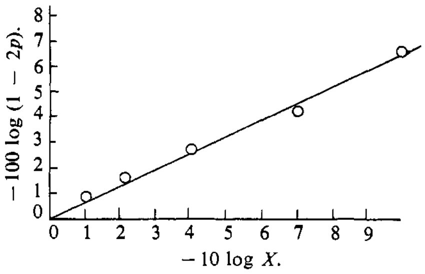

Figure 1.

except for minor air contamination for which trivial corrections were made, and finally because the natural abundance level agreed with the accepted value in cylinder gases as well as in air and various blanks made in the course of the study. Among these blanks were several degradations of α-labeled diazonium salts which had not been subjected to partial hydrolysis; these gave only natural abundance of ^{15}N in the β position within the experimental error, showing that the degradation was effective. The extent of rearrangement can be quantitatively related to the extent of hydrolysis by the equations derived previously,[1] assuming that the reaction is kinetically first order and neglecting the isotope effect (this is certainly larger than was estimated by direct rate measurement, as shown by reliable competitive methods,[4] but still not large enough to cause concern in this connection). A convenient form of the relationship is the readily derived eq 1, in which $R = k_{\text{rearr}}/k_{\text{hydrol}}$ and p is the fraction of the label in the β position when the fraction of remaining total diazonium salt is x.

$$2R \log x = \log (1 - 2p) \qquad (1)$$

Figure 1 shows a plot of log (1 − 2 p) $vs.$ log x for p-toluenediazonium ion at extents of completion from 20 to 90%, and the line is drawn from eq 1 with $R = 0.033$, in satisfactory agreement with $R = 0.029$ from many runs to 80% completion. The satisfactory fit to the line demonstrates the first-order kinetics and provides as well information not easily ascribed to experimental error.[5]

[4] L. L. Brown and J. S. Drury, *J. Chem. Phys.*, 43, 1688 (1965).

[5] A referee comments that a minor isotopically rearranged product other than diazonium ion may be responsible for these results. If so, this substance must have the following characteristics in common with the diazonium ion $Ar^+N{\equiv}^{15}N$: a reaction with azide ion to give no ^{15}N in primary nitrogen, giving secondary nitrogen after warming, and leaving a product which gives nitrogen with arsenite; the relative yields must be similar; a very similar rate of destruction, necessitated by the kinetics, and closely similar activation energy for formation and destruction; all the above similarities are unaltered when the substitution on the diazonium ion is changed. We feel that this identification is compelling.

[6] R. E. H. thanks the National Aeronautics and Space Administration for a traineeship; we also thank the Robert A. Welch Foundation for support of much of this work.

Edward S. Lewis, Robert E. Holliday[6]
Department of Chemistry, William Marsh Rice University
Houston, Texas 77001

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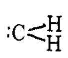
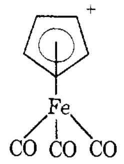
Evidence for a Novel Metal–Carbene System

Sir:

It has recently been recognized that carbene (I) may be capable of acting as a ligand in certain organo-transition metal complexes. The lone pair electrons in I could act as a donor pair and the vacant p_z carbon orbital would be available for back-donation of electrons from the metal. The species could thus be classified with carbon monoxide and triphenylphosphine as far as donor–acceptor capabilities are concerned and could, in principle, replace such ligands in their stable complexes. The validity of this reasoning has recently been convincingly demonstrated by Fischer and Maasböl[1] through the isolation of methoxymethylcarbene–tungsten pentacarbonyl. We now wish to report evidence for the formation of a very reactive metal complex containing the parent unsubstituted carbene ligand.

