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REACTIONS OF IRIDIUM AND PLATINUM COMPLEXES WITH *N*-SULFINYL COMPOUNDS

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Summary

The reactions of substituted *N*-sulfinylanilines with the complexes $\{Pt[P(C_6H_5)_3]_2O_2\}$ and $\{IrClCO[P(C_6H_5)_3]_2\}$ have been reinvestigated. The former complex yields $\{Pt[P(C_6H_5)_3]_2SO_4\}$ as the only isolable product in reactions with *N*-sulfinylaniline. In contrast to a previous report, Vaska's complex has been found not to react with C_6H_5NSO under anhydrous conditions. $\{Pt[P(C_6H_5)_3]_2(C_2H_4)\}$ reacts with *N*-sulfinyl compounds to give complexes of formula $\{Pt[P(C_6H_5)_3]_2(RNSO)\}$ where R = C_6H_5, p-$O_2NC_6H_4$, p-$CH_3C_6H_4$, or p-$CH_3C_6H_4SO_2$. $\{Pt[P(C_6H_5)_3]_3\}$ reacts with C_6H_5NSO to give the same product obtained from reaction with the ethylene complex. Vaska's complex and its bromo analog form 1 : 1 adducts with p-$O_2NC_6H_4NSO$.

Introduction

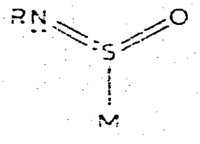
N-Sulfinylamines, R—N=S=O, are analogs of sulfur dioxide and sulfur diimides, RN=S=NR. Transition metal complexes of SO_2 [1,2] are well known and aryl- and alkyl-sulfur diimide complexes of platinum have been characterized [3]. There have been two brief communications on reactions of *N*-sulfinylanilines with complexes of platinum [4] and iridium [5].

In the first case dioxygenbis(triphenylphosphine)platinum was reported to form a 1 : 1 adduct with C_6H_5NSO. The IR bands reported for the complex however are identical to those of the sulfato complex $\{Pt(PPh_3)_2SO_4\}$ [6]. In the second case Vaska's complex was reported to react with C_6H_5NSO to give $\{IrClCO(PPh_3)_2 \cdot SO_2\}$ and aniline. The products reported could be accounted for by reaction with adventitious sulfur dioxide rather than *N*-sulfinylaniline. *N*-Sulfinylaniline is quite moisture sensitive and it is difficult to remove sulfur dioxide and aniline that can be introduced by hydrolysis [7]. This prompted a reinvestigation of these systems and a search for authentic metal complexes of this class of compounds.

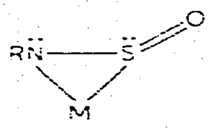
In this paper is reported the preparation and characterization of 1 : 1 adducts of *para*-substituted *N*-sulfinylanilines with bis(triphenylphosphine)platinum(0) and Vaska's complex and reactions of C_6H_5NSO with dioxygen complexes of platinum and iridium.

Results and discussion

N-sulfinyl amines can potentially coordinate to a metal in three ways. Mode A would be analogous to the behavior of sulfur dioxide [1]; mode B would correspond to the behavior of unsaturated compounds such as olefins, carbonyl sulfide, or carbon disulfide [8]; and mode C is like that suggested for sulfurdiimides (RN=S=NR) [3]. A fourth mode of reaction, oxidative addition at the C—N bond, shown in D, is possible but we have found no evidence in this work which would indicate that this has occurred in the systems studied.



(A)



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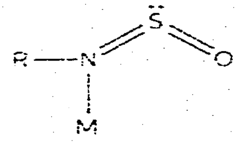

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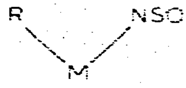
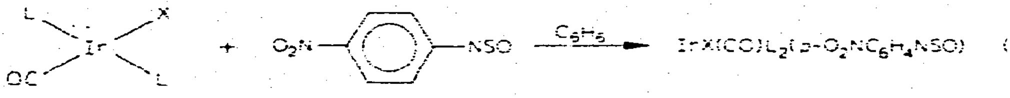


(D)

