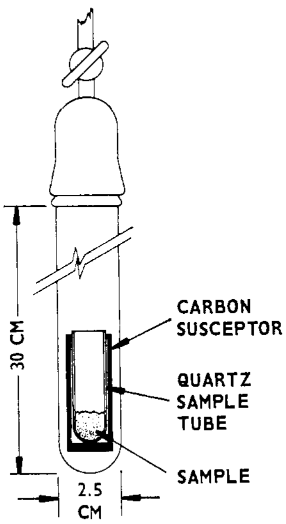

Figure 2. Apparatus for purification of elemental carbon.

and to leave a residual hydrogen pressure of about 100 torr in the apparatus. The reaction is complete when the pressure no longer decreases with time.

At this point the carbon contains all of the iron catalyst charged to the reaction tube. Exploratory experiments showed that the iron content (determined by neutron activation analysis) could not be reduced much below 2% by prolonged extraction with boiling hydrochloric acid. The iron can be removed, however, by treatment with HCl gas at 0.5 to 1 atm and 1000°. The apparatus used for this step is depicted in Figure 2. The impure carbon is placed in a quartz crucible, inside a carbon susceptor. The carbon susceptor is lowered to the bottom of a long vertical reaction tube. After the reaction tube is evacuated and filled to 0.5 atm with dry HCl, the device is placed in the field of a 1-kw induction furnace. The temperature is raised to 1000–1100°. At this temperature iron chloride vaporizes as it is formed and condenses on the walls of the reaction tube. At the end of a 1-hr period the device is cooled and the solids are removed from the walls of the reaction vessel. The purification process is then repeated.

Table I. Preparation and Purification of Elemental Carbon

	Composite results[a]
Carbon-13 enrichment, %	93.4
Carbon content of starting material, g	0.871
Elemental carbon recovered, g	0.828
Elemental carbon recovered, %	95.1
Emission spectrographic analysis, ppm	
B	50
Si	300
Mg	<2
Fe	<5
Ca	100
Cu	50
Be	<20
Na	<200

[a] Highly enriched carbon; three runs.

In a test run with 4.5% of $C^{13}O_2$, 96% of the carbon content of the CO_2 charge was recovered as purified elemental carbon. After the successful test run, three additional runs were made to prepare 0.83 g of carbon enriched to 93.4 ± 0.7% in C^{13}. The composite results of these three runs are given in Table I.

The recovered carbon was essentially identical in isotopic composition with the starting material. Purity of the material was quite satisfactory; however, it seems likely that higher purities could be attained easily by greater care in the choice of materials of construction of the conversion apparatus and by the use of an iron catalyst of higher purity. (The iron catalyst used in this work was Mallinckrodt NF. Neutron activation analysis showed that it contained 0.16% silicon.)

(5) Mound Laboratory is operated by Monsanto Research Corporation for the U. S. Atomic Energy Commission under Contract No. AT-33-1-GEN-53.

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Iridium(III) S-Sulfinates. Preparation of an Iridium(III) Aryl

Sir:

The general concept of oxidative addition of covalent molecules to transition metal complexes having a d^8 configuration is currently being investigated in our laboratories.[1] A great variety of molecules combine with "unsaturated" four-coordinate complexes of iridium(I) to form saturated six-coordinate complexes of iridium(III).[2]

The ready addition of pseudo-halogens such as arylsulfenyl chlorides to the planar iridium complex **1** prompted us to attempt the addition of other sulfur-halogen bonds. Subsequently, alkyl- and arylsulfonyl chlorides were found to combine readily with **1** to afford a new type of complex formulated as iridium(III) sulfinate derivatives **2** (eq 1).

During the course of our experiments, Wojcicki[3] prepared several π-cyclopentadienyliron dicarbonyl sulfinate compounds by insertion of SO_2 into iron-carbon σ bonds and also by a metathetical reaction. Cyclopentadienylmolybdenum tricarbonyl sulfinates have also been reported.[3] Our conclusions concerning the probable nature of the metal–sulfinate bonds were reached independently and are in agreement with those of Wojcicki. At the present time these two systems constitute the only known examples of transition metal S-sulfinate derivatives.

The infrared spectra of the iridium sulfinates (Table I) reveal two intense absorptions centered near 1235 and 1065 cm^{-1}, ascribed to the asymmetric and symmetric stretching modes of the $-SO_2-$ group bound to the metal through sulfur. In several cases these absorptions are doublets. This same splitting, especially of the asymmetric mode, is commonly found in organic sulfones.[4]

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(1) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **87**, 4008 (1965).

(2) A summary of examples of this type of reaction is given in ref 1.

(3) J. P. Bibler and A. Wojcicki, *J. Am. Chem. Soc.*, **86**, 5051 (1964); Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 36M.

(4) P. M. G. Bavin, G. W. Gray, and A. Stephenson, *Spectrochim. Acta*, **16**, 1312 (1960).

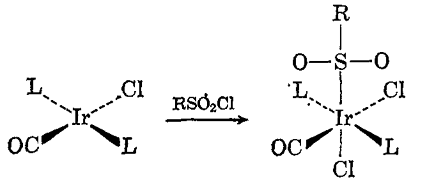
The average ratio of asymmetric to symmetric sulfonyl frequencies in Table I is 1.16. This is exactly the same ratio found in organic sulfones.[5] It is significant that the sulfonyl absorption modes are displaced by almost 100 cm^{-1} to lower frequency from the values typically found in the spectra of organic sulfonyl derivatives—even though this absorption is usually insensitive to conjugative effects.[6] This displacement is undoubtedly a reflection of dπ–dπ back bonding from the metal to the sulfonyl group. The CO frequency is shifted from 1950 cm^{-1} in the starting material (**1**) to a value of about 2080 cm^{-1} in the sulfinates (**2**).

