34]. A similar reaction was found to take place between $[OsCl(NO)(PPh_3)_3]$ and cyclo-octasulphur in toluene, the major product being the green disulphur complex $[OsCl(NO)(PPh_3)_2(S_2)]$, which was isolated in ca. 70% yield by column chromatography. The compound is spectroscopically identical to that obtained from the reaction of $[OsCl(NO)(PPh_3)_2(OSN\text{-}tosyl)]$ and H_2S/DBU. Thus it appears that the reaction proceeds in a manner completely analogous to that observed for the iridium system, but under the strongly reducing conditions (SH^-) the initially formed disulphur monoxide ligand is further reduced to the corresponding disulphur complex. In this context it is relevant to note that the archetypal S_2O complex prepared by Schmid and Ritter [31] was obtained by reduction of the disulphur S,S'-dioxide complex cation $[Ir(dppe)_2(S_2O_2)]^+$ [dppe = 1,2-bis(diphenylphosphino)ethane].

With the disulphur complex available it was a trivial step to reoxidise the ligand to S_2O by using a suitable oxygen atom transfer reagent, such as 3-chloroperbenzoic acid (mCPBA). Other reagents which have been used successfully in related systems include peracetic acid, periodate ion, and even adventitious air [28-32]. Thus a green chloroform solution of $[OsCl(NO)(PPh_3)_2(S_2)]$ cooled to $-40\,^\circ C$ and treated with mCPBA quantitatively gave the orange disulphur monoxide complex $[OsCl(NO)(PPh_3)_2(S_2O)]$. The loss of mirror symmetry which accompanies this transformation renders the reaction amenable to study by $^{31}P\{^1H\}$ NMR spectroscopy: The singlet at -4.0 ppm is replaced by an AB-quartet (4.7, -12.5 ppm, $J(AB)$ 372 Hz). The reaction stops at the disulphur monoxide stage and there is no

evidence for the formation of a disulphur dioxide complex even in the presence of a threefold excess of peracid. Use of stronger oxidants was not investigated.

The synthetic scope made available by this reaction is vast. Complexes of *p*-tosyliminooxosulphurane may thus be considered synthetically equivalent to $[M=SO]^{2+}$ in reaction with the wide range of potential diprotic nucleophiles which could be employed. The synthesis in our laboratory of group 7 complexes of S_2O by this method hints at the generality of the S_2O complex synthetic strategy [35].

A complex of sulphine

The parent species of the alkylideneoxosulphurane or aldehyde-*S*-oxide class of compounds, sulphine CH_2SO, is not independently stable, and rapidly decomposes when formed. Nevertheless it has been generated by flash vacuum pyrolysis of suitable precursors, e.g., methyl allyl sulphone, dimethyl sulphoxide, and methyl sulphinyl chloride. The sulphine thus formed has been spectroscopically characterised [5,9,36] and its molecular geometry established. Of all the analogues of sulphur dioxide to be discussed here, this species is distinguished by having the highest energy associated with the π-bonding molecular orbital [10], and accordingly is expected to show a strong disposition towards, π-coordination.

Substituted sulphines have been found to coordinate to metals in one of two modes, corresponding to A (planar, η^1 through sulphur) and C (π pseudo olefinic through C and S) (Scheme 2) [37]. The synthetic strategy which has led to these complexes has involved the interaction of preformed alkylideneoxosulphuranes with coordinatively unsaturated metal-ligand fragment precursors. This method is clearly unsuitable for the synthesis of a complex of unsubstituted sulphine owing to the transient nature of such a complex.

Guided by the previous synthesis of a complex of disulphur monoxide by oxidation of the corresponding disulphur ligand, we investigated the possibility of oxidising a coordinated thioaldehyde [13]. Thioaldehydes are themselves not particularly stable entities although thioformaldehyde, the parent ligand has been prepared within the protective environment of a transition-metal coordination sphere. Thus the reaction of the osmium methylene complex $[OsCl(NO)(PPh_3)_2(CH_2)]$ with elemental sulphur leads to the thioformadehyde complex $[OsCl(NO)(PPh_3)_2(CH_2S)]$. Similar reactions with selenium and tellurium provide the selenoformaldehyde and telluroformaldehyde species [18]. Treatment of $[OsCl(NO)(PPh_3)_2(CH_2S)]$ with mCPBA in dichloromethane at $-78°C$ gives an orange complex of composition $[OsCl(NO)(PPh_3)_2(CH_2SO)]$ in good yield.

