

structuredness¹⁷ are involved in the transition state. The more favorable enthalpy due to increased hydrogen bonding under these conditions can only partly compensate the entropic loss. In the n_{H_2O} region from 0.900 to 0.700 long-range order is rapidly destroyed as reflected in rates of hydrolysis which are now slowed down through rather smooth changes in ΔH^\ddagger and ΔS^\ddagger .

Our findings may well have biochemical implications of some generality, since it has long been recognized that "water structure" may be either appreciably increased or decreased (compared to pure water) around the active sites of enzymes.¹⁸ One of the consequences will be that for water-dependent enzymic processes involving hydrolysis of activated esters or mechanistically related reactions, there may occur a strong interdependence of *substituent effects* in the substrate and *solvent effects* due to changes in "water structure." Therefore, substituent effects obtained with the aid of suitable model reactions¹⁹ in water may be substantially modified at the active site.

In the light of the present results we are encouraged to believe that the effect of "water structure" and its concomitant influence on thermodynamic parameters will become part of all theories for processes in aqueous solutions. However, at the moment complete separation of these effects from other influences and quantitative predictions must await further development in our understanding of the peculiar nature of water.²⁰

Further studies of reactions which respond to perturbation of the structuredness of aqueous media are in progress.

(17) We leave open the question whether or not the enhanced structuredness is the one characteristic of pure water.

(18) H. J. C. Berendsen, "Theoretical and Experimental Biophysics," A. Cole, Ed., Marcel Dekker, New York, N. Y., 1967, p 1.

(19) For excellent reviews, see ref 5 and 6. We find that the ratio of k_{obsd} values for the hydrolysis of 1 and *p*-methoxyphenyl dichloroacetate changes from 22 in pure water to 43 at $n_{H_2O} = 0.950$ in aqueous *tert*-butyl alcohol (30°C).

(20) Important theories have been developed recently: (a) A. Rahman and F. H. Stillinger, *J. Chem. Phys.*, **57**, 1281 (1972); (b) O. Weres and S. A. Rice, *J. Amer. Chem. Soc.*, **94**, 8983 (1972); (c) A. T. Hagler, H. A. Scheraga, and G. Némethy, *J. Phys. Chem.*, **76**, 3229 (1972).

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A 2,2'-Bipyridine Derivative of Diiron Nonacarbonyl, $Fe_2(CO)_7dipy$. Some Observations on the Nature and Function of Semibridging Carbonyl Groups

Sir:

Simple substitution products of the iron carbonyls in which the substituents are organic amines are previously unreported,^{1,2} although $Fe(CO)_4NH_3$ has been described.³ We have found that use of THF as solvent for reactions of $Fe_2(CO)_9$ allows the isolation of a number of unusual products not otherwise obtainable, in-

(1) Cf. F. Calderazzo, R. Ercoli, and G. Natta in "Organic Syntheses via Metal Carbonyls," Vol. 1, I. Wender and P. Pino, Ed., Interscience-Wiley, New York, N. Y., 1968, p 127.

(2) Studies by Hieber and coworkers found that direct reactions between the iron carbonyls and amines yield only disproportionation products, *i.e.*, salts containing amine-coordinated ferrous ion and carbonylate anions. Cf. W. Hieber and A. Lipp, *Chem. Ber.*, **92**, 2075, 2085 (1959), and earlier work cited there.

(3) W. Hieber and H. Beutner, *Z. Anorg. Allg. Chem.*, **317**, 63 (1962).

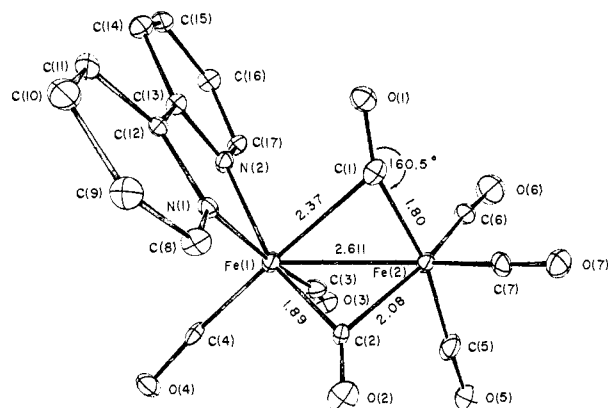


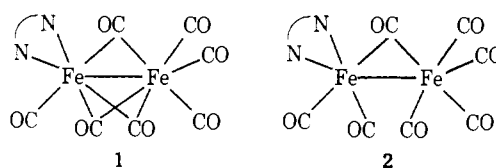
Figure 1. The structure of $Fe_2(CO)_7dipy$. The ellipsoids representing amplitudes of thermal vibration enclose 50% of the electron density. An atom numbering scheme is indicated.

cluding novel olefin complexes⁴ and $Fe(CO)_4py$.⁵ Another product readily obtained is $Fe_2(CO)_7dipy$, a red-purple, crystalline solid. We have characterized this compound fully by X-ray crystallography.⁶ The structure is shown in Figure 1.