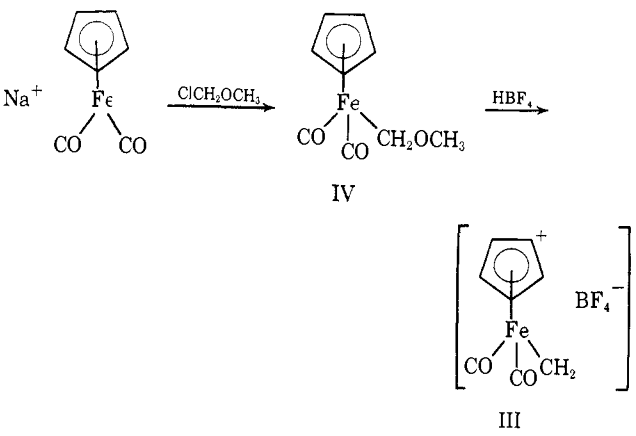


I



II

Salts of the cyclopentadienyliron tricarbonyl cation (II) have been isolated[2] and the above reasoning suggests that the cyclopentadienyliron dicarbonyl carbene cation (III) might also be stable. Reaction of the sodium salt of the cyclopentadienyliron dicarbonyl anion with chloromethyl methyl ether produced (methoxymethyl)cyclopentadienyliron dicarbonyl[3] (IV). Ether cleavage of IV with acids would be expected to yield the carbene complex III if the latter were to be stable. Complex IV reacted rapidly with HBF_4 and both cyclopentadienylmethyliron dicarbonyl (V) and the cyclopentadienylethyleneiron dicarbonyl cationic complex (VI) were isolated as products. Both V and VI are known species,[2a,4] and their formation can be reasonably formulated through intermediacy of the cation III. When conducted at 0° in the presence of cyclohexene, the reaction of IV with HBF_4 produced norcarane (46% yield based on IV) together with other species, predominantly II and V. The methylene transfer reaction

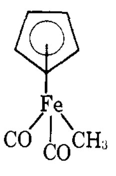


[1] (a) E. O. Fischer and A. Maasböl, *Angew. Chem.*, 76, 645 (1964); (b) O. S. Mills and A. D. Redhouse, *ibid.*, 77, 1142 (1965).

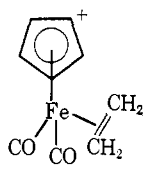
[2] (a) E. O. Fischer and K. Fichtel, *Chem. Ber.*, 94, 1200 (1961); (b) A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961).

[3] The elemental analysis and nmr spectrum of this new product agree with the proposed formulation.

[4] (a) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3, 104 (1956). (b) In a recent personal communication Professor M. L. H. Green has informed us that he has also observed compounds V and VI to be produced upon treatment of IV with acids; he also interprets this reaction as proceeding *via* the carbene complex III.



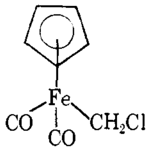
V



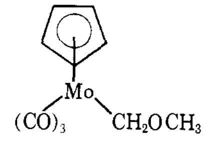
VI

appears to be general and stereospecific; in the presence of *cis*-2-butene reaction of IV with HBF_4 produces *cis*-1,2-dimethylcyclopropane, while with *trans*-2-butene the sole cyclopropane product is the *trans*-1,2-dimethyl isomer.

Reaction of the methoxymethyl complex IV and HCl in pentane caused immediate formation of cyclopentadienyl(chloromethyl)iron dicarbonyl (VII).[3] The complex VII reacts instantly with $AgBF_4$, precipitating silver chloride and forming complexes II, V, and VI in solution. When this reaction was performed at −60°, the AgCl was removed and cyclohexene was added to the supernatant and allowed to warm; small amounts of norcarane were produced. These reactions, especially the latter, strongly imply intermediacy of the carbene complex III.



VII



VIII

$(CO)_5ReCH_2OCH_3$

IX

The chloromethyliron complex VII, upon heating with cyclohexene at 50° for several hours, produces cyclopentadienyliron dicarbonyl chloride and high yields of norcarane (80%). This reaction appears to be analogous to the Simmons–Smith reaction or the pyrolysis of the halomethylmercury systems studied by Seyferth and co-workers.[5,6]

Other transition metal complexes appear to behave in an analogous manner to the iron complex IV. Thus, cyclopentadienyl(methoxymethyl)molybdenum tricarbonyl[3] (VIII) also produces norcarane upon treatment with HBF_4 in the presence of cyclohexene.

