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Desulfonation of Sulfinatoiridium(III) Complexes

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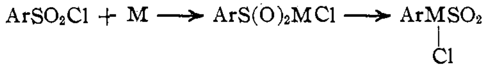
The reactions of $Ir(N_2)Cl[P(C_6H_5)_3]_2$ with alkyl- and arylsulfonyl chlorides lead to evolution of nitrogen and formation of five-coordinated *S*-sulfinato complexes, $IrCl_2[P(C_6H_5)_3]_2RSO_2$, **4**, where R is methyl, ethyl, *n*-propyl, phenyl, etc. These complexes rearrange under mild conditions to the corresponding alkyl or aryl complexes $RIrCl_2[P(C_6H_5)_3]_2SO_2$, **7**. Kinetic studies indicate that electron-withdrawing substituents on R enhance the rate of this rearrangement. The five-coordinated sulfinato complexes are readily carbonylated to give $IrCl_2(CO)[P(C_6H_5)_3]_2RSO_2$, **5**. Sulfur dioxide in the alkyl or aryl complexes **7** is displaced by carbon monoxide to give $RIrCl_2(CO)[P(C_6H_5)_3]_2$, **8**.

Introduction

The activation of simple molecules by their interactions with transition metal atoms and their subsequent reactions at the metal sites are of interest because of their involvement in reactions which are homogeneously catalyzed.[2] The reactions of sulfur dioxide with complexes of metals with d^8 and d^{10} electronic configuration have been widely investigated.[3] Recently, the reactions of sulfur dioxide with oxygen at metal sites have been reported by Valentine, Valentine, and Collman.[4] The insertion of sulfur dioxide into alkyl–iron and alkyl–manganese bonds has been extensively studied by Wojcicki and coworkers.[5] The reaction which is the reverse of sulfur dioxide insertion, that is the extrusion of sulfur dioxide from alkyl- or arylsulfinato-(transition metal) complexes with formation of metal–carbon bonds, has not been studied as extensively, and in fact, desulfonation has been effected only in a few examples.[6]

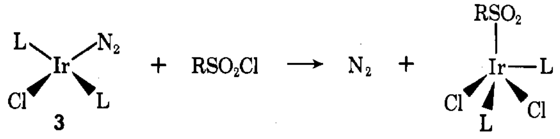
Just as complexes of metals with d^8 electronic configuration are effective homogeneous catalysts for decarbonylation of acyl chlorides,[7] complexes of soft metals are also effective catalysts for desulfonation of arylsulfonyl halides.[8] Wilkinson's catalyst $Rh[P(C_6H_5)_3]_3Cl$ and Vaska's compound $Ir(CO)[P(C_6H_5)_3]_2Cl$ were shown to be the most effective desulfonation catalysts. The most significant steps in the mechanism for desulfonation include the oxidative addition[6a,9] of the sulfonyl chloride to give the metal–sulfinato complex (1) and the actual desulfonation step in which the arylsulfinato–metal bond is converted to the arylmetal–sulfur dioxide bond (2). In this paper, we describe results of a study of the desulfonation reaction, that is the rearrangement of the sulfinato complex 1 to the sulfur dioxide complex 2.



$$ArSO_2Cl + M \longrightarrow \underset{\mathbf{1}}{ArS(O)_2MCl} \longrightarrow \underset{\mathbf{2}}{Ar\underset{\substack{|\\ Cl}}{M}SO_2}$$

Results and Discussion

Reactions of the iridium–dinitrogen complex **3** and alkyl- and arylsulfonyl chlorides in benzene solution proceed with immediate evolution of nitrogen and formation of dark brown to black solutions. This intense color is diagnostic of the presence of five-coordinated d^6 complexes and such complexes have been isolated in reactions of the dinitrogen complex **3** with hydrogen chloride,[10] carbon disulfide,[11] and acyl chlorides.[12]



3 **4**

L = triphenylphosphine

The five-coordinated alkyl- and arylsulfinato complexes **4** were isolated and characterized by elemental analyses (Table I). Molecular weight measurements indicate that the complexes are monomeric in chloroform or benzene solution. The structures of these complexes are presumably square pyramidal with the sulfinato ligand in the apical position analogous to related five-coordinated complexes of d^6 metal ions.[13] The infrared spectra of these complexes consist of bands due to triphenylphosphine and the organic moiety R and, additionally, bands shown in Table II. The intense bands in the 1240- and 1060-cm^{-1} regions, assigned to the asymmetric and symmetric S–O stretching modes of the *S*-sulfinato ligand,[6,14] are shifted by approximately 100 cm^{-1} to lower frequencies compared to the absorption in organic sulfonyl derivatives. This shift has been ascribed to the π back-bonding from the metal to the *S*-sulfinato ligand.[6a,14a] More recently, Chatt and Mingos have stressed the significance of inductive electron release from sulfur to the metal.[14c]

That the sulfinato complexes **4** are five-coordinated is strongly indicated by their facile carbonylation to give the six-coordinated carbonylsulfinato complexes **5**.