The sulphine complex, $[OsCl(NO)(PPh_3)_2(CH_2SO)]$, has no plane of symmetry owing to the presence of the pyramidal sulphur atom in the equatorial plane. Accordingly, the phosphine environments are chemically distinct, and this is manifest in the AB quartet observed in the $^{31}P\{^1H\}$ NMR spectrum and centred at 1.9 and -1.0 ppm ($J(AB)$ 297 Hz). The methylenic protons of the sulphine ligand are also inequivalent, and are each coupled to two chemically distinct phosphorus atoms, giving rise to a 16-line ABXY system in the ^1H NMR spectrum [13]. This simplified to a four line AB quartet upon phosphorus decoupling, allowing the identification of $J(HH)$ (7.9 Hz) (Table 2).

The band at 1035 cm^{-1} (Nujol), absent in the case of the precursor complex, may be assigned primarily to $\nu(SO)$ whilst the nitrosyl-associated band at 1719 cm^{-1} is consistent with the fragment $OsCl(NO)(PPh_3)_2$ coordinated by a moderately strong

π-acid. It is perhaps noteworthy that whereas oxidation of the disulphur complex [OsCl(NO)(PPh$_3$)$_2$(S$_2$)] to [OsCl(NO)(PPh$_3$)$_2$(S$_2$O)] is accompanied by virtually no change in ν(NO), the nitrosyl stretching frequency actually decreases upon oxidation of [OsCl(NO)(PPh$_3$)$_2$(CH$_2$S)]. These changes are comparatively small, and observed only in solid-state measurements. Accordingly caution should be excercised in drawing inferences about relative π-acid strengths.

Whilst ^{31}P{^{1}H} NMR evidence suggested that similar oxidation reactions occurred with the seleno- and telluro-formaldehyde complexes [OsCl(NO)(PPh$_3$)$_2$-(CH$_2$E)], these reactions were much more complicated and no conclusive results in respect of the complexation of CH$_2$SeO and CH$_2$TeO could be obtained. The reaction of [OsCl(NO)(PPh$_3$)$_3$] with fluorene-thione-S-oxide was investigated to establish whether substituted sulphines might also coordinate to the OsCl(NO)(PPh$_3$)$_2$ fragment. Fluorene-thione-S-oxide has been shown to coordinate to zerovalent platinum metal-ligand fragments [37b], but in the present case no evidence for adduct formation was obtained. This may be due to the steric pressures associated with the comparatively crowded coordination sphere.

Interconversions

In support of the idea of a strong parallel between the complexes of the SO$_2$-analogues, it is worth noting that a number of the complexes may be interconverted. Some of these reactions have been discussed above, namely: displacement of SO$_2$ by tosyl-NSO; hydrolysis of coordinated tosyl-NSO to SO$_2$; and reaction of coordinated tosyl-NSO with H$_2$S to give a S$_2$O complex. Finally it should also be noted that the simple aryliminooxosulphurane complexes react rapidly with tosyl-NSO to give [OsCl(NO)(PPh$_3$)$_2$(OSN-tosyl)] and free tolyliminooxosulphurane. Once again it is tempting to invoke an electrophilic substitution mechanism. Scheme 3 summarises the syntheses and interconversions of the osmium series of compounds, whilst Scheme 4 depicts the reactions of the iridium compounds.
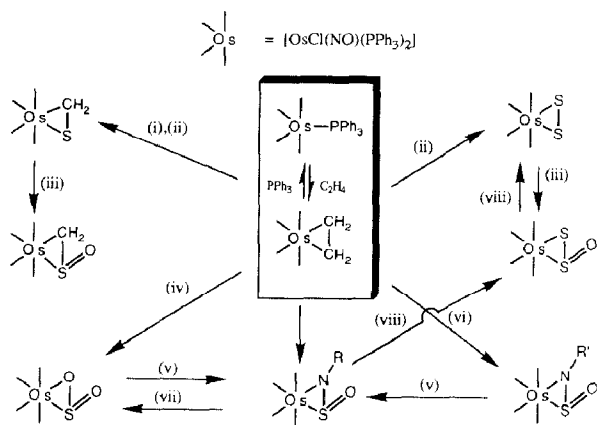
((i) CH$_2$N$_2$; (ii) S$_8$; (iii) mCPBA; (iv) SO$_2$ (v) R-NSO; (vi) R'-NSO; (vii) OH$_2$;
(viii) H$_2$S/base. R = SO$_2$C$_6$H$_4$Me-4; R' = C$_6$H$_4$Me-2, C$_6$H$_4$Me-4)