Although our studies are not yet comprehensive, it appears that the stability of carbene–transition metal complexes will prove to be very dependent upon the nature of the metal and especially its accompanying ligands. An indication of this is seen in the fact that whereas complex IV reacts practically instantly with HCl in pentane to produce the chloromethyl complex VII, (methoxymethyl)rhenium pentacarbonyl[3] (IX) produces the corresponding chloromethyl system only after several hours of treatment with HCl. The manganese compound analogous to IX forms the chloromethyl derivative even more slowly.

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(5) D. Seyferth and M. A. Eisert, *J. Am. Chem. Soc.*, **86**, 121 (1964).

(6) A chloromethyliridium complex appears to act analogously; *cf.* F. D. Mango and I. Dvoretzky, *ibid.*, **88**, 1654 (1966).

(7) The authors thank the National Science Foundation, the U. S. Army Research Office (Durham), and the Robert A. Welch Foundation for financial assistance. Generous gifts of $Fe(CO)_5$ from General Aniline and Film Corp. are also gratefully acknowledged.

P. W. Jolly, R. Pettit[7]
Department of Chemistry, The University of Texas
Austin, Texas 78712

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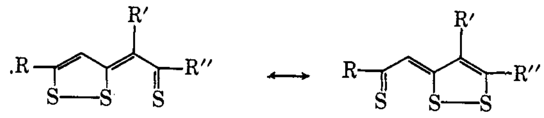
Selenium in the "No-Bond Resonance" System

Sir:

The three sulfur atoms in dimethylthiothiophthene (Ia) are reported to be collinear and equally spaced at 2.36 A. This exceptionally high bond length, as compared to the generally accepted S–S distance of 2.08 A, has been explained in terms of "no-bond resonance" between two equivalent structures, Ia and Ib.[1] This hypothesis has been supported by nmr studies[2] and by the finding that IIa and IIb are not isomers; one and the same compound is given by syntheses that would give both if they had distinct existence.[3]



Ia, R = R″ = Me, R′ = H
IIa, R = R′ = Ph, R″ = H

Ib
IIb

However, current X-ray crystallographic work by Hordvik, Sletten, and Sletten shows that equal spacing is not present in II.[4] Its shorter S–S bond, and thus its more important resonance structure, is represented by IIb; the corresponding S–S bond distance is found to be 2.22 A, 0.14 A above normal. The S–S bond distance corresponding to IIa is 2.51 A, higher than in Ia–Ib but still, of course, much below the van der Waals distance (3.70 A for two sulfur atoms), and thus indicative of a significant contribution from IIa. The obvious explanation for this result is, of course, that the symmetrical sulfur spacing in I is perturbed by unsymmetrical substitution in II. The possibility should also be noted, however, that the results reported for I may be partly due either to random packing of the molecules (since their shape is not altered much upon flipping over) or to an ordered superstructure. This is supported by the anisotropy in the direction of the S–S bonds exhibited by the S atoms as observed in the electron density maps of I. If this were due to a preferred thermal vibration, the much lighter carbon atoms attached to the sulfur atoms might reasonably be expected to move together with them. Yet the electron density distribution of the carbon atoms does not indicate this to be the case,[5] implying dissimilar S–S bonds even in I. The question might be further investigated by low-temperature high-resolution nmr.

In III, the oxygen analog of I, the remaining S–S bond length is 2.12 A, close to normal.[6] We are investigating other isosteres of thiothiophthene, and report herewith the selenium compound V, obtained in good yield by refluxing IV[3] for 4 hr in chlorobenzene with freshly ground phosphorus pentaselenide; it crystallizes as purple rods from methylcyclohexane, mp 130.5–131.5°.

The absorption spectra of II and IV in hexane conform to the established pattern for such pairs of com-

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(1) S. Bezzi, M. Mammi, and C. Garbuglio, *Nature*, **182**, 247 (1958).

(2) H. G. Hertz, G. Traverso, and W. Walter, *Ann.*, **625**, 43 (1959).

(3) E. Klingsberg, *J. Am. Chem. Soc.*, **85**, 3244 (1963).

(4) A. Hordvik, E. Sletten, and J. Sletten, *Acta Chem. Scand.*, in press.

(5) M. Mammi, private communication, 1966.

(6) M. Mammi, R. Bardi, G. Traverso, and S. Bezzi, *Nature*, **192**, 1282 (1961).