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[1] National Science Foundation Undergraduate Research Participant.

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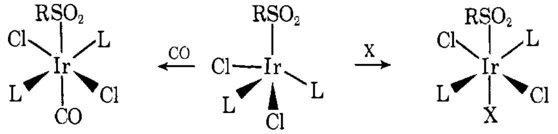
TABLE I

ANALYTICAL DATA FOR COMPLEXES

No.	Compound	% C Calcd	% C Found	% H Calcd	% H Found	% S Calcd	% S Found	% Cl Calcd	% Cl Found	Mp,[f] °C
4a	$IrCl_2[P(C_6H_5)_3]_2CH_3SO_2$[a]	51.3	52.1	3.84	3.85	3.69	3.67			170–200
4b	$IrCl_2[P(C_6H_5)_3]_2C_2H_5SO_2$[b]	51.4	52.4	3.97	3.98	3.61	2.62			185
4c	$IrCl_2[P(C_6H_5)_3]_2C_3H_7SO_2$[c]	52.3	51.8	4.17	4.20	3.57	3.48			202
4d	$IrCl_2[P(C_6H_5)_3]_2C_7H_7OSO_2$[d]	53.9	54.7	3.89	3.61	3.35	3.38	7.40	8.32	204
4e	$IrCl_2[P(C_6H_5)_3]_2C_7H_7SO_2$	54.8	55.4	3.96	3.97			7.53	7.59	219–221
4f	$IrCl_2[P(C_6H_5)_3]_2C_6H_5SO_2$[e]	54.4	55.9	3.81	3.89	3.45	2.74			209
4g	$IrCl_2[P(C_6H_5)_3]_2C_6H_4ClSO_2$	52.4	52.5	3.56	3.76	3.34	3.21	11.0	10.8	190–200
4h	$IrCl_2[P(C_6H_5)_3]_2C_6H_4NO_2SO_2$	51.9	50.9	3.53	3.56	3.30	2.48	7.30	7.98	137–145
5a	$IrCl_2(CO)[P(C_6H_5)_3]_2CH_3SO_2$[h]	50.0	48.9	3.76	3.72	3.59	3.38			220–229
5b	$IrCl_2(CO)[P(C_6H_5)_3]_2C_2H_5SO_2$[i]	53.4	53.4	3.73	4.14	3.40	2.93			
5e	$IrCl_2(CO)[P(C_6H_5)_3]_2C_7H_7SO_2$[h]	52.0	53.3	3.81	3.86	3.20	2.13	10.6	10.1	206–209
5f	$IrCl_2(CO)[P(C_6H_5)_3]_2C_6H_5SO_2$	53.8	53.4	3.70	3.71	3.35	3.34			259–264
7b	$C_2H_5IrCl_2[P(C_6H_5)_3]_2SO_2$	51.4	52.1	3.97	3.98	3.61	2.62			164–184
7c	$C_3H_7IrCl_2[P(C_6H_5)_3]_2SO_2$	52.3	52.6	4.17	3.99	3.57	3.38			
7f	$C_6H_5IrCl_2[P(C_6H_5)_3]_2SO_2$	54.4	58.5	3.81	3.90	3.45	1.37			213–220
7h	$O_2NC_6H_4IrCl_2[P(C_6H_5)_3]_2SO_2$	57.8[g] 51.9	55.2	4.09[g] 3.53	4.09	1.72[g] 3.30	0.93	7.30	8.00	
7i	$C_6F_5IrCl_2[P(C_6H_5)_3]_2SO_2$	54.3[g] 49.6	48.2	3.69[g] 2.98	2.71	1.08[g] 3.16	3.10	7.64[g]		273–276
8d	$CH_3OC_6H_4IrCl_2[P(C_6H_5)_3]_2(CO)$	57.4	57.3	4.04	3.96					211
8e	$CH_3C_6H_4IrCl_2[P(C_6H_5)_3]_2(CO)$	58.3	58.1	4.11	4.19			7.86	7.89	225–230
8f	$C_6H_5IrCl_2[P(C_6H_5)_3]_2(CO)$	58.0	57.8	3.96	3.88			7.94	7.94	264–268
8g	$ClC_6H_4IrCl_2[P(C_6H_5)_3]_2(CO)$	55.7	55.5	3.70	3.67					

[a] Molecular weight: calcd, 866.8; found, 830 (in $CHCl_3$). [b] Molecular weight: calcd, 880.9; found, 916 (in $CHCl_3$). [c] Molecular weight: calcd, 895.9; found, 807 (in $CHCl_3$). [d] Molecular weight: calcd, 958.9; found, 855 (in benzene). [e] Molecular weight: calcd, 928.9; found, 790 (in $CHCl_3$). [f] Compounds decompose upon melting. [g] Calculated for $[RIrCl_2(P(C_6H_5)_3)_2]_2SO_2$. [h] Solvate of 0.5 CH_2Cl_2 [i] Solvate of 0.5 C_6H_6.



