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# CLEAVAGE OF THE SULFUR–SULFUR BOND IN 2,4-DINITROPHENYL 4-SUBSTITUTED PHENYL DISULFIDES BY *trans*-$[IrX(CO)(PPh_3)_2]$

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## SUMMARY

A series of 2,4-dinitrophenyl 4-Y-phenyl disulfides ($Y = NO_2$, Br, F, H, $CH_3$, or $CH_3O$) have been shown to react with *trans*-$IrX(CO)(PPh_3)_2$ (X = Cl, Br, or I) in refluxing benzene to form "oxidative-elimination" products of the type, $[IrX(SC_6H_4\text{-}Y)(SC_6H_3(NO_2)_2)(CO)(PPh_3)]_2$. The physical properties of these complexes are discussed in relation to their structure in the solid state and in solution. In particular, available infrared spectral data indicate that these complexes contain 2,4-dinitrobenzenethiolato bridging groups and that the substituted arenethiolato ligand is *trans* to carbon monoxide.

## INTRODUCTION

The sulfur–sulfur bond in organic disulfides may be cleaved by nucleophilic, electrophilic, photolytic, or thermolytic processes[1,2]. In addition, several transition metal complexes have been shown to be effective reagents for the cleavage of a sulfur–sulfur bond[3]. In this latter instance, the thiolato fragments which are produced as a result of the scission of the sulfur–sulfur bond normally appear as bridging ligands in the product(s) of reaction. As part of a general interest in the chemistry of transition metal complexes containing at least one sulfur donor atom[4–11], we decided to investigate the feasibility of cleaving a sulfur–sulfur linkage via oxidative-addition to some low-valent iridium complexes which are known to cleave a number of other homonuclear bonds via oxidative-addition[12–15]. The results of our study are herein reported.

## RESULTS AND DISCUSSION

No apparent reaction was observed between *trans*-$IrX(CO)(PPh_3)_2$ (X = Cl, Br, or I) and diphenyl disulfide at room temperature. The original iridium(I) complex could be readily recovered intact even upon prolonged exposure to diphenyl disulfide. However, it was found that *trans*-$IrCl(CO)(PPh_3)_2$ slowly reacted with diphenyl disulfide in refluxing benzene. The product which was isolated from this particular reaction exhibited two bands, assigned to $\nu(CO)$ at 2057 and 1959 $cm^{-1}$. The latter band at 1959 $cm^{-1}$ may be ascribed to unreacted *trans*-$IrCl(CO)(PPh_3)_2$[16] while the

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the other band may be attributed to the product of reaction. The higher energy band was invariably lesss intense than the band at 1959 $cm^{-1}$ which may be taken to indicate that the reaction had not proceeded to completion.

In order to induce a reaction between these iridium(I) complexes and the sulfur–sulfur bond, one phenyl ring was substituted in the 2- and 4-positions by $NO_2$ in order to "activate" the sulfur–sulfur bond. At room temperature, this substitution was not sufficiently effective to induce cleavage of the sulfur–sulfur bond. However, the sulfur–sulfur bond was found to be readily cleaved in reflucing benzene. Consequently, these reaction conditions were extended to the reaction between a series of 2,4-dinitrophenyl 4-substituted-phenyldisulfides, $C_6H_3(NO_2)_2SSC_6H_4Y$, where $Y =$ 4-$NO_2$, 4-Br, 4-F, 4-H, or 4-$CH_3O$ and *trans*-$IrX(CO)(PPh_3)_2$ ($X = Cl$, Br, or I). The sulfur–sulfur bond in this series of unsymmetrically substituted diphenyl disulfides was found to be cleaved by *trans*-$IrX(CO)(PPh_3)_2$ according to eqn. (1);

$$\underset{(I)}{2\,IrX(CO)(PPh_3)_2} + 2\,ArSSAr' \rightarrow \underset{(II)}{[IrX(SAr)(SAr')(CO)(PPh_3)]_2} + 2\,PPh_3 \qquad (1)$$

where $X = Cl$, Br, or I; $Ar =$ a *para*-substituted benzene ring and $Ar' =$ 2,4-dinitrophenyl. The analytical data given in Table 1 confirm that the fragments resulting from the cleavage of the sulphur–sulphur bond in the disulfide have coordinated to the metal to form a dimeric iridium(III) complex. The osmometric molecular weight data obtained in benzene are consistent with the formulation of these complexes as dimers and also

