ing the position of the ring, the crystal structure results may not represent the preferred ring orientation for the compound in solution. As a consequence spectral data taken in solution may not be compatible with data in the solid state.

An X-ray crystal structure of selected tungsten compounds would be useful in checking some of the ideas expressed in this paper. In addition, the assumption that molybdenum and tungsten atoms will have equivalent electronic environments for identical ligands is not necessarily valid. In fact, recent evidence indicates that tungsten and molybdenum are not stereochemically or electronically equivalent since it has been shown that under the same experimental conditions the synthesis of $Mo(CO)_3L_3$ and $W(CO)_3L_3$ (where L = tris(3,3-dimethylbutynyl)phosphine) gives the mer isomer for the tungsten compound and gives the fac isomer for the molybdenum compound.[23]

An alternative method for assigning stereochemistry in these compounds is the use of their carbon-13 nmr spectra. Future work using this technique will be forthcoming in a subsequent paper.

Registry No. Triphenyl phosphite, 101-02-0; $[C_5H_5W(CO)_3]_2Hg$, 12289-72-4; $[C_5H_5W(CO)_2P(OC_6H_5)_3]_2Hg$, 37188-06-0; $C_5H_5W(CO)_2P(CH_3)_3I$, 37449-00-6; $C_5H_5W(CO)_2P(CH_3)_2(C_6H_5)I$, 37449-01-7; $C_5H_5W(CO)_2PCH_3(C_6H_5)_2I$, 37474-46-7; $C_5H_5W(CO)_2P(CH_3)_3Sn(CH_3)_3$, 37583-10-1; $C_5H_5W(CO)_2P(CH_3)_2(C_6H_5)Sn(CH_3)_3$, 37583-11-2; $C_5H_5W(CO)_2PCH_3(C_6H_5)_2Sn(CH_3)_3$, 37583-13-4; $C_5H_5W(CO)_2P(C_6H_5)_3Sn(CH_3)_3$, 37583-12-3; $C_5H_5W(CO)_2P(OCH_3)_3Sn(CH_3)_3$, 37583-14-5; $C_5H_5W(CO)_2P(OC_6H_5)_3Sn(CH_3)_3$, 37583-15-6; $C_5H_5W(CO)_3I$, 31870-69-6; $P(CH_3)_3$, 594-09-2; $P(CH_3)_2(C_6H_5)$, 672-66-2; $PCH_3(C_6H_5)_2$, 1486-28-8; $P(C_6H_5)_3$, 603-35-0; $C_5H_5W(CO)_2P(C_6H_5)_3I$, 37474-48-9; $C_5H_5W(CO)_3Sn(CH_3)_3$, 12093-29-7.

Acknowledgments. The authors thank the National Science Foundation for financial support in the form of a Science Faculty Fellowship, Grant No. 61200, for C. D. Turnipseed. The authors acknowledge the assistance of Dr. David Thoennes in the recording of the phosphorus-31 and carbon-13 nmr spectra and for helpful discussions. The XL-100 spectrometer was purchased from funds provided by NSF Grants GP-10293 and GP-18383. We also thank Ron Aerni for preliminary investigation of the synthetic procedures used in preparing these compounds.

[23] A. D. George, T. A. George, and D. O. Wiebers, to be submitted for publication.

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Synthesis and Characterization of Sulfenato and Alkoxysulfenato Complexes of Iridium(III)

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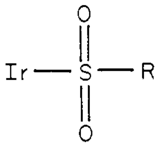
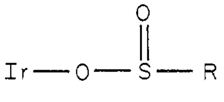
The preparation of what we believe to be the first sulfenato and alkoxysulfenato complexes with a transition metal is reported. The sulfenato complexes $IrCl_2(CH_3SO)(CO)L_2$ ($L = P(C_6H_5)_3$ or $P(C_6H_5)_2CH_3$) were prepared by the reaction of $CH_3S(O)Cl$ with $IrCl(CO)L_2$. Alkoxysulfenato complexes of the type $IrCl_2(ROSO)(CO)L_2$ were prepared by treating $ROS(O)Cl$ with $IrCl(CO)L_2$ ($L = P(C_6H_5)_3$, $R = CH_3$ or C_2H_5; $L = P(C_6H_5)_2CH_3$, $R = CH_3$, C_2H_5, or $i\text{-}C_3H_7$; $L = P(CH_3)_2C_6H_5$, $R = CH_3$). These alkoxysulfenato compounds do not rearrange to yield sulfinato complexes even when refluxed in toluene for 1 hr. The preparation of the new sulfinato complex $IrCl_2(CH_3SO_2)(CO)[P(C_6H_5)_2CH_3]_2$ and the new thio complexes $IrCl_2(p\text{-}CH_3C_6H_4S)(CO)L_2$ ($L = P(C_6H_5)_3$ or $P(C_6H_5)_2CH_3$) is also reported. The infrared and ^1H nmr spectral data indicate that the phosphine ligands are trans to each other, the chlorine atoms are mutually cis, and the sulfur atom is bonded directly to the metal in all of these compounds.