5 **4** **6**

$R = C_6H_5$; X = pyridine, benzonitrile

TABLE II

INFRARED DATA (cm^{-1}) FOR THE SULFINATO COMPLEXES

R	ν_{SO_2}(asym)	ν_{SO_2}-(sym)	δ_{SO_2}	ν_{Ir-Cl}
CH_3	1238	1082		333
C_2H_5	1246, 1211	1077	580	335, 325
n-C_3H_7	1237, 1204	1088	580	330
p-$CH_3OC_6H_4$	1244	1062	572	334
p-$CH_3C_6H_4$	1243	1064	570	330
C_6H_5	1243	1061	576	326, 312
p-ClC_6H_4	1243	1063	586	323
p-$O_2NC_6H_4$	1249	1072	579	326

Pertinent infrared spectral bands for these complexes are given in Table III. The CO frequencies in the 2075-cm^{-1} region indicate that CO is bonded to iridium(III).[15] Absorption bands in the 1215- and 1060-cm^{-1} regions are indicative of iridium-*S*-sulfinato bonding as mentioned above for the sulfinatoiridium complexes **4**.

The phosphine ligands are almost always trans to each other in related complexes.[9,15] It has been observed that there is a correlation[16] between stereochemistry of the cis,trans arrangement of triphenylphosphine ligands on four-coordinated metal atoms and the relative intensities of two weak bands at 1586 and 1572 cm^{-1}. When the triphenylphosphine ligands are cis, the band at 1586 cm^{-1} is more intense than that at 1572 cm^{-1}. In trans complexes the intensities of the bands are reversed. The 1572-cm^{-1} band is more intense than the band at 1586 cm^{-1} for all the six-coordinated bis(triphenylphosphine) complexes described in this paper. This may be a good indication of the trans arrangement of triphenylphosphine ligands. The trans arrangement of methyldiphenylphosphine and dimethylphenylphosphine ligands in related complexes has been established by nmr studies.[9,15] The presence of a single absorption band in the 330-cm^{-1} region is indicative of the trans Cl–Ir–Cl geometry.[9] The CO is thus stereodirected trans to the strongly trans-labilizing[9,14] RSO_2 ligand. Nucleophilic addition to a five-coordinated d^6 complex was previously shown to be stereodirected trans to a strongly trans-labilizing hydrido ligand.[17] The *trans*-dichlorosulfinato complexes **5** are isomeric with the *cis*-dichlorosulfinato complexes obtained by the oxidative addition reactions of sulfonyl chlorides and *trans*-chlorobis(organophosphine)carbonyliridium complexes.[6a,9] The C–O and S–Os tretching frequencies for the *trans*-dichlorosulfinato complexes **5** shown in Table III are very similar.

TABLE III

INFRARED DATA (cm^{-1}) FOR THE CARBONYLSULFINATO COMPLEXES $IrCl_2(CO)[P(C_6H_5)_3]_2RSO_2$

R	ν_{CO}	ν_{SO_2}-(asym)	ν_{SO_2}-(sym)	δ_{SO_2}	ν_{Ir-Cl}
CH_3	2087	1215	1071	. . .	334
C_2H_5	2075	1236	1064	589	332
n-C_3H_7	2073	1214	1063	590	331
p-$CH_3OC_6H_4$	2074	1211	1053	579	331
p-$CH_3C_6H_4$	2077	1211	1053	572	334
C_6H_5	2074	1211	1052	584	331
p-ClC_6H_4	2084	1213	1055	593	335, 311 w
p-$O_2NC_6H_4$	2088	1216	1062	588	338

Lewis bases such as pyridine and nitriles nucleophilically attack the five-coordinated *S*-sulfinato complex **4** to give six-coordinated complexes **6**. The *S*-

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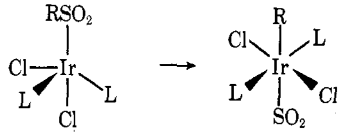
(16) W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc. A*, 2062 (1969); W. H. Baddley, private communication.