TABLE 1

ANALYTICAL DATA

| *Complex*[a] | *Found (calcd.)(%)* | | *Mol. wt. found (calcd.)* |
|---|---|---|---|
| | *C* | *H* | |
| $[IrCl(SAr')(SC_6H_4NO_2)(CO)(PPh_3)]_2$[b] | 44.84 (44.84) | 2.92 (2.75) | 1275 (1742) |
| $[IrCl(SAr')(SC_6H_4Br)(CO)(PPh_3)]_2$[b] | 43.06 (43.23) | 2.71 (2.65) | 1536 (1810) |
| $[IrCl(SAr')(SC_6H_4F)(CO)(PPh_3)]_2$[b] | 46.76 (46.21) | 2.96 (2.83) | 1203[c] (1688) |
| $[IrCl(SAr')(SC_6H_5)(CO)(PPh_3)]_2$[b] | 46.70 (47.17) | 3.06 (3.01) | 1242 (1652) |
| $[IrCl(SAr')(SC_6H_4CH_3)(CO)(PPh_3)]_2$[b] | 47.85 (47.79) | 3.01 (3.19) | 1262[c] (1680) |
| $[IrCl(SAr')(SC_6H_4OCH_3)(CO)(PPh_3)]_2$[b] | 47.53 (46.93) | 3.46 (3.13) | 1434[c] (1712) |
| $[IrBr(SAr')(SC_6H_4NO_2)(CO)(PPh)_3)]_2$[d] | 44.99 (44.70) | 2.78 (2.82) | 1671[c] (1831) |
| $[IrBr(SAr')(SC_6H_4Br)(CO)(PPh_3)]_2$[d] | 43.41 (43.22) | 2.72 (2.73) | 1270[c] (1898) |
| $[IrBr(SAr')(SC_6H_4F)(CO)(PPh_3)]_2$[d] | 45.63 (45.95) | 2.36 (2.90) | 1699[c] (1777) |
| $[IrBr(SAr')(SC_6H_5)(CO)(PPh_3)]_2$[d] | 46.53 (46.82) | 3.99 (3.06) | 1582[c] (1741) |
| $[IrBr(SAr')(SC_6H_4CH_3)(CO)(PPh_3)]_2$[d] | 47.14 (47.39) | 3.77 (3.22) | 1392[c] (1769) |
| $[IrBr(SAr')(SC_6H_4OCH_3)(CO)(PPh_3)]_2$[d] | 46.77 (46.61) | 3.39 (3.17) | 1397 (1801) |
| $[IrI(SAr')(SC_6H_4NO_2)(CO)(PPh_3)]_2$[b] | 40.32 (40.75) | 2.36 (2.50) | 1258 (1925) |
| $[IrI(SAr')(SC_6H_4Br)(CO)(PPh_3)]_2$[e] | 42.75 (43.12) | 2.58 (2.78) | 1338 (1992) |
| $[IrI(SAr')(SC_6H_4F)(CO)(PPh_3)]_2$[d] | 43.82 (43.82) | 2.44 (2.76) | 1102 (1871) |
| $[IrI(SAr')(SC_6H_5)(CO)(PPh_3)]_2$[b] | 42.68 (42.66) | 2.61 (2.72) | 1528 (1835) |
| $[IrI(SAr')(SC_6H_4CH_3)(CO)(PPh_3)]_2$ | 41.81 (41.23) | 2.56 (2.68) | 1586 (1863) |
| $[IrI(SAr')(SC_6H_4OCH_3)(CO)(PPh_3)]_2$ | 41.08 (40.53) | 3.07 (2.64) | 1588 (1895) |

[a] $Ar' =$ 2,4-dinitrophenyl. [b] Complexes contain 1 mole of benzene of solvation. [c] Value obtained by extrapolation to infinite dilution from a plot of apparent molecular weight *versus* concentration. [d] Complexes contain 2 moles of benzene of solvation. [e] Complexes contain 3 moles of benzene of solvation.