Introduction

Various sulfinato complexes of iridium(III) have been prepared by the oxidative addition of sulfonyl chlorides to square-planar iridium(I) compounds.[1,2] In these compounds, the sulfinato group is bonded to the metal through the sulfur atom (configuration I); however, iridium to oxygen bonded sulfinates are also known (II).[3] The oxidative addition of sulfenyl chlorides to square-planar iridium(I) (III) has been reported,[4] but the experimental information on these compounds has not been published.


$\mathrm{Ir{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}R}$

I

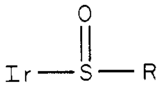

$\mathrm{Ir{-}O{-}\overset{\overset{O}{\|}}{S}{-}R}$

II

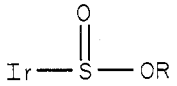
$\mathrm{Ir{-}S{-}R}$

III

This paper reports the first preparation of sulfenato (IV) and alkoxysulfenato (V) complexes of iridium(III). The preparation of a new sulfinato and new thio complexes is also reported.


$\mathrm{Ir{-}\overset{\overset{O}{\|}}{S}{-}R}$

IV


$\mathrm{Ir{-}\overset{\overset{O}{\|}}{S}{-}OR}$

V

Experimental Section

Physical Measurements. The infrared spectra (Tables I and II) were obtained on a Perkin-Elmer Model 621 grating spectrophotometer. The spectra of the metal complexes were taken in potassium bromide pellets (4000–400 cm^{-1}) and in cesium iodide

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(1) J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, **88**, 180 (1966).

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Table I. Infrared Data for $IrCl_2A(CO)L_2$ (cm^{-1})

L	A	ν(C≡O)[a]	ν(S=O)[a]	ν(C–O)[a]	ν(S–O)[a]	ν(IrCl)[b]	
$P(C_6H_5)CH_3$	$CH_3S(O)_2$	2080	1228 asym 1076 sym			318	272
$P(C_6H_5)_2CH_3$	$CH_3OS(O)$	2072	1085	987	643	308	261
$P(C_6H_5)_2CH_3$	$C_2H_5OS(O)$	2075	1078	1011	864	310	259
$P(C_6H_5)_2CH_3$	i-$C_3H_7OS(O)$	2073	1078	900	818	309	260
$P(C_6H_5)_2CH_3$	$CH_3S(O)$	2060	1004			318	257
$P(C_6H_5)_2CH_3$	p-$CH_3C_6H_4S$	2056				302	284
$P(CH_3)_2C_6H_5$	$CH_3OS(O)$	2063	1081	977	645	317	268
$P(C_6H_5)_3$	$CH_3OS(O)$	2080	1085	983	652	306	258
$P(C_6H_5)_3$	$C_2H_5OS(O)$	2080	1085	1014	867	307	257
$P(C_6H_5)_3$	$CH_3S(O)$	2067	1013			316	257
$P(C_6H_5)_3$	p-$CH_3C_6H_4S$	2060				308	287

[a] KBr pellet. [b] CsI pellet.

Table II. Infrared Data for Sulfur Compounds (cm^{-1})[a]

	ν(S=O)	ν(C–O)	ν(S–O)
$CH_3S(O)_2Cl$[b]	1382 vs, asym 1179 vs, sym		
$CH_3OS(O)Cl$[c]	1224 vs	955 vs	725 s, 686 m
$C_2H_5OS(O)Cl$[c]	1220 vs	892 vs	732 s, 717 sh
i-$C_3H_7OS(O)Cl$[c]	1220 vs	892 vs, 878 vs	745 m, 720 s
$CH_3S(O)Cl$[b]	1160 vs		

[a] Key: vs, very strong; s, strong; m, medium; sh, shoulder. [b] CCl_4 solution. [c] CS_2 solution.

