

REACTIONS OF IRIDIUM(I) COMPOUNDS WITH OXIDIZED DERIVATIVES OF ORGANIC DISULFIDES AND WITH THIONYL CHLORIDE

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Summary

The complex *trans*-[IrZ(CO)(PMePh₂)₂] (Z = Cl or Br) undergoes an oxidative addition reaction, at room temperature, at the sulfur—sulfur bond of diphenyl disulfide, (PhSSPh), phenyl benzenethiosulfonate, (PhSSO₂Ph), and phenyl benzenesulfinylsulfonate, (PhS(O)SO₂Ph). Diphenyl disulfone is unreactive at 75° C. Phenyl benzenethiosulfinate (PhSS(O)Ph) disproportionates in the reaction medium. The iridium(I) complex also inserts into the sulfur—sulfur bond of 1,2-dithiolene-1,1-dioxide, (S(O)₂(CH₂)₃S). Thionyl chloride adds to square planar iridium(I) compounds to give iridium(III) complexes containing the chlorosulfinyl group (—S(O)Cl). The remaining sulfur—chlorine bond is reactive toward methanol producing the coordinated methoxy sulfinyl group.

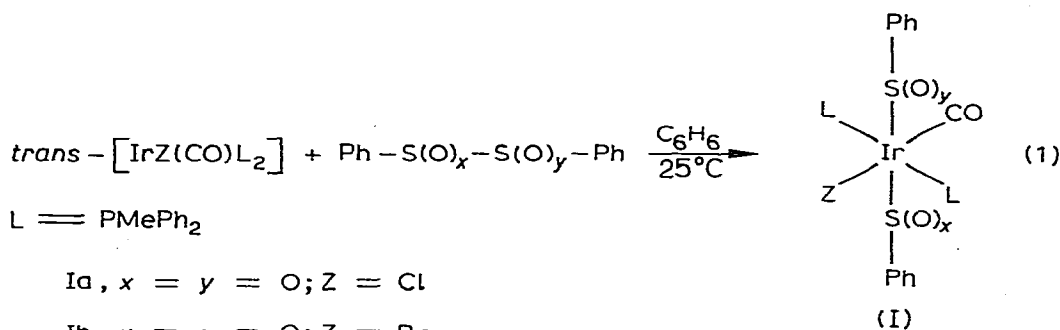
Introduction

The incorporation of sulfur-containing ligands into transition metal complexes has been a subject of interest to chemists for many years [1,2]. Much of this interest has centered around complexes with sulfur containing fragments from the series R \ddot{S} —(sulfide), R \ddot{S} (O)—(sulfenate) and RS(O)₂—(sulfinato). The formation of complexes containing these sulfur moieties via insertion of a metal complex into the sulfur—sulfur bond of disulfide oxide derivatives having the general R—S(O)_x—S(O)_y—R [3] has been utilized only in the case of disulfides themselves (x = y = 0). Platinum(0) [4], iridium(I) [5] and titanium(II) [6] complexes have been found to cleave the disulfide bond and incorporate the two sulfido groups into monomeric or dimeric metal complexes. Cleavage of the sulfur—sulfur bond in the oxidized derivatives by non-metallic nucleophiles has been extensively studied by Kice and his co-workers [3]. Incorporation of sulfido, sulfenato, and sulfinato groups via an

oxidative addition reaction of the appropriate chloride $\text{RS(O)}_n\text{Cl}$ (where $n = 0$ [7], 1 [7], or 2 [7,8,9]) to square planar iridium(I) complexes has been the subject of several reports. We report here the results of our study of the interaction of diphenyldisulfide oxides or thionyl chloride with iridium(I) complexes.

Results and discussion

In contrast to Vaska's complex, *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, which reacts with aromatic disulfides only under forcing conditions [5], the methyl diphenylphosphine analogs, *trans*- $[\text{IrZ}(\text{CO})(\text{PMePh}_2)_2]$ ($Z = \text{Cl}$ or Br), react with phenyl disulfide and some of its oxidized analogs at room temperature. This has allowed the reactivity of the series of compounds $\text{PhS(O)}_x\text{-S(O)}_y\text{Ph}$ (where $x = 0, 1, 2$ and $y = 0, 1, 2$) toward a transition metal nucleophile to be assessed. In this series of disulfide oxides compounds having all combinations of x and y are known except for $x = y = 1$ [3]. The products obtained in the reactions of these with the iridium(I) compounds are shown in eq. 1. Reactions were complete within 60 min at room temperature.