The structural features of greatest interest are the presence of only *one* ordinary bridging CO group (moderately unsymmetrical) and the occurrence of one grossly unsymmetrical carbonyl bridge.⁷

While the compound can be regarded as a substitution product of $Fe_2(CO)_9$, in contradistinction to being the result of a disproportion or other scission process, there has been an extensive rearrangement of the structure. The nature and significance of the rearrangement have been analyzed yielding important new insight into the principles governing the structures of metal carbonyls.

Mere substitution of two *cis* terminal CO groups by *dipy* would have afforded a structure of type 1. We suggest that whether or not it is an actual intermediate this could not be stable relative to 2, for the following reason.



Bridging CO groups are most likely much less efficient π -acids than terminal CO groups, and with the replacement of two terminal CO groups by *dipy*, a good σ -donor but a poor (compared to CO) π -acid, there is need to generate π -acid capacity among the remaining ligands. This is done by opening two CO bridges thereby creating two more terminal CO ligands and affording a structure of type 2.⁹

(4) F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, **95**, 3798 (1973).

(5) F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, in press.

(6) See paragraph at end of paper regarding supplementary material.

(7) As in $(\eta^5-C_5H_5)_2V_2(CO)_8$ there is an ir band ($\sim 1850\text{ cm}^{-1}$) between the normal ranges for bridge and terminal CO groups assignable to the grossly unsymmetrical one; this indicates that this structure persists in solution.

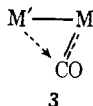
(8) F. A. Cotton, L. Kruczynski, and B. A. Frenz, *J. Amer. Chem. Soc.*, **95**, 951 (1973).

(9) This can be regarded as a simple substitution product of an initially singly bridged structure such as has been proposed for $Os_2(CO)_6$.¹⁰ A $(OC)_4Fe(\mu-CO)Fe(CO)_4$ structure is probably only a few kilocalories less stable than the $(OC)_3Fe(\mu-CO)_2Fe(CO)_3$ for $Fe_2(CO)_8$.

(10) J. R. Moss and W. A. G. Graham, *Chem. Commun.*, 835 (1970).

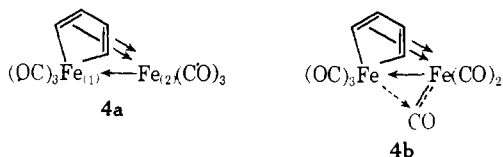
The final step to pass from **2** to the actual structure is to have one of the CO groups on Fe₍₂₎ lean toward Fe₍₁₎ to form the *semibridging CO group*,¹¹ SBCO, first observed^{11a} in 1961.

One of the uniquely important things about this molecule is that it gives a clue to the nature of the bonding in SBCO's and, hence, a prediction of *one* set of circumstances in which they may be expected to occur. We think that in this molecule it is obvious that the relatively electron-rich Fe₍₁₎ atom in **2** is forming a weak $d \rightarrow \pi^*$ dative bond to the C(1)–O(1) group. In short, *the semibridging CO group provides a mechanism for a metal atom otherwise tending to be excessively negative to transfer electron density to a CO group on a less negatively charged metal atom.* A convenient diagrammatic representation, useful in drawing structures, is **3**, imply-



ing that one π^* orbital continues to back-accept $d\pi$ electrons from M, while the other π^* orbital is at least partially used to accept electron density from M'. As this process occurs, the M–C–O chain bends and the acceptor orbital for M' will acquire carbon s character, thus making it a better acceptor.