TABLE 2

INFRARED SPECTRAL DATA

| *Complex* | $\nu(CO)^a$ $(cm^{-1})$ | $\nu(Ir{-}Cl)^b$ $(cm^{-1})$ |
|---|---|---|
| $[IrCl(SAr')(SC_6H_4NO_2)(CO)(PPh_3)]_2$ | 2074 (2064) | 319 |
| $[IrCl(SAr')(SC_6H_4Br)(CO)(PPh_3)]_2$ | 2070 (2064) | 318 |
| $[IrCl(SAr')(SC_6H_4F)(CO)(PPh_3)]_2$ | 2069 (2058) | 320 |
| $[IrCl(SAr')(SC_6H_5)(CO)(PPh_3)]_2$ | 2068 (2060) | 321 |
| $[IrCl(SAr')(SC_6H_4CH_3)(CO)(PPh_3)]_2$ | 2068 (2064) | 319 |
| $[IrCl(SAr')(SC_6H_4OCH_3)(CO)(PPh_3)]_2$ | 2067 (2062) | 320 |
| $[IrBr(SAr')SC_6H_4NO_2)(CO)(PPh_3)]_2$ | 2069 (2063) | |
| $[IrBr(SAr')(SC_6H_4Br)(CO)(PPh_3)]_2$ | 2066 (2064) | |
| $[IrBr(SAr')(SC_6H_4F)(CO)(PPh_3)]_2$ | 2065 (2062) | |
| $[IrBr(SAr')(SC_6H_5)(CO)(PPh_3)]_2$ | 2065 (2063) | |
| $[IrBr(SAr')(SC_6H_4CH_3)(CO)(PPh_3)]_2$ | 2064 (2060) | |
| $[IrBr(SAr')(SC_6H_4OCH_3)(CO)(PPh_3)]_2$ | 2063 (2060) | |
| $[IrI(SAr')(SC_6H_4NO_2)(CO)(PPh_3)]_2$ | 2066 (2062) | |
| $[IrI(SAr')(SC_6H_4Br)(CO)(PPh_3)]_2$ | 2063 (2065) | |
| $[IrI(SAr')(SC_6H_4F)(CO)(PPh_3)]_2$ | 2062 (2058) | |
| $[IrI(SAr')(SC_6H_5)(CO)(PPh_3)]_2$ | 2062 (2063) | |
| $[IrI(SAr')(SC_6H_4CH_3)(CO)(PPh_3)]_2$ | 2061 (2060) | |
| $[IrI(SAr')(SC_6H_4OCH_3)(CO)(PPh_3)]_2$ | 2060 (2060) | |

[a] Value quoted in parentheses was obtained in Nujol. [b] Nujol as medium.

suggest that these complexes are somewhat dissociated in solution. Most of the complexes contain benzene of solvation (Table 1) in the solid state which could not be readily eliminated by heating the complexes *in vacuo* at 110°. Presumably the benzene of solvation is associated with the 2,4-dinitrobenzenethiolato moiety via a weak charge transfer interaction. Reaction (1) may be compared to the reaction between $IrCl(PPh_3)_3$ or $IrCl(AsPh_3)_3$ and a series of *para*-substituted benzenethiols in which the major product is also a dimeric iridium(III) species[17] *viz*., $[IrHCl(SAr)(EPh_3)_2]_2$ or $[IrCl_2(SAr')(EPh_3)_2]_2$ where E=P or As; Ar=$4\text{-}BrC_6H_4$, $4\text{-}FC_6H_4$, $4\text{-}HC_6H_4$, $4\text{-}CH_3C_6H_4$, $4\text{-}CH_3OC_6H_4$ and Ar'=$4\text{-}O_2NC_6H_4$.

Pertinent infrared data are presented in Table 2 and may be used to assist in establishing the structure of the products obtained via reaction (1). Only one band in the $\nu(C{\equiv}O)$ region of the infrared was observed both in solution and in the solid state. It may be noted that the position of the $\nu(C{\equiv}O)$ vibration in these dimeric complexes is somewhat dependent upon the nature of the *para*-substituent, Y, and increases as Y becomes more electron withdrawing (Table 2). In fact, a linear correlation exists between $\nu(C{\equiv}O)$ and the Hammett parameter, $\sigma_p$. This is illustrated in Fig. 1. This observation parallels that observed in the complexes, $IrHX(SC_6H_4Y)(CO)(PPh_3)_2$[4,9] and indicates that the CO ligand is *trans* to the $YC_6H_4S^-$ moiety. However, it may be noted that the variation in $\nu(C{\equiv}O)$ in the complexes (II), is less sensitive to a change in the nature of the substituent, Y, *vis à vis* $IrHX(SC_6H_4Y)(CO)(PPh_3)_2$. Also, the position of the $\nu(C{\equiv}O)$ vibration in (II) is ≈20–30 $cm^{-1}$ higher than that observed for $IrHX(SC_6H_4Y)(CO)(PPh_3)_2$ suggesting that a coordinated 2,4-dinitrobenzenethiolato moiety is causing only a slight reduction in electron density at iridium.