pellets (400–200 cm^{-1}). Proton nmr spectra (Table III) were obtained by means of a Varian Associates Model A-60 spectrometer, using tetramethylsilane as an internal standard. Molecular weight data were taken in benzene or dichloromethane solutions using a Hewlett-Packard Model 302B vapor pressure osmometer. Mass spectra were taken using a Perkin-Elmer Hitachi RMU-6D double-focusing spectrometer at 70-eV ionizing energy. A Cahn 1-g electrobalance was used to determine weight losses for $IrCl_2(CH_3SO)(CO)[P(C_6H_5)_3]_2 \cdot 0.5CH_2Cl_2$ and $IrCl_2(p\text{-}CH_3C_6H_4S)(CO)[P(C_6H_5)_3]_2 \cdot 0.5CH_2Cl_2$ after they were heated on a Perkin-Elmer DSC B1. Melting points were determined in sealed capillary tubes using a Mel-Temp melting point apparatus and are uncorrected. Microanalyses (Table IV) were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Materials. Chlorocarbonylbis(triphenylphosphine)iridium(I) ($IrCl(CO)[P(C_6H_5)_3]_2$) was purchased from Alfa Chemical Co. Methanesulfonyl chloride was purchased from Eastman Organic Chemicals. Chlorocarbonylbis(diphenylmethylphosphine)iridium(I) ($IrCl(CO)[P(C_6H_5)_2CH_3]_2$),[5] methyl chlorosulfinate ($CH_3OS(O)Cl$),[6] ethyl chlorosulfinate ($C_2H_5OS(O)Cl$),[6] isopropyl chlorosulfinate (i-$C_3H_7OS(O)Cl$),[6] p-toluenesulfinyl chloride (p-$CH_3C_6H_4S(O)Cl$),[7] benzenesulfinyl chloride ($C_6H_5S(O)Cl$),[7] bis(methylsulfinato)zinc(II) dihydrate [$(CH_3SO_2)_2Zn \cdot 2H_2O$],[8] and p-toluenesulfenyl chloride (p-$CH_3C_6H_4SCl$)[9] were prepared by published methods. Chlorocarbonylbis(dimethylphenylphosphine)iridium(I) ($IrCl(CO)[P(CH_3)_2C_6H_5]_2$) was prepared by the displacement of $P(C_6H_5)_3$ from $IrCl(CO)[P(C_6H_5)_3]_2$ with $P(CH_3)_2C_6H_5$[10] and identified by published infrared and proton nmr spectroscopy.[11] Methanesulfinyl chloride was prepared by the dropwise addition of 14.4 g (0.12 mol) of thionyl chloride to a magnetically stirred mixture of 7.2 g (0.026 mol) of $(CH_3SO_2)_2Zn \cdot 2H_2O$ in 100 ml of diethyl ether at 0°. The sulfur dioxide and hydrogen chloride formed were swept out of the reaction vessel by a slow stream of nitrogen. After addition of the thionyl chloride was completed, the reaction vessel was warmed to room temperature and stirred for 1 hr more. The ether was distilled off at atmospheric pressure using a simple distillation head. When the temperature reached 40°, the distillation head was replaced by a Vigreux column and the residue distilled at a reduced pressure of 40 Torr. The fraction distilling at 54–55° was collected (4.0 g, 73%). The product was identified by previously published boiling point,[12] infrared,[13] and nmr data.[14] All solvents were reagent grade and were deoxygenated by bubbling nitrogen through for at least 15 min before use. Benzene and heptane were distilled from calcium hydride and dichloromethane was distilled from phosphorus pentoxide. All reactions and recrystallizations involving the metal complexes were carried out under a nitrogen atmosphere.

General Procedure. All of the oxidative addition reactions were carried out by dissolving the iridium(I) complex in benzene and then freezing the solution by putting the reaction vessel in a 2-propanol–Dry Ice bath. The sulfur compound, in benzene, was then added dropwise and frozen on top of the metal–benzene mixture. This mixture was allowed to warm slowly to room temperature with stirring and then stirred for an additional 15–30 min. The solvent was then removed under vacuum (0.01 Torr) at room temperature to yield the crude product.

Dichloro(S-methylsulfinato)carbonylbis(diphenylmethylphosphine)iridium(III), $IrCl_2(CH_3SO_2)(CO)[P(C_6H_5)_2CH_3]_2$. A mixture of 0.16 g (0.24 mmol) of $IrCl(CO)[P(C_6H_5)_2CH_3]_2$ in 10 ml of benzene was treated with 0.032 g (0.28 mmol) of $CH_3S(O)_2Cl$ in 8 ml of benzene by the given procedure. The crude product was dissolved in 10 ml of benzene and filtered. To the filtrate, 70 ml of heptane was added and the volume of the solution was reduced to 30 ml under vacuum. Filtration of the mixture yielded the tan product.

The following compounds were prepared similarly.

Dichloro(S-methoxysulfenato)carbonylbis(diphenylmethylphosphine)iridium(III), $IrCl_2(CH_3OSO)(CO)[P(C_6H_5)_2CH_3]_2$. The yellow product was obtained upon reducing the volume of a benzene–methanol (4:5) solution containing the crude material.

Dichloro(S-ethoxysulfenato)carbonylbis(diphenylmethylphosphine)iridium(III), $IrCl_2(C_2H_5OSO)(CO)[P(C_6H_5)_2CH_3]_2$. The yellow product was obtained upon reducing the volume of a benzene–methanol (1:5) solution containing the crude material.

Dichloro(S-isopropoxysulfenato)carbonylbis(diphenylmethylphosphine)iridium(III), $IrCl_2(i\text{-}C_3H_7OSO)(CO)[P(C_6H_5)_2CH_3]_2$. Addition of methanol to a benzene solution of the crude material yielded the yellow product.