(17) D. N. Blake and M. Kubota, *J. Amer. Chem. Soc.*, **92**, 2578 (1970).

sulfinato ligand in these complexes is characterized by infrared absorption in the 1210-, 1052-, and 582-cm^{-1} regions similar to those shown for the carbonyl complexes **5** in Table III. These complexes also have a singlet band in the 335-cm^{-1} region which is indicative of the trans Cl–Ir–Cl geometry. The structures of the complexes are thus as depicted for **6**. In accord with our earlier observation,[17] the nucleophile is stereodirected trans to the strong trans-labilizing *S*-sulfinato ligand. An indication of the trans-labilizing property of the *S*-sulfinato ligand is given by the relatively low Ir–Cl stretching frequencies in compounds with the trans Cl–Ir–SO_2R geometry.[9]



4 **7**

TABLE IV

INFRARED DATA (CM^{-1}) FOR THE COMPLEXES $RIrCl_2[P(C_6H_5)_3]_2(SO_2)$

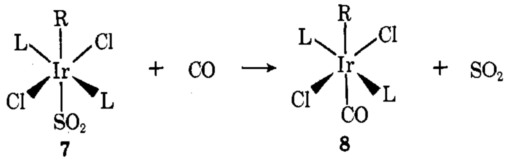
R	ν_{SO_2}- (asym)	ν_{SO_2}- (sym)	δ_{SO_2}	ν_{Ir-Cl}
CH_3	1181	955, 935	565 w	333
C_2H_5	1166	965, 937	584 w	325 w
n-C_3H_7	1165	969, 941	582 w	
p-$CH_3OC_6H_4$	1057	1001	585	312
p-$CH_3C_6H_4$[a]	1048	1011	575 w	309
C_6H_5	1054	1020		312
p-ClC_6H_4	1044	1006	562 w	327, 308
p-$O_2NC_6H_4$[a]	1037	1022	579	325
C_6F_5	1060	967, 959	...	330

[a] Analytical data indicates stoichiometry $\{RIrCl_2[P(C_6H_5)_3]_2\}_2SO_2$.

When the five-coordinated sulfinato complexes **4** were warmed in benzene solution, the intense green color faded and the pale yellow complexes **7** were isolated. The addition of methanol was observed to accelerate this reaction. Six-coordinated d^6 complexes of iridium are generally colorless or pale yellow.[15] The absorption bands in the 1240-cm^{-1} region in the spectra of the sulfinato complexes disappeared and were replaced by bands at lower frequencies. These bands (Table IV) are assigned to the coordinated sulfur dioxide ligand. The SO_2 stretching frequencies in **7** are substantially lower than those observed in related complexes.[4] These reduced frequencies may be attributed to the greater extent of π back-bonding or inductive electron release from the metal to the sulfur dioxide, which might be expected when sulfur dioxide is trans to an alkyl or aryl group, which is a poor π acceptor. The strong σ-trans-labilizing influence of the alkyl or aryl groups contributes to rather weak Ir–SO_2 bonding and low sulfur analyses were obtained for these complexes. For R = C_6H_5 and *p*-$O_2NC_6H_4$, the analytical data indicate the presence of compounds with the stoichiometry $\{RIrCl_2[P(C_6H_5)_3]_2\}_2SO_2$. Compounds with related stoichiometry apparently with bridging SO_2 ligands have been previously reported.[8] These compounds may have bridging SO_2 ligands. The compound $K_6[(CN)_5CoSO_2Co(CN)_5]$ has sulfur–oxygen stretching frequencies[18] which are relatively low compared to the frequencies in most SO_2 complexes.[4] The symmetric and asymmetric S–O stretching frequencies for the complexes **7** when R is alkyl are separated by 200 cm^{-1}, whereas when R is aryl, the separation is much smaller (15–56 cm^{-1}). This difference may be due to the π-acceptor capabilities of the aryl ligands or to structural differences such as mentioned previously, where the sulfur dioxide molecule can serve as a bridging ligand.

Absence of absorption in the 250–280-cm^{-1} region indicates the absence of trans Cl–Ir–R or trans Cl–Ir–L geometry in **7** and an intense band in the 312–330-cm^{-1} region in the spectrum of each of the complexes indicates the presence of the trans Cl–Ir–Cl bonding.[17] The relative intensities of the 1573- and 1582-cm^{-1} bands as in the previously mentioned complexes indicate that the triphenylphosphine ligands are trans to each other. The rearrangement of the sulfinato complex **4** thus leads to the complex **7** in which R and SO_2 are in trans positions. One possible route to such a complex is the formation of an intermediate complex with R and SO_2 in cis positions, followed by dissociation of SO_2 and reassociation of SO_2 trans to the R group. It was noted in an earlier study that rearrangement of acyl complexes to carbonyl–alkyl or –aryl complexes generally leads to complexes with R and CO in cis positions.[12]

The sulfur dioxide ligand trans to the alkyl or aryl group in complex **7** is readily displaced by carbon monoxide to give the *trans*-dichlorocarbonyl complex **8**.