Scheme 3. Synthesis and interconversion of sulphur dioxide-analogue complexes of osmium(O).
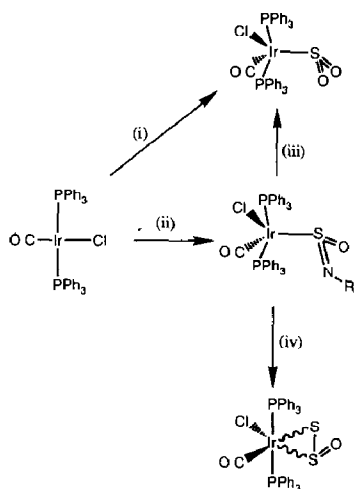
((i) SO$_2$; (ii) RNSO; (iii) H$_2$O; (iv) H$_2$S; R = SO$_2$C$_6$H$_4$Me-4)

Scheme 4. Synthesis of sulphur dioxide-analogue complexes of iridium(I).

Comparison and conclusions

Two series of adducts of sulphur dioxide analogues have been prepared, involving the metal-ligand fragments OsCl(NO)(PPh$_3$)$_2$ and IrCl(CO)(PPh$_3$)$_2$. The two metal-ligand fragments are isoelectronic, but subtle differences in their properties lead to some differences in the coordination geometry and reactivity of ligands to which they are bound. The former series [OsCl(NO)(PPh$_3$)$_2$(OSA)] (A = O, S, CH$_2$, NR; R = C$_6$H$_4$Me-2, C$_6$H$_4$Me-4, SO$_2$C$_6$H$_4$Me-4), appears to be iso-structural on the basis of spectroscopic data, with the S=O bond in all cases being exocyclic to a M–S–A ring. The preference for oxygen to be exocyclic follows from a consideration of the frontier molecular orbitals of the molecules A=S=O [8–10], since in every case the A=S π-bonding orbital is a better donor than the corresponding S=O orbital. In all cases π-coordination is observed, but this is perhaps more a property of the metal-ligand fragment than of the heterocumulenes, since in the iridium (and rhodium) series, the strongly electrophilic tosyliminooxosulphurane prefers to bind in a pyramidal manner through sulphur.

In conclusion, a note of caution is appropriate. Although the complexes described herein have been discussed as representing adducts of the molecules SO$_2$, CH$_2$SO, S$_2$O and iminooxosulphuranes, it is clear that the reactivity of these molecules is drastically changed upon coordination, and a comparison of the properties of these molecules as ligands with those of the free molecules is of dubious value. Significant structural and electronic reorganisation occurs in the simplest of cases, SO$_2$, and of all the addenda this shows the weakest interaction with the metal. It is therefore preferable to consider these compounds as strongly covalent metallathiirane-S-oxide derivatives.

Experimental

General experimental procedures and instrumentation [20] and the synthesis of the compounds [OsCl(NO)(PPh$_3$)$_2$(CH$_2$CH$_2$)] [17], [OsCl(NO)(PPh$_3$)$_3$],

[OsCl(NO)(PPh$_3$)$_2$(CH$_2$S)] [18], [IrCl(CO)(PPh$_3$)$_2$] [14], OSNC$_6$H$_4$Me [38] and OSNSO$_2$C$_6$H$_4$Me-4 [39] have been described previously. Physical data for the complexes are listed in Tables 1 and 2.

[OsCl(NO)(PPh$_3$)$_2$(SO$_2$)]

A suspension of [OsCl(OOCO)(NO)(PPh$_3$)$_2$] [40] (0.30 g, 0.36 mmol) and triphenylphosphine (0.20 g, 0.76 mol) in degassed toluene (4 cm^3) was heated under reflux for 5 min. Sulphur dioxide gas was then passed over the dark brown solution for 10 s and the Schlenk tube was then sealed and the mixture allowed to cool to room temperature with stirring. During the cooling the yellow product began to crystallise, and precipitation was completed by addition of pentane (5 cm^3) followed by cooling to −78°C overnight. The yellow crystals were filtered off, washed with pentane (25 cm^3), and dried under high vacuum. Yield 0.25 g (83%), M.p. 201°C. The compound is air sensitive in the solid state but may be stored indefinitely in the dark under nitrogen.