Dichloro(S-methylsulfenato)carbonylbis(diphenylmethylphosphine)iridium(III), $IrCl_2(CH_3SO)(CO)[P(C_6H_5)_2CH_3]_2$. The crude product was recrystallized twice by dissolving it in benzene and then adding heptane to yield the yellow product.

Dichloro(p-tolylthio)carbonylbis(diphenylmethylphosphine)iridium(III), $IrCl_2(p\text{-}CH_3C_6H_4S)(CO)[P(C_6H_5)_2CH_3]_2$. The yellow product was obtained upon addition of heptane to a benzene solution of the crude material.

Dichloro(S-methoxysulfenato)carbonylbis(dimethylphosphine)iridium(III), $IrCl_2(CH_3OSO)(CO)[P(CH_3)_2C_6H_5]_2$. The yellow product was obtained upon addition of heptane to a benzene solution of the crude material.

Dichloro(S-methoxysulfenato)carbonylbis(triphenylphosphine)iridium(III), $IrCl_2(CH_3OSO)(CO)[P(C_6H_5)_3]_2$. The light yellow product was obtained upon reducing the volume of a benzene–heptane (2:1) solution containing the crude material.

Dichloro(S-ethoxysulfenato)carbonylbis(triphenylphosphine)-

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Table III. ${}^1H$ Nmr Data (τ)[a]

	p-CH_3	Other	Assignment
$CH_3S(O)_2Cl$[b]		6.35 s	SCH_3
$CH_3OS(O)Cl$[b]		5.95 s	OCH_3
$CH_3CH_2OS(O)Cl$[b]		5.55 q, 5.58 q	OCH_2C
		8.54 t	$OCCH_3$
$(CH_3)_2CHOS(O)Cl$[c]		4.92 sp	$OCH(C)_2$
		8.78 d, 8.84 d	$OC(CH_3)_2$
$CH_3S(O)Cl$[b]		6.66 s	SCH_3
$CH_3C_6H_4SCl$[b]		7.62 s	CCH_3
$IrCl_2(CH_3SO_2)(CO)[P(C_6H_5)_2CH_3]_2$[d]	7.52 t	7.82 s	SCH_3
$IrCl_2(CH_3OSO)(CO)[P(C_6H_5)_2CH_3]_2$[d]	7.53 t	7.08 s	OCH_3
$IrCl_2(C_2H_5OSO)(CO)[P(C_6H_5)_2CH_3]_2$[d]	7.53 t	6.33 m	OCH_2C
		9.17 t	$OCCH_3$
$IrCl_2(i\text{-}C_3H_7OSO)(CO)[P(C_6H_5)_2CH_3]_2$[d]	7.57 t	5.98 m	$OCH(C)_2$
		8.93 d, 9.52 d	$OC(CH_3)_2$
$IrCl_2(CH_3SO)(CO)[P(C_6H_5)_2CH_3]_2$[d]	7.45 t	8.43 s	SCH_3
$IrCl_2(p\text{-}CH_3C_6H_4S)(CO)[P(C_6H_5)_2CH_3]_2$[e]	7.63 t	8.03 s	CCH_3
$IrCl_2(CH_3OSO)(CO)[P(CH_3)_2C_6H_5]_2$[e]	8.09 tt	7.03 s	OCH_3

[a] Relative to tetramethylsilane. Key: s, singlet; d, doublet; t, triplet; tt, overlapping triplets; q, quartet; sp, septuplet; m, multiplet. [b] CCl_4 solution. [c] Neat liquid. [d] $CDCl_3$. [e] C_6D_6.

Table IV. Analytical Data for Complexes

$IrCl_2A(CO)L_2$		% C		% H		Mol wt			
L	A	Calcd	Found	Calcd	Found	Calcd	Found	Mp,[a] °C	% yield
$P(C_6H_5)_2CH_3$	$CH_3S(O)_2$	43.63	44.02	3.78	3.96			232–234	85
$P(C_6H_5)_2CH_3$	$CH_3OS(O)$[b]	43.63	43.75	3.78	3.83	771	830[c]	183–184	65
$P(C_6H_5)_2CH_3$	$C_2H_5OS(O)$	44.39	44.63	3.98	4.05			168–170	79
$P(C_6H_5)_2CH_3$	$i\text{-}C_3H_7OS(O)$	45.11	44.96	4.16	4.18			139–141	65
$P(C_6H_5)_2CH_3$	$CH_3S(O)$	44.56	44.46	3.87	3.94	755	742[c]	161–164	48
$P(C_6H_5)_2CH_3$	$p\text{-}CH_3C_6H_4S$	50.12	49.95	4.09	4.27	815	750[c]	83–85	74
$P(CH_3)_2C_6H_5$	$CH_3OS(O)$	33.43	33.34	3.89	3.87	646	640[c]	61–64	67
$P(C_6H_5)_3$	$CH_3OS(O)$	51.01	51.88	3.72	3.75	894	1036[d]	229	49
$P(C_6H_5)_3$	$C_2H_5OS(O)$	51.54	51.85	3.82	4.04	908	830[d]	136–138	70
$P(C_6H_5)_3$	$CH_3S(O)$	50.19[e]	49.80	3.72[e]	3.62			169–172	55
$P(C_6H_5)_3$	$p\text{-}CH_3C_6H_4S$	54.47[e]	54.65	3.90[e]	3.89			213–215	73

[a] Decomposition temperature. [b] Cl analysis (%): calcd, 9.03; found, 9.20. [c] Osmometry in CH_2Cl_2 solution. [d] Osmometry in C_6H_6 solution. [e] Solvate of 0.5 CH_2Cl_2.