In previous work it has been reported that various substituted *N*-sulfinyl anilines react with Vaska's complex in benzene solution to yield the sulfur dioxide complex $IrCl(CO)(PPh_3)_2 \cdot SO_2$ [5]. In contrast to that report it has been found that if moisture and oxygen are excluded there is no reaction between an excess of *N*-sulfinylaniline or 4-methyl-*N*-sulfinylaniline and Vaska's complex within 24 h at room temperature. Infrared spectra of solutions of Vaska's complex and an excess of *N*-sulfinylaniline show only $\nu(C{\equiv}O)$ for the former in the region 1900—2200 cm^{-1}. In contrast a 1 : 1 adduct is rapidly formed in the reaction of Vaska's complex or its bromo analog with an excess of 4-nitro-*N*-sulfinylaniline (eq. 1). Analytical data is shown in Table 1. Compounds Ia and Ib are lemon yellow crystalline solids which readily lose the *N*-sulfinylamine upon washing with benzene or ether indicating that this ligand is quite labile. Compounds Ia and Ib show a strong band at 2000 cm^{-1} due to $\nu(C{\equiv}O)$. This may be compared with 2021 cm^{-1} for the corresponding band in the sulfur dioxide complex, $IrCl(CO)(PPh_3)_2 \cdot SO_2$ [9]. A band at 270 cm^{-1} in Ia and absent in Ib is assigned to $\nu(Ir—Cl)$. This may be compared with a value of 310 cm^{-1} for the SO_2 complex. The infrared data are tabulated in the Experimental Section. The IR spectrum does not provide sufficient information to unambiguously determine the mode of coordination. The similarity of the infrared spectra of free [10] and coordinated 4-nitro-*N*-sulfinylaniline in the $\nu(NSO)$ region of the spectrum may indicate that there is little change in the symmetry of the ArNSO



(1)

(Ia) X = Cl
(Ib) X = Br

TABLE 1

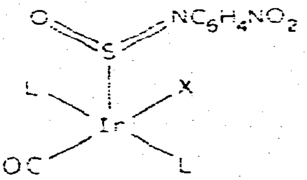
ANALYTICAL DATA

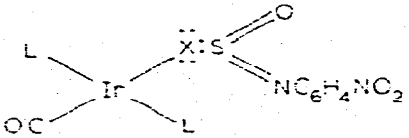
Complex [a]	M.p. (°C)	Color	Analysis found (calcd.) (%)		
			C	H	N
$PtL_2 \cdot CH_3C_6H_4NSO \cdot C_6H_6$	170	yellow	61.12 (61.89)	4.56 (4.56)	1.60 (1.47)
$PtL_2 \cdot NO_2C_6H_4NSO$	170	orange	56.62 (55.81)	3.82 (3.79)	2.61 (3.09)
$PtL_2 \cdot C_6H_5NSO \cdot 1/2\ C_6H_6$	115	yellow	60.16 (60.19)	4.18 (4.26)	1.45 (1.56)
$PtL_2 \cdot CH_3C_6H_4S(O)_2NSO \cdot C_6H_6$	190—194	white	54.29 (55.12)	3.76 (3.98)	1.08 (1.49)
$IrCl(CO)L_2 \cdot NO_2C_6H_4NSO$	140—145	yellow	53.76 (53.55)	3.57 (3.55)	2.96 (2.90)
$IrBr(CO)L_2 \cdot NO_2C_6H_4NSO$	175	yellow	51.96 (51.19)	3.50 (3.40)	2.70 (2.78)

[a] $L = P(C_6H_5)_3$.

group and little alteration of the electronic structure. This is in agreement with the low value of $\nu(C{\equiv}O)$ for the complex and ease of removal of the coordinated ArNSO group.

Two possible structures are consistent with the data *: The first structure is

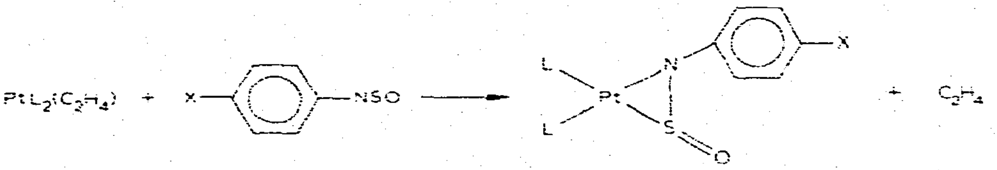




analogous to that found in most complexes of sulfur dioxide [2,11]. The structure in which the ligand is bound via the halide ion would be analogous to that found for $[PtL_2(CH_3)I \cdot SO_2]$ [11]. Coordination to the halide ion may account for the low value of $\nu(Ir{-}Cl)$ in compound Ia.