Table I. Infrared Frequencies[a] of $Ir(CO)Cl_2[P(C_6H_5)_3]_2RSO_2$[b]

R	SO_2 (asym), cm^{-1}	SO_2 (sym), cm^{-1}	CO, cm^{-1}
CH_3	1220	1070	2090
C_2H_5	1235	1070	2080
n-C_3H_7	1225	1070	2080
p-$CH_3C_6H_4$	1240, 1220	1065, 1055	2080
p-ClC_6H_4	1240, 1220	1060	2080
p-$NO_2C_6H_4$[c]	1245, 1225	1065	2080

[a] All compounds were measured as KBr pellets on a Perkin-Elmer Grating Infracord. [b] Satisfactory carbon and hydrogen analyses have been obtained for all compounds reported. Sulfur analyses were determined for aliphatic cases. [c] Aromatic NO_2 bands at 1525 and 1350 cm^{-1}.

In view of the obviously strong back-bonding properties of the sulfonyl group as a ligand, it is likely that it takes up a position *cis* to the carbonyl group. The disposition of the phosphine groups is *trans* as indicated by the proton nmr spectra of a series of octahedral adducts similar to **2** in which the ligand (L) is diphenylmethylphosphine. The nmr spectra of all such complexes reveal a methyl triplet (J = 4 cps) indicating virtual coupling of the two phosphorus nuclei in *trans* positions. The use of this phenomenon to establish the stereochemical relationship of phosphine ligands in diamagnetic complexes was first demonstrated by Shaw.[7] The *trans* disposition of phosphines and the probable *cis* arrangement of carbonyl and sulfonyl groups lead us to suggest the structure depicted for **2**. However, this stereochemical assignment must be considered tentative in the absence of more definitive evidence.



(1)

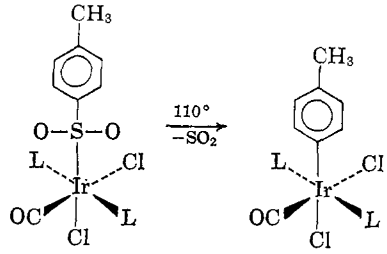
1 **2**

L = $(C_6H_5)_3P$

The alkyl iridium sulfinates are stable thermally and remain unchanged after boiling for 24 hr in solvents such as chloroform or toluene. However, certain of the arylsulfinates undergo loss of SO_2 upon heating 3 hr in boiling toluene. For example, the p-tolylsulfinate **3** is smoothly and quantitatively transformed into the p-tolyl derivative **4** (eq 2), in which the sulfonyl infrared absorptions are completely absent. *Anal.* Calcd for $C_{44}H_{37}OCl_2P_2Ir$: C, 58.28; H, 4.11; P, 6.87; Cl, 7.86. Found: C, 58.23; H, 4.39; P, 7.03; Cl, 8.24. This colorless crystalline compound is very stable as illustrated by its high melting point (259–260°) and represents the first known example of an iridium(III) aryl.[8] The CO frequency in **4** is at 2040 cm^{-1}.

This type of reaction did not prove to be a general method of preparing group VIII aryls inasmuch as other arylsulfinates such as p-chlorophenyl, p-nitrophenyl, and p-methoxyphenyl failed to lose SO_2 under our conditions. However, the benzenesulfinate does lose SO_2.

The elimination of SO_2 represents the third gas-forming elimination reaction whereby transition metal–carbon bonds are formed—the other two involving loss of CO[11] and N_2.[12] The reverse processes are known in the cases of CO and SO_2 but not N_2.



(2)

3 **4**

Experiments in progress are designed to elaborate this transition metal–carbon bond synthesis. For example, arylsulfinic acids have been found to add to ruthenium(0) and iridium(I) complexes.

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(5) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 863 (1957).

(6) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 54.

(7) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

(8) Aryls of the isoelectronic osmium(II) and platinum(IV) are well known from the work of Chatt and Hayter[9] and Chatt and Shaw.[10]

(9) J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 6017 (1963).

(10) J. Chatt and B. L. Shaw, *ibid.*, 705, 4020 (1959).

(11) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3994 (1964), and references therein.

(12) G. W. Parshall, *ibid.*, **87**, 2133 (1965).

(13) Alfred P. Sloan Foundation Fellow. This research was supported by the U. S. Army Research Office, Durham, Grant No. DA-ARO-(D)-318124-G185; by the Advanced Research Projects Agency, Contract SD-100; and by the National Science Foundation.

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Trimethylenecyclopropane

Sir:

We wish to report the synthesis and characterization of trimethylenecyclopropane (I), isomeric with benzene and the simplest member of the class of radialenes.[1,2] Pyrolysis of the appropriate trisquaternary hydroxide IIe has proved to be a superior route for the preparation of this elusive hydrocarbon in a form suitable for characterization, *i.e.*, with a minimum of contamination and dissolved in a solvent of choice; however, **I**, like

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(1) This work was supported by grants from the National Science Foundation (G13759 and GP2543) and partially by the Army Research Office (Durham).

(2) Taken in part from the Ph.D. thesis of L. I. Peterson, Yale University, New Haven, Conn., 1963, and P. A. Waitkus, Tulane University, New Orleans, La., 1966 (in preparation).