This interpretation of the SBCO group serves to explain its occurrence in some other cases. In molecules of type **4**,^{11a,c} the hypothetical structure **4a**, without an SBCO, has Fe₍₁₎ and Fe₍₂₎ formally negative and positive, respectively. Introduction of the SBCO, **4b**,



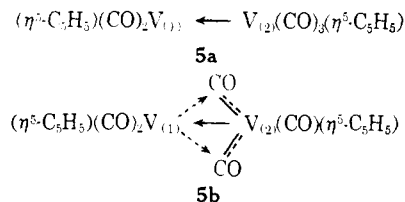
alleviates this by directly removing electron density from Fe₍₁₎ and causing the CO which acts as the SBCO to π -accept less from Fe₍₂₎. Again, in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_2(\text{CO})_8$,^{11b} the Rh atoms tend to bear greater charges than the iron atoms since their ligands are $\eta^5\text{-C}_5\text{H}_5$ groups which donate more than they back-accept, whereas one of the iron atoms, which bears four CO groups, tends to be less electron-rich than the other, which has three. Hence, two appropriately positioned CO groups on the Fe(CO)₄ group become SBCO's and lessen the density on the Rh atoms.

In $(\eta\text{-C}_5\text{H}_5)_2\text{V}_2(\text{CO})_8$ (**5**) a hypothetical structure omitting SBCO formation would be **5a**. Here each V atom has a 16-electron configuration (an acceptable situation in group IV and V compounds), but V₍₁₎ is negative relative to V₍₂₎. The use of two CO groups on V₍₂₎ as SBCO's, **5b** (the actual structure), helps to spread charge more evenly.¹²

In $\alpha\text{-H}_2\text{Ru}_4(\text{CO})_{13}$ ^{11e} the metal atom with the greatest number of CO groups uses two of them as SBCO's to remove electron density from two others.

(11) (a) A. A. Hock and O. S. Mills, *Acta Crystallogr.*, **14**, 139 (1961); (b) R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, **88**, 4847 (1966); (c) H. B. Chin and R. Bau, *J. Amer. Chem. Soc.*, **95**, 5069 (1973); (d) M. R. Churchill and M. V. Veidis, *J. Chem. Soc. A*, 2170 (1971); (e) D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, **11**, 838 (1972).

(12) The V–V bond order may exceed unity because of additional electroneutral V–V bonding. As observed before,⁸ "the order of this bond is uncertain."



In a case such as the $\text{Fe}_4(\text{CO})_{13}^-$ ion^{11b} three SBCO's are so correlated that the associated three metal atoms are charge equivalent in the actual structure but would be also in a structure without the SBCO's (similar to $\text{Ir}_4(\text{CO})_{12}$) as well as one with regular symmetrical bridges (similar to $\text{Co}_4(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$). Charge equalization cannot explain the occurrence of the SBCO's in this or any similar case, e.g., $\text{Fe}_8(\text{CO})_{12}$. Instead, there may simply be a very small variation in the free energy as a function of structure through the entire range covered by concerted shifts of two (in $\text{Fe}_8(\text{CO})_{12}$) or three (in $\text{Fe}_4(\text{CO})_{13}^-$) CO ligands from essentially terminal toward symmetrically bridging positions.

Finally, we note that a need for charge equalization is not a sufficient condition for formation of SBCO's since none exists in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Mo}(\mu\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_4$ where it would seem likely that there is a Mo→Mn bond, thus making Mn appreciably negative relative to Mo.^{13,14} However, there are several features of this molecule, namely, only one CO on the Mo atom, the presence of four CO's on the Mn atom to help disperse its formal charge, and a very long Mo–Mn bond which might militate against the stability of an SBCO.¹⁵

Supplementary Material Available. A table of crystal data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-1233.

(13) R. Hoxmeier, B. Deubzer, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **93**, 536 (1971).

(14) The authors would welcome correspondence concerning any other apparent exceptions.

(15) We are grateful to the National Science Foundation (Grant No. GP33142X) for support and to The Robert A. Welch Foundation for funds to purchase the diffractometer.

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The Chemistry of the Dianisylnitrenium Ion. The Observation of Stable Protonated Nitrenium Ions.

Sir:

We report the direct observation of the dianisyl-nitrenium ion and its conjugate acid, the protonated nitrenium ion. Cyclic voltammetry of di-*p*-anisylamine (**1**) in dichloromethane in the presence of suspended alumina¹ (Figure 1) results in the observation of two reversible one-electron redox couples with oxida-

(1) Aprotic solvents can be rendered "nucleophile free" by suspension of neutral alumina particles which allows for the observation of otherwise very short-lived intermediates such as aromatic dication: O. Hammerich and V. D. Parker, *Electrochim. Acta*, **18**, 537 (1973).