Ethylenebis(triphenylphosphine)platinum(0) reacts with 4-substituted *N*-sulfinylanilines (eq. 2) to give 1 : 1 adducts. Analytical data are shown in Table 1.

Comparison of the IR spectra of the free *N*-sulfinylanilines [10] and the



(2)

(IIa) X = H
(IIb) X = CH_3
(IIc) X = NO_2

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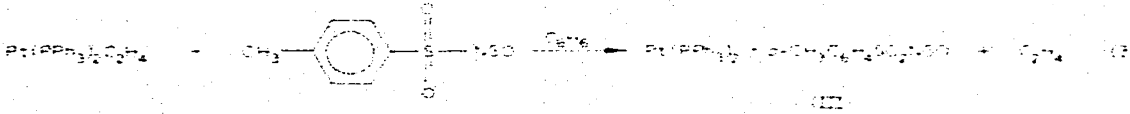
* We thank the referees for reminding us of the possibility of coordination at the halide ion.

complexes in the region of the NSO modes reveals a new, strong band at 1055 cm^{-1} for compound IIa. Corresponding bands appear at 1048 and 1050 cm^{-1} for IIb and IIc respectively. This band is in the region characteristic of $\nu(S{=}O)$ for small ring sulfoxides [12] and metal-*S*-sulfenato complexes [13,14]. This assignment is taken as evidence favoring the tentative assignment of a structure having the ArNSO group coordinated via the N—S π-bond. The bands at 1050 cm^{-1} do not appear in the spectra of the iridium complexes indicating that the mode of coordination is not the same in the platinum and iridium complexes. A strong band at 545 ± 5 cm^{-1} in the spectra of compounds II lends further support to the assigned *cis* structure [15]. Compound IIa is also obtained in high yield in the reaction of C_6H_5NSO with tris(triphenylphosphine)platinum(0).

A 1 : 1 adduct is also obtained in the reaction of *N*-sulfinyl-*p*-toluenesulfonamide with $\{Pt(PPh_3)_2C_2H_4\}$ (eq. 3).



(III)

(3)

The IR spectrum is complex in the region 1000—1400 cm^{-1} making assignment of bands difficult.

The reaction of $\{Pt(PPh_3)_2O_2\}$ with *N*-sulfinylaniline (in vacuo) (eq. 4) produces the sulfato complex as the only isolable platinum-containing product. This is in agreement with the IR data from the previous report of this reaction

$$Pt(PPh_3)_2O_2 + PhNSO \xrightarrow{C_6H_6} Pt(PPh_3)_2SO_4 \qquad (4)$$

in which the bands were erroneously assigned to a 1 : 1 adduct of formula $\{Pt(PPh_3)_2O_2 \cdot (PhNSO)\}$ [4]. Others have also noted the formation of a sulfato complex in this reaction [16]. The origin of the fourth oxygen in the sulfato group is not clear. The only possibilities are: (1) it originated in a second dioxygen complex; or (2) two *N*-sulfinyl groups are involved in the formation of the sulfato ligand. The latter seems the most plausible. This could lead to the formation of ArN=S=NAr as the nitrogen-containing product of the reaction [17]. The mechanism by which sulfate ion is formed in this reaction remains to be illucidated.

The dioxygen adduct of Vaska's complex does not react with *N*-sulfinylaniline but does react with the *para*-nitro derivative to give a mixture containing Ia, unreacted dioxygen complex, and $\{IrCl(CO)(PPh_3)_2SO_4\}$.

Experimental

The compounds *trans*-$\{IrX(CO)[P(C_6H_5)_3]_2\}$ (X = Cl [18] or Br [19]), $\{IrCl(CO)[P(C_6H_5)_3O_2\}$ [20], $\{Pt[P(C_6H_5)_3]_2C_2H_4\}$ [21], $\{Pt[P(C_6H_5)_3]_2O_2\}$ [22], $\{Pt[P(C_6H_5)_3]_2SO_4\}$ [6], $\{IrCl(CO)[P(C_6H_5)_3]_2SO_4\}$ [6], C_6H_5NSO [7], *p*-$CH_3C_6H_4NSO$ [7], *p*-$O_2NC_6H_4NSO$ [7], and *p*-$CH_3C_6H_4SO_2NSO$ [7] were prepared by methods in the literature. The *N*-sulfinylaniline and substituted derivatives were purified by distillation or recrystallization and stored under nitrogen. They were judged to be free of the corresponding amine when IR spectra showed no $\nu(N{-}H)$ bands. The *N*-sulfinylaniline used in vacuo was held under dynamic vacuum at room temperature for 2 h prior to use to insure the absence of sulfur dioxide. Benzene and n-hexane were dried by distillation and storage over molecular sieves. Infrared spectra were obtained on a Perkin—Elmer Model 621 Spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

All of the complexes reported here can be handled briefly in air as solids with no apparent change. The complexes slowly decompose upon storage at room temperature, under nitrogen.