$\text{L} = \text{PMePh}_2$

Ia, $x = y = 0; Z = \text{Cl}$

Ib, $x = y = 0; Z = \text{Br}$

Ic, $x = 0, y = 2, Z = \text{Cl}$

Id, $x = 1, y = 2, Z = \text{Cl}$

Ie, $x = 1, y = 2, Z = \text{Br}$

Attempts to obtain an adduct of phenyl benzenethiosulfinate ($x = 0, y = 1$) with the iridium(I) complex produced only a mixture of compounds Ia and Ic. This is likely to have occurred via a prior disproportionation of the thiosulfinate to phenyl disulfide ($x = y = 0$) and phenyl benzenethiosulfonate ($x = 0, y = 2$) [10] followed by reaction of these compounds with the iridium complex. Diphenyl disulfone ($x = y = 2$) did not react with the iridium complex within one week at 75°C . Spectroscopic data for the compounds are shown in Table 1.

In each of the compounds Ia–e the NMR spectrum contains a triplet for the P-CH_3 group indicating the phosphines are mutually *trans* [11]. The infrared spectra of the compounds containing a sulfinato group (compounds Ic–e) establish the presence of the S-bonded isomer only, $\nu_{\text{as}}(\text{SO}_2)$ ca. 1190 cm^{-1} and $\nu_{\text{sym}}(\text{SO}_2)$ ca. $1050\text{--}1090\text{ cm}^{-1}$ [12]. Compounds Id and Ie show in addition a band at 1042 cm^{-1} which is assigned to $\nu(\text{S=O})$ of the *S*-sulfinato group [7]. The single $\nu(\text{C=O})$ band at ca. $2040\text{--}2065\text{ cm}^{-1}$ for the compounds

TABLE 1
INFRARED (cm^{-1}) AND NMR DATA

Complex ^a	$\nu(\text{C}\equiv\text{O})$	$\nu(\text{SO}_2)$		$\nu(\text{S}=\text{O})$	$\nu(\text{Ir}-\text{Cl})$	$\tau(\text{PCH}_3)$ ^b
		asym	sym			
Ia IrCl(CO)(SPh) ₂ L ₂	2042	—	—	—	315, 298	7.65t
Ib IrBr(CO)(SPh) ₂ L ₂	2040	—	—	—	—	7.72t
Ic IrCl(CO)[SO ₂ Ph](SPh)L ₂	2062	1190	1041	—	312, 306	7.47t
Id IrCl(CO)[SO ₂ Ph][SOPh]L ₂	2070	1195	1095	1042	310	7.48t
Ie IrBr(CO)[SO ₂ Ph][SOPh]L ₂	2070	1193	1095	1042	—	7.38t
IIa IrCl(CO)[—SO ₂ (CH ₂) ₃ S—]L ₂	2045	1210	1056	—	314, 292	8.90d, 7.50 d ^c
IIb IrBr(CO)[—SO ₂ (CH ₂) ₃ S—]L ₂	2050	1213	1060	—	—	—
IIIa IrCl ₂ (SOCl)(CO)L' ₂	2053	—	—	1118	319, 268	—
IIIb IrCl ₂ (SOCl)(CO)L ₂	2073	—	—	1101	312, 271	7.63t
IIIc IrBrCl(SOCl)(CO)L' ₂	2078w, 2048s	—	—	1116	—, 274	—

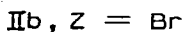
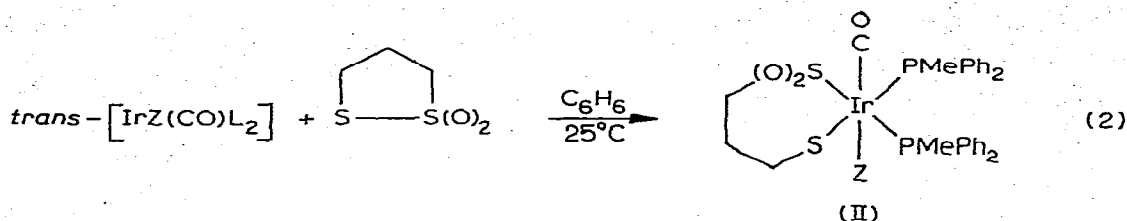
^aL = PMePh₂ and L' = PPh₃. ^bJ(P—CH₃) for the triplets is ca. 11–12 Hz. ^cJ(P—CH₃) for the doublets is 11.0 Hz.