7 **8**

The ir spectra of these complexes are similar to the spectra of the sulfur dioxide complexes **1**, except for the absence of bands shown in Table IV which were assigned to the sulfur dioxide ligand. Pertinent infrared spectral data for the carbonyl complexes are given in Table V. The *trans*-dichloro structure is again indicated by relatively intense absorption in the 310–335-cm^{-1} region and the absence of strong absorption in the 250–270-cm^{-1} region due to Cl trans to R or L. The carbonyl frequencies in the 2040–2070-cm^{-1} region are typical of CO bonded to d^6 iridium(III).[15] These complexes are isomers of the products expected in the oxidative addition reactions of RCl and *trans*-$L_2ClIrCO$.

TABLE V

INFRARED DATA FOR CARBONYL COMPLEXES $RIr(CO)Cl_2[P(C_6H_5)_3]_2$

R	CO	Ir–Cl	R	CO	Ir–Cl
CH_3	2072	323, 255 w	C_6H_5	2044	319
C_2H_5	2075	328	*p*-ClC_6H_4	2059	333, 311
n-C_3H_7	2070, 2040	328 w	*p*-$O_2NC_6H_4$	2076	321
p-$CH_3OC_6H_4$	2053	320	C_6F_5	2075, 2044	317
p-$CH_3C_6H_4$	2056	323, 314			

Kinetics of Desulfonation.—The rates of rearrangements of the sulfinato complexes **4** to the alkyl– or aryl–sulfur dioxide complexes **7** were determined by measuring the visible spectra as a function of time. That the change in the visible spectra reflected the course of the rearrangement was verified by quenching

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(18) A. A. Vlcek and F. Basolo, *Inorg. Chem.*, **5**, 156 (1966).

the reaction mixtures with hexane to precipitate the solid reactants and products and examining their infrared spectra. Strong absorption by solvents such as benzene, tetrahydrofuran, chloroform, or dichloromethane in the 1200–1250 cm^{-1} region precluded the use of infrared spectroscopy for kinetic measurements.

TABLE VI

FIRST-ORDER RATE CONSTANTS FOR THE REARRANGEMENTS OF $IrCl_2[P(C_6H_5)_3]_2RSO_2$ TO $RIrCl_2[P(C_6H_5)_3]_2SO_2$

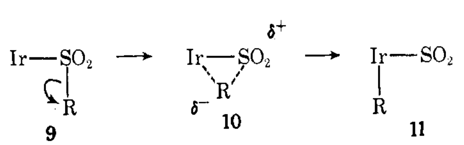
R	10^3k, sec^{-1}	Temp, °C	R	10^3k, sec^{-1}	Temp, °C
		THF Solvent			
p-ClC_6H_4	7.5	35.0	p-$CH_3C_6H_4$	2.4	30.0
C_6H_5	4.3	35.0	C_6H_5	3.1	30.0
p-$CH_3C_6H_4$	3.5	35.0	p-ClC_6H_4	6.9	30.0
p-$CH_3OC_6H_4$	2.8	35.0	p-$CH_3OC_6H_4$	1.3	25.0
CH_3	0.014	35.0	p-$CH_3C_6H_4$	1.5	25.0
C_2H_5	0.009	35.0	C_6H_5	1.7	25.0
n-C_3H_7	0.006	35.0	p-ClC_6H_4	4.8	25.0
p-$CH_3OC_6H_4$	2.0	30.0	p-$O_2NC_6H_4$	26.0[a]	25.0
		Benzene Solvent			
p-$CH_3OC_6H_4$	1.0	35.1	C_6H_5	1.3	35.1
p-$CH_3C_6H_4$	2.0	35.1	p-ClC_6H_4	3.9	35.1

[a] Determined by Guggenheim method.