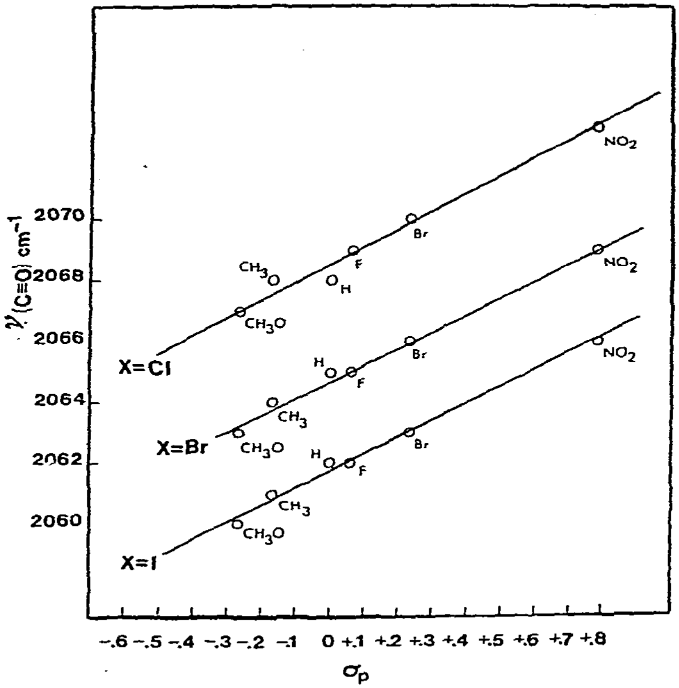
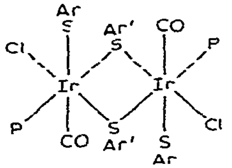


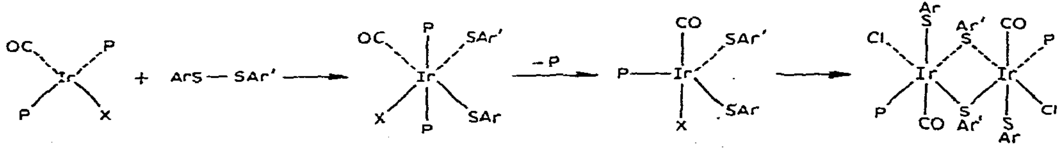
Fig. 1. Plot of $\nu(C{\equiv}O)$ versus $\sigma_p$ for the complexes, $[IrX(SC_6H_4Y)(SC_6H_3(NO_2)_2)(CO)(PPh_3)]_2$

A weak band was observed at ca. 320 cm$^{-1}$ for the dimeric complexes, (II), when X = Cl and has been assigned to the $\nu$(Ir–Cl) vibration. A corresponding band in the bromo and iodo derivatives was absent from this region of the infrared confirming the assignment of the band at ca. 320 cm$^{-1}$. In fact, this band occurs in the region expected for a terminal $\nu$(Ir–Cl) vibration[18]. The infrared spectral data considered above are all consistent with a structure for complexes (II) having 2,4-dinitrobenzenethiolato bridging ligands ($C_i$ local symmetry). This is shown below where Ar = $YC_6H_4$, Ar′ = 2,4-$(O_2N)_2C_6H_3$, P = $PPh_3$ and X = Cl, Br, or I.



The formation of these dimeric iridium(III) complexes may be conceptually rationalized via Scheme 1.

SCHEME 1



The initial step is assumed to be a stereospecific *cis* oxidative-addition of the disulfide to the iridium(I) substrate followed by a loss of triphenylphosphine to form a 5-coordinated iridium(III) species which then dimerizes to form the observed product. Qualitatively at least, the rate of reaction appears to be dependent on the nature of X and increases in the order, Cl < Br < I which is similar to that previously observed for other incoming addenda[4,19–21]. Also, it may be pointed out that this proposed reaction scheme is analogous to that proposed for the formation of $[IrHCl(SC_6H_4Y)(EPh_3)_2]_2$ from the reaction of $IrCl(EPh_3)_3$ and $HSC_6H_4Y$ where E = P or As[17] and the overall reaction represents another example of an "oxidative-elimation" reaction[22].