is also indicative of the presence of only one isomer. In the iridium chlorine stretching region of the IR for compounds Ia and Ic there are two bands in the range 298–315 cm^{-1} for samples run as Nujol mulls. Both bands are absent in the spectra of the bromo analogs. These bands are in the region characteristic of $\nu(\text{Ir}-\text{Cl})$ chloride *trans* to carbon monoxide [9]. The appearance of two bands rather than a single band is probably due to a solid state splitting effect. The spectral data are consistent with the geometry shown in eq. 1 for complexes Ia–e.

Heating of compound Id, {IrCl(CO)[S(O)Ph][S(O)₂Ph](PMePh₂)₂}, for 24 h at 100°C under nitrogen in toluene solution yielded a mixture of products which was only partially resolved. Biphenyl, *trans*-[IrClCO(PMePh₂)₂], some unreacted starting material, and a product whose IR spectrum showed a loss of bands due to the —SO₂— group but still showed a band at 1042 cm^{-1} characteristic of the *S*-sulfenato group were detected by a combination of GLC and IR methods.

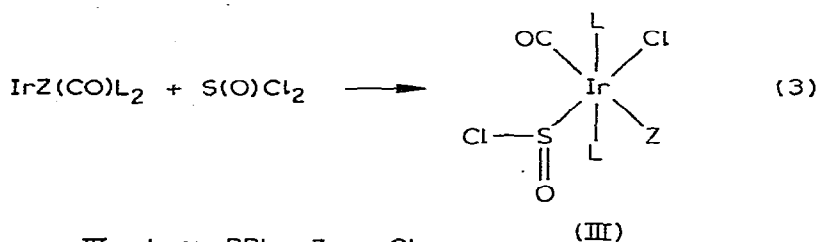
Qualitatively, the reactivity of the sulfur—sulfur bond toward iridium(I) complexes as assessed from reaction 1 was observed to increase in the order PhS(O)·S(O)₂Ph (no reaction) << PhSSPh < PhSS(O)₂Ph ≈ PhS(O)S(O)₂Ph. This parallels trends observed in reactivity toward non-metallic nucleophiles [3].

Reaction of *trans*-[IrZ(CO)(PMePh₂)₂] (Z = Cl or Br) with the cyclic compound 1,2-dithiolane-1,1-dioxide results in insertion of the metal into the ring as is shown in eq. 2. Infrared spectra clearly show that the sulfinate end of the chelate is S-bonded [$\nu_{\text{as}}(\text{SO}_2)$ 1210 cm^{-1} and $\nu_{\text{sym}}(\text{SO}_2)$ 1056 cm^{-1}]. The NMR spectrum of IIa shows two doublets of equal intensity in the region characteristic of the phosphorus methyl group. This indicates the phosphines are *cis* to each other [11]. Bands at 314 and 292 cm^{-1} are observed in the $\nu(\text{Ir}-\text{Cl})$ region. The single sharp band for $\nu(\text{C}\equiv\text{O})$ indicates that only one isomer is present hence one would expect only one $\nu(\text{Ir}-\text{Cl})$. The splitting may be a solid state effect, however solubility limitations prevented the obtaining

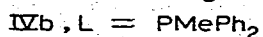
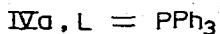
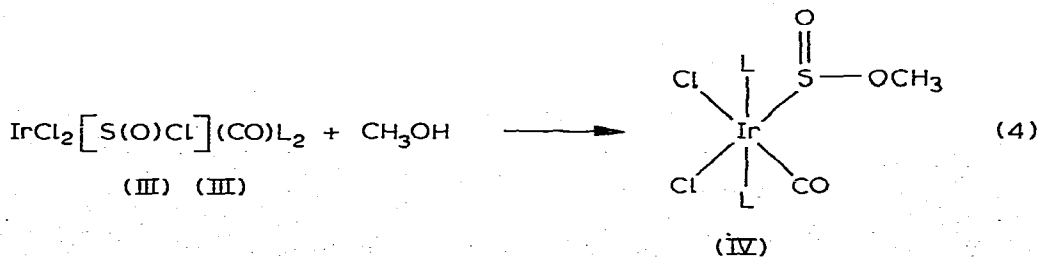


of spectra in solution in this region. Both bands are in a region characteristic of chloride *trans* to carbon monoxide therefore the structure is assigned as is shown [9].