Linear plots of log ($A_\infty - A_t$) *vs.* time indicated that the reactions were first order for at least 2 half-lives. The first-order rate constants are shown in Table VI. Deviation from linearity was observed beyond 2 half-lives for some of the systems. We attribute this to a subsequent loss of sulfur dioxide in 7. For R = CH_3, C_2H_5, and n-C_3H_7 in dioxane solution, the plots of absorbance *vs.* time gave indication of a rapid reaction prior to the primary reaction. That this rapid reaction is not due to the rearrangement was shown by stirring the five-coordinated complex **4** where R is CH_3 for 2 hr in tetrahydrofuran and precipitating the iridium product. This product was shown to be primarily unreacted **4**. The rapid reaction may be due to the formation of a tetrahydrofuran adduct. Activation parameters calculated from the data in Table VI are as follows: R = p-$CH_3OC_6H_4$, $\Delta H^{\ddagger} = 14.1 \pm 0.4$ kcal/mol, $\Delta S^{\ddagger} = -25 \pm 2$ eu; R = p-$CH_3C_6H_4$, $\Delta H^{\ddagger} = 15.3 \pm 0.6$ kcal/mol, $\Delta S^{\ddagger} = -20 \pm 4$ eu; R = C_6H_5, $\Delta H^{\ddagger} = 16.3 \pm 1.2$ kcal/mol, $\Delta S^{\ddagger} = -17 \pm 8$ eu; R = p-ClC_6H_4, $\Delta H^{\ddagger} = 7.5 \pm 1.4$ kcal/mol, $\Delta S^{\ddagger} = -44 \pm 9$ eu.

It is readily apparent that electron-withdrawing substituents on the migrating carbon atom enhance the rate of rearrangement of R from the sulfur to the iridium atom. It is noteworthy that when R is the strongly electron-withdrawing C_6F_5 group, the sulfinato complex **4** could not be isolated or detected. Apparently, the rearrangement to the aryl complex **7** proceeds very rapidly. The complex **4**, with R as p-$O_2NC_6H_4$, could not be isolated in our first attempt, but we were able to isolate the complex by running the reaction at a low temperature and immediately precipitating the product with hexane.

The enhancement of the rates of rearrangement of the sulfinato complexes by electron-withdrawing substituents on R may indicate significant contributions of the carbanionic characteristics of R and the strength of the R–Ir bond to the stabilization of the activated complex **10**. The enhancement of the rates of rearrangement of the sulfinato complexes **4** to the sulfur dioxide complexes 7 by electron-withdrawing substituents on R contrasts to the observation that electron-withdrawing substituents on R lead to decreased rates of migration from carbon monoxide to iridium.[19]



Extrusion of sulfur dioxide from six-coordinated *S*-sulfinato iridium complexes could be accomplished only for a few complexes.[6a] High temperatures were required. The facile desulfonation of the sulfinato complexes observed in this study is attributed to the presence of the vacant sixth coordination site which might be expected to facilitate interaction as depicted in **10**.

Experimental Section

The dinitrogen complex $IrCl(N_2)[P(C_6H_5)_3]_2$ was prepared by the method previously described.[11] The sulfonyl chlorides were reagent grade materials, which were vacuum distilled or sublimed as required. The sulfonyl chlorides were stored and handled in a Vacuum Atmospheres Dri-Lab. Benzene and dioxane were redistilled and stored over molecular sieves. Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer Model 621 spectrophotometer. Molecular weights were determined with a Mechrolab osmometer. Melting points were obtained using a Mel-Temp apparatus and are uncorrected. Microanalyses were performed by Dr. F. Pascher, Bonn, Germany.

Dichloroalkylsulfinatobis(triphenylphosphine)iridium(III) (4).—Methanesulfonyl chloride (0.2 ml) was added to a suspension of 470 mg of the dinitrogen complex **3** in 7 ml of benzene. The reaction mixture which was vigorously stirred immediately turned green and a black solution was formed. After a few minutes when there was no further evidence of gas evolution, 15 ml of hexane was added to precipitate a brown solid which was washed with hexane and diethyl ether. The other sulfinato complexes shown in Tables I and II were prepared in a similar manner. An attempt to recrystallize some of these compounds from benzene–methanol led to formation of rearranged products.

Dichloro(arylsulfinato)carbonylbis(triphenylphosphine)-iridium(III) (5).—A suspension of 100 mg of the five-coordinated sulfinato complex **4** in 30 ml of benzene was carbonylated under 20 psi of carbon monoxide for 5 min. The dark color faded to give a pale yellow solution which was stripped to dryness under reduced pressure. The product was recrystallized from benzene–hexane. An example of a more convenient procedure is described. A solution of 60 mg of p-toluenesulfonyl chloride in 10 ml of benzene was added to 200 mg of the dinitrogen complex **3**. After gas evolution had ceased in 3 min, carbon monoxide was passed over the solution while it was vigorously stirred. The dark brown color of the solution rapidly faded and 10 ml of hexane was added to precipitate a pale yellow solid. The product was recrystallized from dichloromethane–hexane.

