0.02 A and the average deviation of a ligand–cobalt–ligand angle from 90° being less than 2°. The bridging peroxo group is *not* perpendicular to the cobalt–cobalt axis and is *not* joined to the metal atoms by d–π bonds, but each of the oxygen atoms is σ-bonded to one of the cobalt atoms, resulting in the staggered arrangement shown. These four atoms are almost coplanar; thus, in contrast to hydrogen peroxide, there is only a small dihedral angle at the oxygen–oxygen bond. This configuration probably arises because the ammonia molecules close to the bridge tend to keep the cobalt atoms as far apart as possible. The cobalt–cobalt distance, 4.56 A, is comparable to that reported by Vannerberg and Brosset[4] (4.52 A), but the oxygen–oxygen distance is signficantly shorter than theirs (1.31 *vs.* 1.45 A). The oxygen–oxygen distance we find is only slightly longer than that found in alkali metal superoxides, 1.28 A, and is much shorter than the 1.48 A found for most peroxides.[6] It is therefore reasonable to state that the bridging group is more nearly a superoxide radical and to expect that suitable epr measurements may show that the unpaired electron is found more on the oxygen atoms than on the cobalt atoms.

There seems to be no reason to believe that the geometry of the $[(NH_3)_5CoO_2Co(NH_3)_5]^{+5}$ cation should be different in the sulfate and the nitrate. Therefore, in view of the doubts mentioned earlier concerning the validity of Vannerberg and Brosset's structure analysis, we conclude that the structure reported here, rather than that postulated by Vlček, is generally correct for all such compounds.

[6] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 351, 352.

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Preparation of Elemental Carbon-13 in High Yield from $C^{13}O_2$

Sir:

Recent experimental work in this laboratory has resulted in the separation of highly enriched carbon-13 (natural abundance 1.1%) by the thermal diffusion of methane.[1] It was desired that elemental carbon be prepared from a portion of the separated $C^{13}H_4$. The separation of $C^{13}H_4$ is difficult, and the quantities of separated material are very limited; hence, a conversion procedure which would give a high yield was sought. Procedures for the conversion of methane to carbon dioxide or to barium carbonate are quantitative and straightforward; hence, any of these three compounds is satisfactory as a starting material.

Exploratory experiments on direct pyrolysis of methane gave unsatisfactory yields. Published work[2] on the preparation of carbon by fusion of barium carbonate with alkali metals or magnesium indicated that this procedure would also result in poor yields and possibly high contents of refractory impurities. This communication describes a method by which elemental carbon can be prepared from carbon dioxide in high yield and high purity.

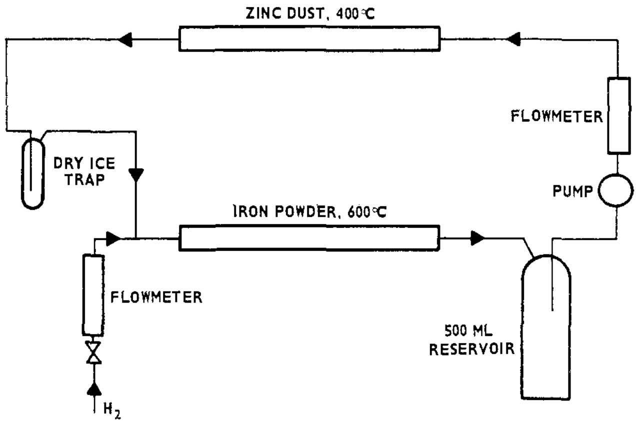

Figure 1. Apparatus for converting carbon dioxide to carbon.

The method is based on two well-known reactions: (1) the reduction of CO_2 to CO by zinc and (2) the reduction of CO over an iron catalyst in the presence of hydrogen.[3] The necessary apparatus is depicted schematically in Figure 1. Two quartz reaction tubes (12 mm i.d. × 50 cm long) are connected in a loop with a circulating pump,[4] a gas reservoir, and a Dry Ice cold trap. In the upper reactor CO_2 is reduced to CO over a 10-g charge of zinc dust. In the lower reactor carbon is formed on 20 mg of powdered iron catalyst *via* the reactions

$$2CO \longrightarrow C + CO_2$$

$$CO + H_2 \longrightarrow C + H_2O$$

The hydrogen content of the circulating gas is maintained at the desired level by continuous addition through a metering valve and a flow meter. The Dry Ice trap removes water formed in the second of the above reactions and also water resulting from reduction of zinc oxide in the upper reactor. When the process is complete, essentially all of the carbon in the starting CO_2 is deposited in the lower reactor, and the oxygen is collected as water in the Dry Ice trap. (Although a quantitative evaluation was not made, it appears that this procedure may also be useful for extracting oxygen isotopes from CO or CO_2.)

The apparatus is charged with CO_2 to an initial pressure of 500 to 600 torr (500 to 600 STP ml of gas in this system). The upper reactor is brought to 400°, and the reduction to CO is allowed to proceed for approximately 0.5 hr as the gas is circulated at a rate of 200–400 cc/min. The lower reactor is then heated to 600°, and the pressure is raised to 800 torr by the addition of hydrogen. After an induction period of 10–20 min, the pressure begins to drop as the reaction proceeds. Hydrogen is added to keep the pressure at 800 torr. The flow of hydrogen continues until enough has been added to satisfy the stoichiometry of the over-all reaction

$$2H_2 + CO_2 \longrightarrow C + 2H_2O$$

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[1] W. M. Rutherford and J. M. Keller, to be published.

[2] I. W. Ruderman and C. S. Wu, USAEC Report AECD-2412, 1948.

[3] P. L. Walter, J. F. Rakszawski, and G. R. Imperial, *J. Phys. Chem.*, **63**, 133 (1959); **63**, 140 (1959).

[4] The circulating pump is a miniature version of that described by J. F. Schultz, *Ind. Eng. Chem.*, **54**, 34 (1962).

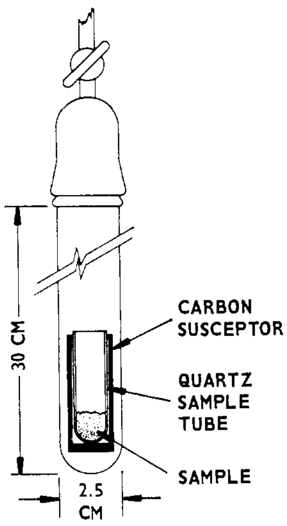

Figure 2. Apparatus for purification of elemental carbon.

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.)

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(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).