The addition of thionyl chloride to Vaska's complex and its methyl-diphenylphosphine analog yields products containing the S-bonded chloro-sulfinyl group. The phosphine ligands in III are *trans* which is established by the NMR spectrum of IIIb. Two bands are present in the $\nu(\text{Ir}-\text{Cl})$ region of the



IR spectra of IIIa and IIIb. The band near 270 cm^{-1} is assigned to chlorine *trans* to sulfur and that in the region $312-319 \text{ cm}^{-1}$ is assigned to chlorine *trans* to carbon monoxide [9]. A band at ca. 380 cm^{-1} is assigned to $\nu(\text{S}-\text{Cl})$



[13] and a strong band at 1118 and 1101 cm^{-1} for compounds IIIa and IIIb respectively is assigned to $\nu(\text{S}=\text{O})$. There is a decrease of about 110 cm^{-1} from $\nu(\text{S}=\text{O})$ for thionyl chloride [13]. The absence of the band at 319 cm^{-1} in the IR spectrum of IIIc is indicative of a *trans* addition of thionyl chloride.

Compounds IIIa and IIIb react with methanol to produce the methoxy-sulfenato complexes, IVa and IVb, which have previously been obtained by the oxidative addition of methylchlorosulfinate to iridium(I) complexes [7]. The coordinated $-\text{S}(\text{O})\text{Cl}$ group in compound III remains reactive and offers the possibility of introducing other substituents at the S-Cl bond.

Experimental

The compounds $\text{PhS}(\text{O})\text{SPh}$ (m.p. 65–67, lit. 69°C) [14], $\text{PhS}(\text{O})_2\text{SPh}$ (m.p. 74–75, lit. 70°C) [14], $\text{PhS}(\text{O})_2\text{S}(\text{O})\text{Ph}$ (m.p. 76, lit. 78°C) [15], $\text{PhS}(\text{O})_2\text{S}(\text{O})_2\text{Ph}$ (m.p. 192–193, lit. 192–196°C) [16], $\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{S}$ [17], *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ [18] and *trans*- $[\text{IrCl}(\text{CO})(\text{PMePh}_2)]$ [19] were prepared by literature methods. Thionyl chloride was distilled from linseed oil and stored in vacuo in a container with a teflon stopcock. Diphenyl disulfide was from Eastman Chemical Company. Infrared spectra were obtained on a Perkin-Elmer Model 621 spectrometer. Samples were prepared as Nujol mulls between CsI plates. ^1H NMR spectra were obtained in deuteriochloroform solution on Varian T60 and HA100 spectrometers. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