[OsCl(NO)(PPh$_3$)$_2$(OSN-tosyl)]

A solution of OSNSO$_2$C$_6$H$_4$Me-4 in toluene (0.10 mol/l, 2.6 cm^3, 0.26 mmol) was added to a solution of either [OsCl(NO)(PPh$_3$)$_3$] (0.26 g, 0.25 mmol) or [OsCl(NO)(PPh$_3$)$_2$(CH$_2$CH$_2$)] (0.20 g, 0.25 mmol) in tetrahydrofuran (50 cm^3). The mixture was stirred for 20 min and then volatile components were removed under reduced pressure. The yellow residue was recrystallised from a mixture of tetrahydrofuran and pentane at −30°C. Yield 0.22 g (92%). Found: C, 55.40; H, 3.60; S, 7.00. C$_{43}$H$_{37}$ClN$_2$O$_4$OsP$_2$S$_2$ calc.: C, 55.20; H, 4.00; S, 6.85%.

For reactions of the complex [OsCl(NO)(PPh$_3$)$_2$(OSN-tosyl)] it was found convenient to prepare it in situ from the ethylene complex and 1.0 equivalents of the iminooxosulphurane, since the reaction is quantitative.

[IrCl(CO)(PPh$_3$)$_2$(OSN-tosyl)]

A solution of OSNSO$_2$C$_6$H$_4$Me-4 in tetrahydrofuran (0.10 mol/l, 10.5 cm^3, 1.05 mmol) was added dropwise to a suspension of [IrCl(CO)(PPh$_3$)$_2$] (0.80 g, 1.01 mmol) in tetrahydrofuran (15 cm^3) and the suspension stirred for 5 min. The solvent was removed in vacuo and the bright orange-yellow microcrystalline residue recrystallised from tetrahydrofuran/pentane (ca. 1/4). The yield was quantitative. In the event that the sample thus obtained contains unchanged [IrCl(CO)(PPh$_3$)$_2$] (IR spectrum) the mixture may be treated with further OSNSO$_2$C$_6$H$_4$Me-4 until no starting material remains. Found: C, 56.80; H, 3.70; S, 6.70. C$_{44}$H$_{37}$ClIrNO$_4$P$_2$S$_2$ calc.: C, 56.50; H, 4.00; S, 6.85%.

[OsCl(NO)(PPh$_3$)$_2$(OSNC$_6$H$_4$Me-4)] and [OsCl(NO)(PPh$_3$)$_2$(OSNC$_6$H$_4$Me-2)]

A solution of [OsCl(NO)(PPh$_3$)$_2$(CH$_2$CH$_2$)] (0.20 g, 0.25 mmol) in tetrahydrofuran (20 cm^3) was treated with OSNC$_6$H$_4$Me-4 or OSNC$_6$H$_4$Me-2 (0.04 g, 0.27 mmol). The mixture was stirred for 10 min, during which the colour darkened to a deep red. Infrared spectroscopy indicated quantitative conversion. The solvent volume was reduced to 5 cm^3 under reduced pressure and pentane added to complete crystallisation of the deep red air-sensitive product. Yield 0.23 g (98%). [OsCl(NO)(PPh$_3$)$_2$(OSNC$_6$H$_4$Me-4)], m.p. 126°C; [OsCl(NO)(PPh$_3$)$_2$(OSN-C$_6$H$_4$Me-2)], m.p. 122°C.

[OsCl(NO)(PPh₃)₂(S₂O)]

A solution of [OsCl(NO)(PPh$_3$)$_2$(S$_2$)] (0.25 g, 0.30 mmol) in chloroform (40 cm^3) was cooled to $-40°$C and treated with solid 3-ClCH$_6$H$_4$CO$_3$H (0.08 g, 0.38 mmol) (the commercial peracid contains 15% of the benzoic acid as stabiliser). The initially dark green solution immediately became orange. It was allowed to warm to room temperature, solvent was removed under reduced pressure, and the orange residue recrystallised from dichloromethane-ethanol (ca. 1:4). The yield was quantitative according to the ^{31}P{^{1}H} NMR spectrum of a reaction carried out in CDCl$_3$; the isolated yield was 0.24 g (93%). Found: C, 49.75; H, 3.25; S, 7.70. C$_{36}$H$_{30}$ClNO$_2$OsP$_2$S$_2$ calc.: C, 50.15; H, 3.50; S, 7.45%.