$\{Pt[P(C_6H_5)_3]_2[C_6H_5NSO]\}$. Method A: *N*-Sulfinylaniline (0.07 ml) was added via syringe to a solution of $\{Pt[P(C_6H_5)_3]_2(C_2H_4)\}$ (0.4 g) in benzene (5 ml) under an atmosphere of dry nitrogen. The solution initially turned lemon yellow in color. Within 10 min a heavy yellow precipitate formed. The mixture was filtered, open to the atmosphere. The solid was washed with benzene (6 ml) and ether (4 ml), then dried in vacuo. Yield: 0.39 g.

Method B: *N*-Sulfinylaniline (0.3 ml) and toluene (6 ml) were condensed onto 0.55 g of tris(triphenylphosphine)platinum(0) at 77 K in vacuo. The mixture was allowed to warm to ice temperature and stirred. Within 5 min a heavy yellow precipitate formed. This was recovered as in Method A. Yield: 0.47 g. IR *: 1255s, 1055vs, 930w cm^{-1}.

$\{Pt[P(C_6H_5)_3]_2[p\text{-}CH_3C_6H_4NSO]\}$. *N*-Sulfinyl-*p*-toluidine (0.07 ml) was added via syringe to a solution of $\{Pt[P(C_6H_5)_3]_2(C_2H_4)\}$ (0.4 g) in benzene (5 ml) as for the previous compound. The solution turned dark yellow in color. n-Hexane (2 ml) was added with stirring. within 1 h clusters of yellow needles had formed. The mixture was filtered, open to the atmosphere. The solid was washed with benzene (2 ml) and ether (4 ml) then dried in vacuo. Yield: 0.35 g. IR *: 1500s, 1240m(br), 1048vs, 920w, 820w cm^{-1}.

$\{Pt[P(C_6H_5)_3]_2[p\text{-}O_2NC_6H_4NSO]\}$. A solution of $\{Pt[P(C_6H_5)_3]_2C_2H_4\}$ (0.3 g) in benzene (5 ml) was added to *N*-sulfinyl-*p*-nitroaniline in a nitrogen atmosphere. The resulting orange solution was stirred for 10 min. Dry n-hexane (0.5 ml) was added dropwise. The resulting orange precipitate was recovered by filtration, in air. The solid was washed with ether (5 ml) and dried in vacuo. Yield: 0.4 g. IR *: 1575vs, 1290vs, 1280vs, 1175m, 1108s, 1050vs, 918s, 830w cm^{-1}.

$\{Pt[P(C_6H_5)_3]_2[p\text{-}CH_3C_6H_4SO_2NSO]\}$. To a mixture of *N*-sulfinyl-*p*-toluenesulfonamide (0.1 g) and $\{Pt[P(C_6H_5)_3]_2C_2H_4\}$ (0.3 g) under dry nitrogen was added benzene (3 ml). The resulting light yellow solution was stirred for 3—4 min. Diethyl ether (4 ml) from a freshly opened can was added dropwise. A heavy white precipitate formed over the period of 15 min. The solid was recovered by filtration, in air, washed with ether and dried in vacuo. Yield: 0.2 g. IR *: 1525vs, 1350s, 1308m, 1150vs, 1070s, 880m(br), 850m cm^{-1}.

$\{IrX(CO)[P(C_6H_5)_3]_2(p\text{-}O_2NC_6H_4NSO)\}$ (X = Cl or Br). The iridium complex, *trans*-$\{IrX(CO)[P(C_6H_5)_3]_2\}$ (0.25 g) and *p*-nitro-*N*-sulfinylaniline (0.15 g) were transferred in a dry box to a flask fitted with a serum cap. Benzene (5 ml) was added and the mixture was stirred for 1 h. Filtration, open to air, gave a bright yellow product. This was washed with n-hexane (2 ml). Washing with benzene or ether results in extraction of the *N*-sulfinylamine from the compound. The yields are: X = Cl, 0.38 g; X = Br, 0.27 g. IR *: (X = Cl) 2000vs (ν(CO)), 270w

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* Infrared bands due to coordinated $P(C_6H_5)_3$ are not listed. Samples were run as Nujol mulls.