Nucleophilic Addition to Dichlorobenzenesulfinatobis(triphenylphosphine)iridium(III) (4).—A solution of 0.1 ml of benzenesulfonyl chloride in 5 ml of benzene was added to 200 mg of the dinitrogen complex **3**. The sample was vigorously stirred until gas evolution ceased. The Lewis base (1 ml at 0.5 g of solid) was added and the solution was stirred until the black solution became yellow. In some trials a pale yellow solid precipitated, but in all cases, 10 ml of hexane was added to precipitate the pale yellow products (6). When the products were warmed in dichloromethane, green solutions were formed, which turned yellow upon addition of excess base. *Anal.* Calcd for the pyridine adduct $C_6H_5SO_2IrCl_2[P(C_6H_5)_3]_2 \cdot C_5H_5N$: C, 56.0; H, 4.00; N, 1.40. Found: C, 55.2; H, 4.31; N, 1.51. Pertinent ir bands (cm^{-1}): 1602 (m), 1202 (vs), 1052 (s), 585 (s), 332 (m). *Anal.* Calcd for the benzonitrile adduct $C_6H_5SO_2IrCl_2[P(C_6H_5)_3]_2 \cdot C_6H_5CN$: C, 57.0; H, 3.91; N, 1.36. Found: C, 57.7; H, 3.92; N, 1.36. Pertinent ir bands (cm^{-1}): 2280 (w), 1212 (s), 1060 (m), 587 (s), 340 (w).

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[19] M. Kubota, D. N. Blake, and S. A. Smith, *Inorg. Chem.*, **10**, 1430 (1971).

Anal. Calcd for the acetonitrile adduct $C_6H_5SO_2IrCl_2[P(C_6H_5)_3]_2 \cdot CH_3CN$: C, 54.5; H, 3.95; N, 1.44. Found: C, 52.1; H, 3.84; N, 1.28. Pertinent ir bands (cm^{-1}): 2322 (w), 1208 (s), 1050 (m), 588 (s), 330 (w). The addition of other Lewis bases such as diethyl sulfide, triphenylphosphine, and triphenyl phosphite was also observed to discolor the brown solutions of the sulfinatoiridium complex **4**.

Alkyl– or Aryl–Sulfur Dioxide Complexes (7).—The sulfinato complex **4** (100 mg) was refluxed in 10 ml of benzene until the brown color faded to a pale yellow. A small amount of methanol was added to accelerate the slower reactions. A solution of 10 ml of dichloromethane and 5 ml of methanol was also found to be a suitable solvent for these reactions. The solvent was stripped under reduced pressure and the product was recrystallized from benzene–methanol or dichloromethane–methanol.

Alkyl- or Aryldichlorocarbonylbis(triphenylphosphine)iridium(III) (8).—A solution of the sulfur dioxide complex **7** (100 mg) in 30 ml of dichloromethane or benzene was treated with carbon monoxide at 20 psi for 24 hr. The solvent was removed under reduced pressure and the product was recrystallized from dichloromethane–methanol.

Kinetic Measurements.—The rates of the rearrangement of the sulfinato complexes **4** to the sulfur dioxide complexes **7** were followed spectrophotometrically with a Cary 16 spectrometer with a thermostated cell compartment. The rates of disappearance of the sulfinato complexes $RSO_2IrCl_2[P(C_6H_5)_3]_2$ **4** were monitored by recording the absorbances at the following wavelengths for various R: CH_3, 468 nm; C_2H_5, 471 nm; *n*-C_3H_7, 473 nm; *p*-$CH_3OC_6H_4$, 480 nm; *p*-$CH_3C_6H_4$, 493 nm; C_6H_5, 478 nm; *p*-ClC_6H_4, 482 nm; *p*-$O_2NC_4H_6$, 483 nm.

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Oxidative Addition Reactions of the Dihalodicarbonyliridate(I) Ions

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Oxidative addition reactions of the $Ir(CO)_2X_2^-$ ions with halogens, alkyl halides, acetyl halides, mercuric halides, hydriodic acid, and tetracyanoethylene are described. Two isomers of the $Ir(CO)_2Br_2I_2^-$ ion have been prepared, one by oxidative addition of iodine to $Ir(CO)_2Br_2^-$ and the other by addition of bromine to the $Ir(CO)_2I_2^-$ ion. Infrared data for the new complexes are presented.

Introduction

Studies on oxidative addition reactions of d^8 iridium(I) have been concentrated almost exclusively on iridium–phosphine complexes.[1] However, in many ways the $Ir(CO)_2X_2^-$ ions may be considered as more fundamental iridium(I) species insofar as they are the ultimate species formed in a system Ir–halide–CO in a hydroxy solvent[2] and are presently used as intermediates in routes to iridium(I)–phosphine complexes.[3] We report here the results of a study of the oxidative addition reactions of the $Ir(CO)_2X_2^-$ ions.