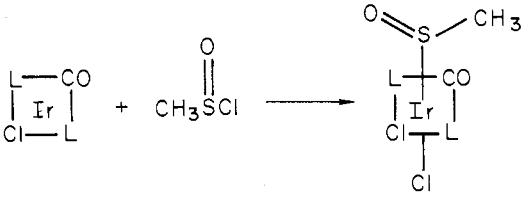
iridium(III), $IrCl_2(C_2H_5OSO)(CO)[P(C_6H_5)_3]_2$. Addition of heptane to a benzene solution of the crude material yielded the light yellow product.

Dichloro(*S*-methylsulfenato)carbonylbis(triphenylphosphine)-iridium(III), $IrCl_2(CH_3SO)(CO)[P(C_6H_5)_3]_2$. The bright yellow product was obtained upon reducing the volume of a dichloromethane–heptane (1:4) solution containing the crude material. The compound crystallized with 0.5 mol of CH_2Cl_2/mol of product.

Dichloro(*p*-tolylthio)carbonylbis(triphenylphosphine)iridium(III), $IrCl_2(p\text{-}CH_3C_6H_4S)(CO)[P(C_6H_5)_3]_2$. The orange product was obtained upon reducing the volume of a dichloromethane–heptane (1:3) solution containing the crude material. The compound crystallized with 0.5 mol of CH_2Cl_2/mol of product.

Results and Discussion

Sulfenato Complexes. Methanesulfinyl chloride reacts with $IrCl(CO)L_2$ ($L = P(C_6H_5)_3$ or $P(C_6H_5)_2CH_3$) to yield $IrCl_2(CH_3SO)(CO)L_2$ (eq 1). A new strong band in the infrared spectrum near 1000 cm^{-1} (Table I) is assigned to the sulfur–oxygen stretching mode. The S–O stretching frequency is only 50 cm^{-1} lower than that found for organic sulfoxides[15] and is not nearly so low as the 855 cm^{-1} found for the *O*-sulfinates where the oxygen is bonded to both the sulfur and the iridium atoms (II).[3] Since the S–O stretching frequency is lower in $CH_3S(O)Cl$ than in $CH_3S(O)_2Cl$ (Table II) and it is lower in organic sulfoxides than in organic sulfones,[16] one would expect an oxygen-bonded complex formed with CH_3SO to have a $\nu_{as}(SOIr)$ frequency lower than 855 cm^{-1}. Thus, the complex must be bonded through the sulfur and not the oxygen (IV). The ${}^1H$ nmr spectrum (Table III) of $IrCl_2(CH_3SO)(CO)[P(C_6H_5)_2CH_3]_2$ also supports this structure as the value of τ 8.43 is too high for the methyl group to be bonded to the oxygen and too low for it to be bonded to the metal. The protons on methyl groups bonded directly to iridium resonate at τ 9-10[17] while the methoxy protons in this study resonate below τ 7.1.



(1)

VI

The stereochemistry of the $IrCl_2(CH_3SO)(CO)[P(C_6H_5)_2CH_3]_2$ complex can be determined from ${}^1H$ nmr and infrared spectral data. The ${}^1H$ nmr spectrum of the complex shows a triplet at τ 7.53 which is due to the methyl protons on trans phosphine ligands.[18] Proton nmr spectra could not be obtained for the triphenylphosphine complex due to its low solubility. However, we find that the infrared band at 1572 cm^{-1} is more intense than the band at 1586 cm^{-1} which Kubota has suggested may indicate a trans arrangement.[19] The ir spectra (400-200 cm^{-1}) show two absorptions attrib-

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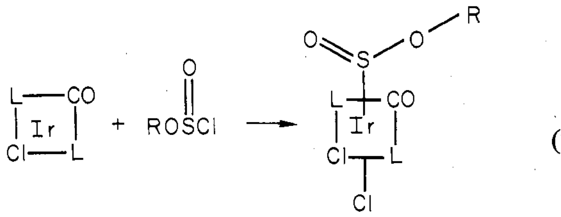
(19) M. Kubota and B. Loeffler, *Inorg. Chem.*, 11, 469 (1972).

utable to iridium-chlorine stretching frequencies (Table I). The higher frequency (316-318 cm^{-1}) is associated with the chlorine trans to the carbonyl[17] and the lower frequency (257 cm^{-1}) is associated with the chlorine trans to the sulfur-containing ligand (VI).[2]