[IrCl(CO)(PPh₃)₂(S₂O)]

A suspension of [IrCl(CO)(PPh$_3$)$_2$(OSN-tosyl)] (0.50 g, 0.50 mmol) in tetrahydrofuran (20 cm^3) was treated with a stream of hydrogen sulphide for 20 s and then the Schlenk tube was sealed. The mixture was stirred for 20 min, by which the starting complex had dissolved. The solvent was removed under reduced pressure and the yellow residue was dissolved in the minimum of dichloromethane and chromatographed on a column of silica gel. Elution with dichloromethane gave [IrCl(OC)(PPh$_3$)$_2$] (10–15%). The column was then eluted with dichloromethane/tetrahydrofuran (10/1) and the major yellow band was collected, and the solvent removed. The yellow residue was then purified by preparative thin-layer chromatography on silica gel with dichloromethane/tetrahydrofuran (10/1) as eluent, the bright yellow complex recrystallised from tetrahydrofuran/ethanol (ca. 1/4). Yield 0.33 g (76%). Found: C, 50.90; H, 3.45; Cl, 4.20; S, 7.65. C$_{37}$H$_{30}$ClIrO$_2$P$_2$S$_2$ calc.: C, 51.65; H, 3.50; Cl, 4.10; S, 7.45%.

[OsCl(NO)(PPh₃)₂(CH₂SO)]

A rapidly stirred solution of [OsCl(NO)(PPh$_3$)$_2$(CH$_2$S)] · $\frac{1}{2}$CH$_2$Cl$_2$ (0.16 g, 0.18 mmol) in dichloromethane (100 cm^3) was cooled to $-78°$C and treated with solid 3-ClC$_6$H$_4$CO$_3$H (0.04 g, 0.19 mmol). The solution became yellow. It was allowed to warm to room temperature and volatiles were removed under reduced pressure. The residue was purified by preparative thin-layer chromatography on silica gel with dichloromethane as eluent. The major yellow zone was collected and the isolated solid recrystallised from a mixture of dichloromethane and ethanol to give the product (0.10 g, 65%), m.p. 228°C.

Acknowledgements

References

1 W.P. Ehrenreich, M. Herberhold and A.F. Hill, J. Organomet. Chem., 371 (1989) 303.
2 B. Zwanenburg, Rec. Trav. Chim. Pays-Bas, 102 (1982) 1.
3 R. Bussas, G. Kresze, H. Münsterer and A. Schwöbel, Sulphur Reports, 2 (1983) 215.
4 P.W. Schenk, Z. Anorg. Allg. Chem., 233 (1937) 385.
5 E. Block, R.E. Penn, R.J. Olsen and P.F. Sherwin, J. Am. Chem. Soc., 98 (1976) 1264; R.E. Penn and R.J. Olsen, J. Mol. Spectr., 61 (1976) 21.

6   O.J. Scherer and R. Schmitt, Chem. Ber., 101 (1968) 3302; M. Becke-Goering, R. Schwarz and W. Spiess, Z. Anorg. Allg. Chem., 293 (1958) 294; H. Richert, Z. Anorg. Allg. Chem., 309 (1961) 171; P.W. Schenk, Chem. Ber., 75 (1942) 94; P.O. Tchir and R.D. Spratley, Can. J. Chem., 53 (1973) 2311; W.H. Kirchhoff, J. Am. Chem. Soc., 91 (1969) 2437.

7   M. Herberhold, W. Jellen, W. Bühlmeyer and W. Ehrenreich, Z. Naturforsch. B, 40 (1985) 1233 and refs. cited therein.

8   H. Bock, B. Solouki, P. Rosmus and R. Steudel, Angew. Chem., 85 (1973) 987; Angew. Chem., Int. Ed. Engl., 12 (1973) 933; D.J. Meschi and R.H. Myers, J. Mol. Spectr. 3 (1959) 405.

9   E. Block, H. Bock, S. Mohmand, P. Rosmus and B. Solouki, Angew. Chem., 88 (1976) 380; Angew. Chem., Int. Ed. Engl., 15 (1976) 383; H. Bock, B. Solouki, S. Mohmand, E. Block and L.K. Revelle, J. Chem. Soc., Chem. Commun., (1977) 287.