Experimental Section

Infrared spectra were obtained with a Beckman IR-12 spectrophotometer. Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer.

Preparation of Compounds. Tetraphenylarsonium Dihalodicarbonyliridate(I).—These compounds were prepared as described elsewhere.[2]

Tetraphenylarsonium Tetrahalodicarbonyliridate(III).—These compounds were prepared by the general method of treating the salt of the $Ir(CO)_2X_2^-$ ion dissolved in chloroform with a slight excess of the corresponding halogen and then precipitating the iridium(III) species by addition of excess diethyl ether; yield 80–90%. *Anal.* Calcd for $C_{26}H_{20}AsCl_4IrO_2$ ($[(C_6H_5)_4As][Ir(CO)_2Cl_4]$, pale yellow crystals): C, 40.36; H, 2.59; Cl, 18.34. Found: C, 39.79; H, 2.53; Cl, 18.66. Calcd for $C_{26}H_{20}AsBr_4IrO_2$ ($[(C_6H_5)_4As][Ir(CO)_2Br]_4$, lemon yellow crystals): C, 32.82; H, 2.10; Br, 33.62. Found: C, 32.60; H, 1.92; Br, 33.27. Calcd for $C_{26}H_{20}AsI_4IrO_2$ ($[(C_6H_5)_4As][Ir(CO)_2I_4]$, dark brown crystals): C, 27.40; H, 1.76; I, 44.58. Found: C, 27.88; H, 1.91; I, 44.13.

Tetraethylammonium Dibromodiiododicarbonyliridate(III) (Isomer A).—$[(C_6H_5)_4As][Ir(CO)_2Br_2]$ (0.5 g) and $(C_2H_5)_4NBr$ (0.15 g) were dissolved in chloroform (3 ml). Iodine (0.16 g) was dissolved in chloroform (~4 ml) and added to the above solution. Orange crystals rapidly separated and were filtered off, washed with a small volume of chloroform and then diethyl ether, and air-dried; yield 0.33 g. *Anal.* Calcd for $C_{10}H_{20}IrBr_2I_2NO_2$: C, 15.15; H, 2.52; Br, 20.20; I, 32.05. Found: C, 15.33; H, 2.47; Br, 20.19; I, 32.07.

Tetraethylammonium Dibromodiiododicarbonyliridate(III) (Isomer B).—$[(C_6H_5)_4As][Ir(CO)_2I_2]$ (0.5 g) and $(C_2H_5)_4NI$ (0.13 g) were dissolved in chloroform (1.5 ml). One milliliter of a 5% solution of bromine in chloroform was added with stirring. [Note: it is necessary to use a deficiency of bromine in this experiment (~75% of molar requirement).] A dark orange solid precipitated and was filtered off, washed with a small amount of chloroform, and air-dried; yield 0.2 g. *Anal.* Calcd for $C_{10}H_{20}IrBr_2I_2NO_2$: C, 15.15; H, 2.52; Br, 20.20; I, 32.05. Found: C, 15.10; H, 2.44; Br, 20.70; I, 32.55.

Tetraphenylarsonium Triiododicarbonylmethyliridate(III).—$[(C_6H_5)_4As][Ir(CO)_2I_2]$ (0.40 g) was dissolved in methyl iodide and then the solution was evaporated to dryness. The resulting yellow solid was collected and dried *in vacuo;* yield 0.42 g; mp 123°. *Anal.* Calcd for $C_{27}H_{23}AsI_3IrO_2$: C, 31.54; H, 2.24; I, 37.06. Found: C, 32.20; H, 2.26; I, 36.78.

Tetraphenylarsonium Dichloroiododicarbonylmethyliridate(III).—$[(C_6H_5)_4As][Ir(CO)_2Cl_2]$ (0.5 g) was dissolved in methyl iodide and then the solution was evaporated to dryness. The resulting solid was collected and dried in air; yield 0.53 g. *Anal.* Calcd for $C_{27}H_{23}AsCl_2IIrO_2$: C, 38.39; H, 2.73; Cl, 8.40; I, 15.04. Found: C, 38.19; H, 2.64; Cl, 8.68; I, 15.51.

Tetraphenylarsonium Trichlorodicarbonylallyliridate(III).—$[(C_6H_5)_4As][Ir(CO)_2Cl_2]$ (0.5 g) was dissolved in chloroform (5 ml) and excess allyl chloride (~1 ml) was added. After 2 min excess diethyl ether was added to the mixture. The white precipitate which formed was separated and recrystallized from

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