Alkoxysulfenato Complexes. Alkyl chlorosulfinates ($\mathrm{ROS(O)Cl}$) add oxidatively to $\mathrm{IrCl(CO)L_2}$ ($\mathrm{L = P(C_6H_5)_3}$, $\mathrm{R = CH_3}$ or $\mathrm{C_2H_5}$; $\mathrm{L = P(C_6H_5)_2CH_3}$, $\mathrm{R = CH_3, C_2H_5}$, or i-$\mathrm{C_3H_7}$; $\mathrm{L = P(CH_3)_2C_6H_5}$, $\mathrm{R = CH_3}$) to yield $\mathrm{IrCl_2(ROSO)(CO)L_2}$ (eq 2). A strong band in the infrared spectrum at approximately 1080 cm^{-1} (Table I) is assigned to a terminal oxygen to sulfur stretching frequency and is in close agreement to the value of 1085 cm^{-1} found for *O*-sulfinato complexes (II).[3] We, however, do not find any new band in the 800-900 cm^{-1} range which can be attributed to a S-O-Ir stretching frequency for an *O*-sulfinato complex. Thus, there is not any rearrangement of the ROSO groups to yield sulfinato complexes. The assignment of additional bands to carbon-oxygen and sulfur-oxygen stretching modes (Table I) supports an *S*-alkoxysulfenato complex being formed (V).



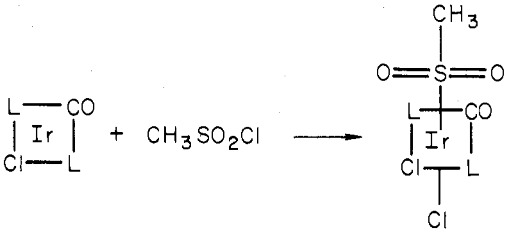
(2)

VII

The ^{1}H nmr spectral data also indicate that the R group is still bonded to the oxygen as shown by the greater deshielding of the methoxysulfenato protons in $\mathrm{IrCl_2(CH_3OSO)(CO)[P(C_6H_5)_2CH_3]_2}$ (τ 7.08) as compared to the methylsulfinato protons in $\mathrm{IrCl_2(CH_3SO_2)(CO)[P(C_6H_5)_2CH_3]_2}$ which resonate at τ 7.82. Different chemical shifts are found for each of the two isopropoxy methyl groups in $\mathrm{IrCl_2}$(i-$\mathrm{C_3H_7OSO)(CO)[P(C_6H_5)_2CH_3]_2}$ and in i-$\mathrm{C_3H_7OS(O)Cl}$ (Table IV). The different chemical shifts for the methyl groups on the same central carbon are probably due to the presence of the asymmetric sulfur atom.[20] This effect is also observed for the methylene protons in $\mathrm{CH_3CH_2OS(O)Cl}$. The methylene protons in $\mathrm{IrCl_2(C_2H_5OSO)(CO)[P(C_6H_5)_2CH_3]_2}$ give a broad multiplet which is unresolved. All of the alkoxysulfenato compounds which have methyl-containing phosphine ligands give rise to triplets in the ^{1}H nmr spectra indicating trans phosphines. We also find the infrared band at 1572 cm^{-1} to be more intense than the band at 1586 cm^{-1} for the triphenylphosphine complexes which may again indicate trans phosphines.[19] The ir spectra (400-200 cm^{-1}) again show two bands which can be assigned to iridium-chlorine stretching frequencies where the higher band (306-317 cm^{-1}) is associated with the chlorine trans to the carbonyl and the lower band (257-268 cm^{-1}) is associated with the chlorine trans to the sulfur atom. This shows that these complexes have the configuration VII.

When a 0.01 *M* toluene solution of $\mathrm{IrCl_2(ROSO)(CO)L_2}$ ($\mathrm{L = P(C_6H_5)_3}$, $\mathrm{R = CH_3}$ or $\mathrm{C_2H_5}$; $\mathrm{L = P(C_6H_5)_2CH_3}$, $\mathrm{R = CH_3}$ or i-$\mathrm{C_3H_7}$) is refluxed for 1 hr, vacuum evaporation of the solvent yields various mixtures of $\mathrm{IrCl(CO)L_2}$, $\mathrm{IrCl_2H(CO)L_2}$, $\mathrm{IrCl_3(CO)L_2}$, and the starting material $\mathrm{IrCl_2(ROSO)(CO)L_2}$. Infrared spectra of the resulting products do not reveal any band in the 1150-1250-cm^{-1} region which can be assigned to the $\mathrm{-SO_2-}$ asymmetric stretching mode found in sulfinato complexes.[1,2] This indicates that these alkoxysulfenato complexes do not rearrange to form sulfinato complexes under these conditions. This is in agreement with Wojcicki's prediction that alkoxysulfenato complexes are not intermediates in sulfur dioxide insertion reactions.[21]