## EXPERIMENTAL

### *Physical measurements*

Infrared spectra were recorded on a Beckmann IR-12 spectrophotometer as Nujol mulls between NaCl discs in the region 4000–650 $cm^{-1}$. In the region 650–200 $cm^{-1}$ Nujol mulls between CsI discs were used. Solution spectra ($CHCl_3$) were recorded with 0.2 or 0.4 mm NaCl liquid cells. Molecular weight measurements were determined by Dornis u. Kolbe or A. Bernhardt, West Germany. Microanalyses were carried out by Chemalytics, Inc., Tempe, Arizona. Melting points were determined with a Fisher–Johns melting point apparatus and are uncorrected.

### *Materials*

Triphenylphosphine was purchased from Strem Chemicals, Inc., Danvers, Massachussetts, and was recrystallized from ethanol. Unless otherwise stated all other chemicals used were commercially available samples. All reactions were normally carried out under an atmosphere of nitrogen.

### *trans-Halocarbonylbis(triphenylphosphine)iridium(I)*

These complexes were prepared as previously reported[4].

### *μ,μ-Bis(2,4-dinitrobenzenethiolatodi(arenethiolato)dichlorodicarbonylbis(triphenylphosphine)diiridium(III)*

The following general procedure was used to prepare these complexes. A sample (0.3 g) of *trans*-$IrX(CO)(PPh_3)_2$ was dissolved in oxygen-free benzene (100–150 ml) whereupon the appropriate 2,4-dinitrophenyl 4-Y-phenyl disulfide (0.3 g) was added to the solution. This was then heated under reflux for 5 h when X = Cl, 4 h when X = Br and 3 h when X = I. Also, care was taken to exclude light during the course of reaction with *trans*-$IrI(CO)(PPh_3)_2$. During the course of reaction the solutions became dark reddish-brown in color. After the appropriate period of reflux, the solution was allowed to cool to room temperature, filtered by gravity, and n-pentane slowly added to the filtrate to precipitate the desired product as a reddish-brown solid. The product was then filtered off, washed successively with n-pentane, ligroin (b.p. 63–75°), and dried *in vacuo* over boiling toluene for 24 h. Analytical data are given in Table 1.

### 2,4-*Dinitriphenyl 4-Y-phenyl disulfides*

These were prepared by the reaction of 2,4-dinitrobenzenesulfenyl chloride with the appropriate arenethiol following the general procedure of Campaigne *et al.*[23]. Analytical data are given in Table 3.

TABLE 3

ANALYTICAL DATA FOR 2,4-DINITROPHENYL 4-Y-PHENYL DISULFIDES

| *Y* | *Found (calcd.)(%)* | | *M.p. (°C)* |
|---|---|---|---|
| | *C* | *H* | |
| $NO_2$ | 41.48 (40.77) | 1.97 (1.98) | 176–177 |
| Br | 37.17 (37.20) | 1.80 (1.81) | 127–128 |
| F | 44.38 (44.14) | 2.31 (2.15) | 136–137 |
| H | 46.96 (46.72) | 2.72 (2.60) | 86–87 |
| $CH_3$ | 48.08 (48.42) | 3.18 (3.10) | 114 |
| $CH_3O$ | 45.81 (46.13) | 2.90 (2.96) | 97 |

### *Reaction of diphenyl disulfide with trans-IrCl(CO)(PPh$_3$)$_2$*

To an oxygen-free benzene solution (100 ml) containing 0.5 g of *trans*-IrCl(CO)(PPh$_3$)$_2$ was added 0.4 g of diphenyl disulfide. The resulting solution was then heated under reflux for 5 h during which time it changed in colour from lemon-yellow to orange-brown. A 20 ml aliquot of this solution was then allowed to cool to room temperature whereupon an excess of n-pentane was added. The orange precipitate was then filtered off, washed with a small amount of n-pentane, and air-dried. $\nu(C\equiv O)$, 2057 s and 1959 vs cm$^{-1}$.

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