(ν(Ir—Cl)); (X = Br) 2000vs (ν(CO)); other bands (same for X = Cl and X = Br) 1585s, 1290vs(br), 1178m, 1110m(sh), 1080m(sh), 940w, 850w cm^{-1}.

Reaction of trans-$\{IrCl(CO)[P(C_6H_5)_3]_2\}$ *with N-sulfinylaniline.* Benzene, (5 ml) and *N*-sulfinylaniline (0.4 ml) were transferred in vacuo to a flask containing Vaska's complex (0.2 g) held at 77 K. The mixture was warmed to room temperature and the suspension stirred in vacuo for 26 h. During this time there was no visible evidence of the formation of the characteristic lime green color of the SO_2 adduct of Vaska's complex. The unreacted Vaska's complex (0.2 g) was recovered by filtration.

Reaction of $\{IrCl(CO)[P(C_6H_5)_3]_2O_2\}$ *with N-sulfinylaniline and p-nitro-N-sulfinylaniline.* Benzene (4 ml) and *N*-sulfinylaniline (0.3 ml) were condensed onto the iridium complex in vacuo at 77 K. The mixture was warmed to room temperature and the suspension stirred for 24 h. Filtration gave nearly a quantitative yield of the unreacted dioxygen adduct of Vaska's complex.

Reaction with *p*-nitro-*N*-sulfinylaniline under similar conditions gave a mixture of unreacted dioxygen complex, $\{IrCl(CO)(PPh_3)_2SO_4\}$ and the *p*-$O_2NC_6H_4NSO$ adduct of Vaska's complex.

Acknowledgement

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References

1 A. Wojcicki, Account Chem. Res., 4 (1971) 344.
2 J.P. Linsky and C.G. Pierpont, Inorg. Chem., 12 (1973) 2959.
3 J. Kuyper and K. Vrieze, J. Organometal. Chem., 74 (1974) 289.
4 I.S. Kolomnikov, Y.D. Koreshkov, T.S. Lobura, and M.E. Volpin, Izv. Akad. Nauk. SSSR, (1972) 1181.
5 G. De Luca, C. Panattoni and L. Toniolo, Chem. and Ind., (1973) 742.
6 R.W. Horn, E. Weissberger and J.P. Collman, Inorg. Chem., 9 (1970) 2367.
7 G. Kresze, R. Albrecht, K. Bederke, H.P. Patzschke, H. Smalla and A. Trede, Angew. Chem. Int. Ed., 1 (1962) 89.
8 R. Ugo, Coord. Chem. Rev., 3 (1968) 319.
9 L. Vaska and S.S. Bath, J. Amer. Chem. Soc., 88 (1966) 2616.
10 G. Kresze and A. Maschke, Chem. Ber., 94 (1961) 450.
11 M.R. Snow and J.A. Ibers, Inorg. Chem., 12 (1973) 224.
12 G.E. Hartzell and J.N. Page, J. Amer. Chem. Soc., 88 (1966) 2616.
13 T.A. George and D.D. Watkins, Jr., Inorg. Chem., 12 (1973) 398.
14 S.J. Markham, Y.L. Chung, G.D. Branum and D.M. Blake, J. Organometal. Chem., 107 (1976) 121.
15 S.H. Mastin, Inorg. Chem., 13 (1974) 1003.
16 C.G. Pierpont, private communication.
17 H.W. Roesky in A. Senning (Ed.), Sulfur in Organic and Inorganic Chemistry, Vol. 1, Marcel Dekker, Inc., New York, 1971, p. 24.
18 J.P. Collman, C.T. Sears and M. Kubota, Inorg. Syn., 11 (1968) 102.
19 J.P. Collman, M. Kubota, F.D. Vastine, J.Y. Sun and J.W. Kang, J. Amer. Chem. Soc., 90 (1968) 5430.
20 L. Vaska, Science, 140 (1963) 809.
21 D.M. Blake, S. Shields and L. Wyman, Inorg. Chem., 13 (1974) 1595.
22 C.D. Cook and G.S. Jauhal, Inorg. Nucl. Chem. Lett., 3 (1967) 31.