10 B. Solouki, P. Rosmus and H. Bock, Angew. Chem., 88 (1976) 381; Angew. Chem., Int. Ed. Engl., 15 (1976) 384.

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

12 M. Herberhold and A.F. Hill, J. Chem. Soc., Dalton Trans., (1988) 2027.

13 M. Herberhold and A.F. Hill, J. Organomet. Chem., 309 (1986) C29.

14 L. Vaska and J.W. DiLuzio, J. Am. Chem. Soc., 84 (1962) 679.

15 L. Vaska and S.S. Bath, J. Am. Chem. Soc., 88 (1966) 1333.

16 S.J. LaPlaca and J.A. Ibers, Inorg. Chem., 6 (1966) 405.

17 A.H. Wright, Ph.D. Thesis, University of Auckland, 1983; W.R. Roper, J. Organomet. Chem., 300 (1986) 167.

18 A.F. Hill, W.R. Roper, J.M. Waters and A.H. Wright, J. Am. Chem. Soc., 105 (1983) 5939.

19 (a) M.B.H. Stiddard and R.E. Townsend, Chem. Comm, (1969) 1372; (b) R.D. Wilson and J.A. Ibers, Inorg. Chem., 17 (1978) 2134.

20 M. Herberhold, A.F. Hill, N. McAuley and W.R. Roper, J. Organomet. Chem., 310 (1986) 95.

21 M. Herberhold and A.F. Hill, in preparation.

22 D.M. Blake and J.R. Reynolds, J. Organomet. Chem., 113 (1976) 391.

23 M. Herberhold, A.F. Hill, G.R. Clark, C.E.F. Rickard, W.R. Roper and A.H. Wright, Organometallics, 8 (1989) 2483.

24 H.C. Ashton and A.R. Manning, Inorg. Chem., 22 (1983) 1440.

25 M. Herberhold and A.F. Hill, J. Organomet. Chem., 368 (1989) 111.

26 R. Meij, D.J. Stufkens, K. Vrieze, E. Roosendaal and H. Schenk, J. Organomet. Chem., 155 (1978) 323.

27 D.C. Moody and R.R. Ryan, J. Chem. Soc., Chem. Commun., (1980) 1230.

28 J.E. Hoots, D.A. Lesch and T.B. Rauchfuss, Inorg. Chem., 23 (1984) 3130 and refs. cited therein.

29 M. Herberhold, B. Schmidkonz, M.L. Ziegler and T. Zahn, Angew. Chem., 97 (1985) 517; Angew. Chem., Int. Ed. Engl., 24 (1985) 515.

30 M. Herberhold and B. Schmidkonz, J. Organomet. Chem., 308 (1986) 35.

31 G. Schmid and G. Ritter, Angew. Chem., 87 (1975) 673; Angew. Chem., Int. Ed. Engl., 14 (1975) 645.

32 J. Dirand-Colin, M. Schappacher, L. Ricard, and R. Weiss, J. Less-Common Met., 54 (1977) 91.

33 M. Herberhold and A.F. Hill, J. Organomet. Chem., 363 (1989) 371.

34 G.R. Clark, D.R. Russel, W.R. Roper and A. Walker, J. Organomet. Chem., 136 (1977) C1; D.H. Farrar, K.R. Grundy, N.C. Payne, W.R. Roper and A. Walker, J. Am. Chem. Soc., 101 (1979) 6577.

35 B. Schmidkonz, Dissertation, Universität Bayreuth, 1987.

36 D.E. Powers, C.E. Arrington, W.C. Harris, E. Block and V.F. Kalasinski, J. Phys. Chem., 83 (1979) 1890.

37 (a) J.W. Gosselink, G. van Koten, K. Vrieze, B. Zwanenburg and B.H.M. Lammerink, J. Organomet. Chem., 179 (1979) 411; (b) J.W. Gosselink, G. van Koten, A.L. Spek and A.J.M. Duisenberg, Inorg. Chem., 20 (1981) 877; (c) J.W. Gosselink, G. van Koten, A.M.F. Brouwers and O. Overbeek, J. Chem. Soc., Dalton Trans., (1981) 342; (d) J.W. Gosselink, H. Bulthuis, G. van Koten, J. Chem. Soc., Dalton Trans., (1981) 1342; (e) J.W. Gosselink, A.M.F. Brouwers, G. van Koten, K. Vrieze, J. Chem. Soc., Dalton Trans., (1982) 397.

38 H.F. van Woerden and S.H. Bijl-Vlieger, Recl. Trav. Chim. Pays-Bas, 93 (1974) 85.

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

40 K.R. Laing and W.R. Roper, Chem. Commun., (1968) 1568.

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