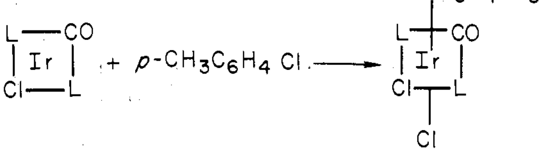
Dichloro(*S*-methylsulfinato)carbonylbis(diphenylmethylphosphine)iridium(III). Methanesulfonyl chloride adds oxidatively to $\mathrm{IrCl(CO)[P(C_6H_5)_2CH_3]_2}$ to yield $\mathrm{IrCl_2(CH_3SO_2)(CO)[P(C_6H_5)_2CH_3]_2}$ (eq 3). Two new bands in the ir spectrum (Table I) are assigned to the asymmetric and symmetric stretching frequencies of the $\mathrm{-SO_2-}$ group indicating the metal is bonded to the sulfur atom as in $\mathrm{IrCl_2(CH_3SO_2)(CO)[P(C_6H_5)_3]_2}$[1] and $\mathrm{IrCl_2(CH_3SO_2)(CO)[P(CH_3)_2C_6H_5]_2}$.[2] The ^{1}H nmr spectrum gives a triplet due to the methyl groups on the phosphine ligands which indicates again that the phosphines are trans to each other. The singlet at τ 7.82 is assigned to the methyl group attached directly to the sulfur atom. The ir spectrum (400-200 cm^{-1}) shows two iridium-chlorine stretching frequencies and as before, the higher one (318 cm^{-1}) is associated with the chlorine trans to the carbonyl group and the lower frequency (272 cm^{-1}) is associated with the chlorine trans to the sulfur atom (VIII).



(3)

VIII

Thio Complexes. The oxidative addition of p-$\mathrm{CH_3C_6H_4SCl}$ to $\mathrm{IrCl(CO)L_2}$ ($\mathrm{L = P(C_6H_5)_3}$ or $\mathrm{P(C_6H_5)_2CH_3}$) yields $\mathrm{IrCl_2}$(p-$\mathrm{CH_3C_6H_4S)(CO)L_2}$ (eq 4). The increase in carbonyl stretching frequency from 1960 cm^{-1} in the iridium(I) complexes to approximately 2060 cm^{-1} (Table I) indicates the formation of an iridium(III) compound. The formation of these thio complexes is supported by the elemental analyses (Table IV) and the ^{1}H nmr spectrum (Table III) of the compound where $\mathrm{L = P(C_6H_5)_2CH_3}$ which gives a singlet at τ 8.03 that is assigned to the methyl group on the p-tolyl group. The ^{1}H nmr spectrum of $\mathrm{IrCl_2}$(p-$\mathrm{CH_3C_6H_4S)(CO)[P(C_6H_5)_2CH_3]_2}$ gives a triplet at τ 7.63 again indicating trans phosphines. The infrared spectrum of the triphenylphosphine complex may also indicate a trans arrangement for the phosphines (the band at 1572 cm^{-1} is more intense than the band at 1586 cm^{-1}).[19] The ir spectra (400-200 cm^{-1}) show two iridium-chlorine stretching frequencies (Table I) with the higher band associated with the chlorine trans to the carbonyl and the lower band associated with the chlorine trans to the sulfur atom (IX).



(4)

IX

The presence of dichloromethane in the crystalline $\mathrm{IrCl_2}$-

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(20) J. W. Wilt and W. J. Wagner, *Chem. Ind.* (*London*), 1389 (1964).

(21) S. E. Jacobson, P. Reich-Rohrwig, and A. Wojcicki, *Chem. Commun.*, 1526 (1971).

$(CH_3SO)(CO)[P(C_6H_5)_3]_2$ and $IrCl_2(p\text{-}CH_3C_6H_4S)(CO)[P(C_6H_5)_3]_2$ complexes is shown by inletting a solid sample into the mass spectrometer and slowly raising the temperature of the sample. At slightly above 100°, both samples give rise to *m/e* peaks characteristic of dichloromethane. The heating of 2.92 mg of $IrCl_2(CH_3SO)(CO)[P(C_6H_5)_3]_2$ to 150° in a vented capsule in a differential scanning calorimeter does not show a transition point but does result in a 0.14-mg weight loss. This corresponds to a 4.8% weight loss (calcd 4.6% for 0.5 mol of CH_2Cl_2/mol of complex). The heating of a 3.74-mg sample of $IrCl_2(p\text{-}CH_3C_6H_4S)(CO)[P(C_6H_5)_3]_2$ to 150° results in a 0.16-mg (4.3%) weight loss (calcd 4.3% for 0.5 mol of CH_2Cl_2/mol of complex). The infrared spectra of the heated samples are identical with spectra taken before heating.