The general method used to react the square planar iridium(I) complexes

TABLE 2
ANALYTICAL RESULTS

	M.p. (°C)	Found (calcd.) (%)			
		C	H	Cl	S
$\text{IrCl}(\text{CO})(\text{SPh})_2(\text{PMePh}_2)_2$	225	52.98 (53.57)	4.08 (4.15)	3.80 (4.05)	7.48 (7.33)
$\text{IrBr}(\text{CO})(\text{SPh})_2(\text{PMePh}_2)_2$	213	51.35 (50.98)	3.94 (3.95)	—	6.61 (6.98)
$\text{IrCl}(\text{CO})(\text{SO}_2\text{Ph})(\text{SPh})(\text{PMePh}_2)_2$	202	51.49 (51.67)	3.96 (4.00)	(4.00) (3.91)	7.21 (7.08)
$\text{IrCl}(\text{CO})(\text{SO}_2\text{Ph})(\text{SOPh})(\text{PMePh}_2)_2$	188	51.15 (50.78)	3.83 (3.93)	—	6.47 (6.95)
$\text{IrBr}(\text{CO})(\text{SO}_2\text{Ph})(\text{SOPh})(\text{PMePh}_2)_2$	180	49.52 (48.49)	3.26 (3.76)	—	6.24 (6.64)
$\text{IrCl}(\text{CO})[-\text{SO}_2(\text{CH}_2)_3\text{S}-](\text{PMePh}_2)_2$	193	44.59 (45.36)	4.05 (4.06)	5.06 (4.46)	8.03 (8.07)
$\text{IrBr}(\text{CO})[-\text{SO}_2(\text{CH}_2)_3\text{S}-](\text{PMePh}_2)_2$	187	43.01 (42.96)	4.02 (3.85)	—	8.25 (7.66)
$\text{IrCl}_2(\text{SOCl})(\text{CO})(\text{PPh}_3)_2$	255	49.09 (49.42)	3.40 (3.36)	11.80 (11.83)	3.57 (3.30)
$\text{IrCl}_2(\text{SOCl})(\text{CO})(\text{PMePh}_2)_2$	166-167	41.81 (41.81)	3.37 (3.38)	13.92 (13.72)	4.08 (4.14)
$\text{IrBrCl}(\text{SOCl})(\text{CO})(\text{PPh}_3)_2 \cdot \text{C}_6\text{H}_6$	251	49.61 (50.55)	3.36 (3.55)	7.69 (6.94)	2.36 (3.13)

with phenyl disulfide or its oxide derivatives is given below. In the case of phenyl benzenesulfonylsulfonate ($\text{PhS(O)}_2\text{S(O)}_2\text{Ph}$) the mixture was stirred at 75°C for seven days with no effect. The reaction with phenyl benzenethiosulfinate (PhSS(O)Ph) yielded a mixture of diphenyl disulfide (PhSSPh) and phenyl benzenethiosulfonate ($\text{PhSS(O)}_2\text{Ph}$) adducts (ca. 40–50% total yield). Analytical data are given in Table 2.

Formation of adducts of trans-[IrZ(CO)(PMePh₂)] (Z = Cl or Br) with phenyl disulfide derivatives

The iridium (I) complex (300 mg) and the sulfur compound (150 mg) were placed in a "pop bottle" which was then closed with a Buna N cap and purged with dry, oxygen-free nitrogen gas. Benzene (10 ml) was added and the mixture stirred for 2 h. During this time a yellow precipitate formed. This was recovered by filtration open to the atmosphere, washed with benzene and ether and dried in vacuo. The adducts were recrystallized from hot benzene by slow addition of n-hexane.

$\text{IrZ}[-\text{S(O)}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{S}-](\text{CO})(\text{PMePh}_2)$ (Z = Cl or Br). *trans*-[IrZCO-(PMePh₂)₂] (300 mg) was placed in a 25 ml "pop bottle" under a nitrogen atmosphere. A solution of 1,2-dithiolene-1,1-dioxide (65 mg) in benzene (3 ml) was added and the solution stirred at 55°C for 12 h. The resulting yellow precipitate was recovered, washed with ether and dried in vacuo (yield 98%).

Attempts to recrystallize the product from benzene produced oils.

$\{\text{IrCl}_2[\text{S(O)Cl}](\text{CO})\text{L}_2\}$ (L = PPh₃ or PMePh₂). Thionyl chloride (0.5 ml) and dry benzene (10 ml) were condensed at 77 K, in vacuo, onto the iridium(I) complex (500 mg). The mixture was warmed to room temperature and stirred for 30–45 min. During this period the color faded from bright yellow to nearly colorless. The volatile components of the mixture were removed in vacuo. The remaining solid was washed from the flask onto a filter with ether then dried in vacuo. The product was recrystallized from benzene/n-hexane to give the pale yellow solid.

$\{\text{IrCl}_2[\text{S(O)OCH}_3](\text{CO})\text{L}_2\}$ (L = PPh₃ or PMePh₂). The analogous thionyl chloride adduct (200 mg) was stirred with methanol (0.5 ml) in methylene chloride (5 ml) for 5 min. The resulting colorless precipitate was recovered (yield 90%). The physical properties were identical to those reported by George and Watkins for samples prepared by addition of $\text{CH}_3\text{OS(O)Cl}$ to iridium(I) compounds [7].

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