Each reaction of RS(O)Cl ($R = C_6H_5$ or $p\text{-}CH_3C_6H_4$) with $IrCl(CO)L_2$ ($L = P(C_6H_5)_3$ or $P(C_6H_5)_2CH_3$) results in the formation of a compound in which the carbonyl stretching frequency (2060–2080 cm^{-1}) indicates the formation of an iridium(III) complex. However, no absorption in the infrared spectrum can be attributed to a sulfur–oxygen stretching frequency. Also, the carbon analyses are 1.4–2.4% low and the hydrogen analyses are 0.13–0.24% high, from those calculated for the expected sulfenato complexes. At present we do not know why these compounds behave differently from those formed with $CH_3S(O)Cl$. Since both the thio and sulfinato complexes are formed and are stable, it does not seem reasonable to expect a different reaction due to the comparatively small change in electronegativity of the sulfenyl group caused by the replacement of the methyl group in $CH_3S(O)Cl$ by the phenyl or *p*-tolyl group.

All of the iridium(III) compounds formed are air and light stable while the parent alkyl chlorosulfinates, methanesulfinyl chloride, benzenesulfinyl chloride, *p*-toluenesulfinyl chloride, and *p*-toluenesulfenyl chloride slowly decompose with time.

It is of interest to note the trends in the carbonyl and sulfur–oxygen stretching frequencies. The carbonyl stretching frequency decreases, for a given phosphine ligand, as the oxidation number of the sulfur is reduced. This indicates a greater electron density on the iridium available to back-bond into the antibonding orbitals on the carbonyl, lowering the effective C–O bond order. The ranges are 2090 cm^{-1} for $IrCl_2(CH_3SO_2)(CO)L_2$ [1] to 2060 cm^{-1} for $IrCl_2(p\text{-}CH_3C_6H_4S)(CO)L_2$, where $L = P(C_6H_5)_3$, and 2080 cm^{-1} for $IrCl_2(CH_3SO_2)(CO)L_2$ to 2056 cm^{-1} for $IrCl_2(p\text{-}CH_3C_6H_4S)(CO)L_2$, where $L = P(C_6H_5)_2CH_3$. This effect is also evident for the phosphines. For a given sulfur ligand, the carbonyl stretching frequency decreases as the basicity of the phosphine increases. The S–O stretching frequencies increase in the order $RS(O)Ir < ROS(O)Ir < RS(O)_2Ir$ showing that increasing the positive charge on the sulfur increases the S–O stretching frequency. The S–O compounds given in Tables I and II show an increase of 60–80 cm^{-1} for each +1 increase in the formal oxidation state of the sulfur (average of asymmetric and symmetric frequencies used for $-SO_2-$ compounds).

Registry No. Methanesulfonyl chloride, 124-63-0; methanesulfinyl chloride, 676-85-7; $IrCl(CO)[P(C_6H_5)_2CH_3]_2$, 15318-32-8; $CH_3OS(O)Cl$, 13165-72-5; $C_2H_5OS(O)Cl$, 3678-11-6; $i\text{-}C_3H_7OS(O)Cl$, 22598-56-7; $p\text{-}CH_3C_6H_4S(O)Cl$, 10439-23-3; $C_6H_5S(O)Cl$, 4972-29-6; $[(CH_3SO_2)_2Zn\cdot 2H_2O]$, 37475-63-1; $p\text{-}CH_3C_6H_4SCl$, 933-00-6; $IrCl(CO)[P(CH_3)_2C_6H_5]_2$, 21209-82-5; $IrCl(CO)[P(C_6H_5)_3]_2$, 14871-41-1; $IrCl_2(CH_3SO_2)(CO)[P(C_6H_5)_2CH_3]_2$, 37534-39-7; $IrCl_2(CH_3OSO)(CO)[P(C_6H_5)_2CH_3]_2$, 37477-99-9; $IrCl_2(C_2H_5OSO)(CO)[P(C_6H_5)_2CH_3]_2$, 37478-00-5; $IrCl_2(i\text{-}C_3H_7OSO)(CO)[P(C_6H_5)_2CH_3]_2$, 37478-01-6; $IrCl_2(CH_3SO)(CO)[P(C_6H_5)_2CH_3]_2$, 37478-02-7; $IrCl_2(p\text{-}CH_3C_6H_4S)(CO)[P(C_6H_5)_2CH_3]_2$, 37478-03-8; $IrCl_2(CH_3OSO)(CO)[P(CH_3)_2C_6H_5]_2$, 37534-40-0; $IrCl_2(CH_3OSO)(CO)[P(C_6H_5)_3]_2$, 37662-29-6; $IrCl_2(C_2H_5OSO)(CO)[P(C_6H_5)_3]_2$, 37480-69-6; $IrCl_2(CH_3SO)(CO)[P(C_6H_5)_3]_2$, 37480-70-9; $IrCl_2(p\text{-}CH_3C_6H_4S)(CO)[P(C_6H_5)_3]_2$, 37480-71-0.

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