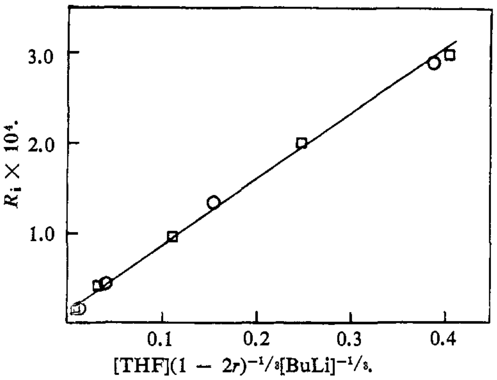

Figure 2. Initial rates of reaction 4 as the function of $[THF]_e$ given in eq 11 with [BuLi] 0.15 *M* (○) and 0.30 *M* (□).

not be a function of the concentration of the source for those electrons (at least above a certain lower limit of source concentration), but rather may be a function of the number of available basic molecules. One could even say that, for a given system, each CT process requires a certain volume of the system.

If our hypothesis is valid, an obvious consequence is that *some reactions of lithium reagents will be kinetically independent of reagent concentrations.* Precisely this result is found in BuLi addition (eq 4) rates in excess THF, *i.e.*, when $r > 1/2$; the published[4] data show that $R_i$ does not increase with increasing [BuLi]. With [THF] constant and $r > 1/2$, additional $R_i$ values are essentially constant with increasing [BuLi], until this reagent concentration approaches $^1/_2$[THF], and then $R_i$ decreases; *i.e.*, when a significant portion of the base is consumed in complexation, $R_i$ decreases. Another critical test of the hypothesis can be made with $R_i$ values from runs without excess THF, *i.e.*, $r < 1/2$.

Equation 11, derived by a conventional algebraic treatment of equilibrium 2, gives $[THF]_e$ when $r < 1/2$. Although the effective base concentration is then extremely small, because $K_e$ for (2) is large, the addition (4) rate is still clearly proportional to $[THF]_e$ as shown in Figure 2. The addition rates plotted show their linear dependence on $[THF]_e$ and their independence of [BuLi]; the data cover runs at two [BuLi] values, 0.15 and 0.30 *M*, with a 30-fold variation in total THF concentration, 0.0025 to 0.074 *M*.

$$[THF]_e = \frac{[THF]}{(6)^{1/3}(K_e)^{1/3}(1 - 2r)^{1/3}[BuLi]^{1/3}} \qquad (11)$$

Elucidation of every detailed step in SET reactions may prove difficult, but we feel the general concept of solvent support of CT has obvious utility in rationalizing many diverse phenomena now.

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## The Novel Structure of $\mathrm{Me_2As}\overline{\mathrm{C{=}C(AsMe_2)CF_2C}}\mathrm{F_2\{Fe(CO)_3\}_2}$

*Sir:*

The chelating properties of ditertiary arsines and phosphines have been extensively studied, most notably by Chatt, Nyholm, and their co-workers.[1,2] Two new ligands of this type, $\mathrm{R}\overline{\mathrm{C{=}C(R)CF_2C}}\mathrm{F_2}$ (R = $AsMe_2$, $PPh_2$) are being investigated. These cyclobutenes are similar to the *o*-phenylene compounds, in that they displace carbon monoxide from simple metal carbonyls to give compounds of the type $LMo(CO)_4$, $LFe(CO)_3$, $LNi(CO)_2$; reaction also occurs with noble metal halides yielding complexes of the expected type. Details of these compounds will be given elsewhere, the purpose of the present note being to report the isolation, during the preparation of $LFe(CO)_3$ (L = the diarsine), of an unusual compound for which X-ray crystal analysis has given the molecular formula $L\{Fe(CO)_3\}_2$ and the structure shown in Figure 1.

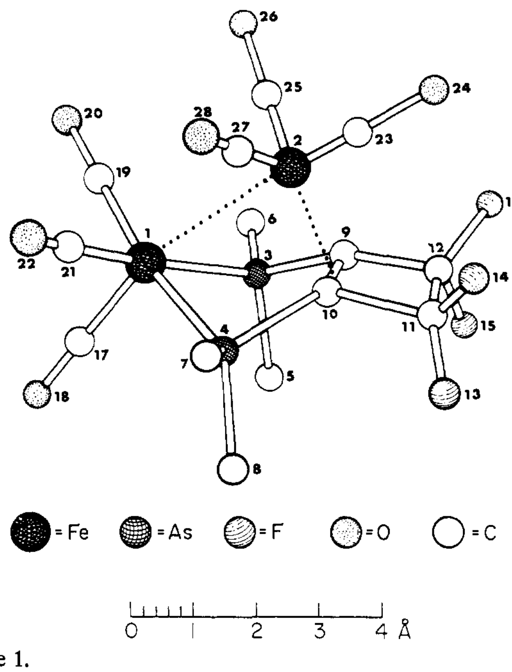

Figure 1.

Crystals of the compound are monoclinic: $a$ = 9.37, $b$ = 14.15, $c$ = 14.82 A; $\beta$ = 96.1°; space group Cc or C2/c. The density, 2.02 g $cm^{-3}$ by flotation, is consistent with a unit cell content of four molecules of molecular weight 614 (later mass spectrometric measurement gave 612). The structure was determined from the three-dimensional Patterson function, which indicated space group Cc, and from electron-density maps, using Mo K$\alpha$ scintillation counter data for 900 reflections. Least-squares refinement has given $R$ = 0.057.

The geometry of the molecule is illustrated in Figure 1, which, together with the bond distances and angles given in Table I, indicates that the structure may best be described in terms of two linked iron atoms. One iron atom is octahedrally coordinated to three carbonyl groups and the two arsenic atoms, with the sixth position occupied by the Fe–Fe bond. The second iron atom has trigonal bipyramidal coordination, the equatorial positions involving two carbonyl groups and the $\pi$ bond from the cyclobutene system, with the apical positions occupied by the third carbonyl group and the Fe–Fe bond. The molecule has approximately $C_s$ symmetry.

The Fe–Fe distance, 2.88 A, is longer than those of about 2.69 A in other compounds with nonbridged

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(1) G. Booth, *Advan. Inorg. Chem. Radiochem.*, 6, 1 (1964).
(2) T. A. Manuel, *Advan. Organometal. Chem.*, 3, 181 (1965).

Table I. Bond Distances (A) and Angles (deg)

| Bond | Std dev, A | Angle | Std dev, deg |
|---|---|---|---|
| Fe–Fe | 0.006 | As–Fe–As | 0.2 |
| Fe–As | 0.005 | Other ∠s at Fe | 1.0–1.3 |
| Fe–C | 0.03 | ∠s at As | 1.0–1.3 |
| As–C | 0.03 | ∠s at C | 2–3 |
| C–O | 0.04 | | |
| C–C | 0.04 | | |
| C–F | 0.03 | | |

| Bond | Distance, A | Bond | Distance, A |
|---|---|---|---|
| Fe(1)–Fe(2) | 2.89 | Fe(2)···C(9) | 2.09 |
| | | Fe(2)···C(10) | 1.99 |
| Fe(1)–As(3) | 2.47 | Fe(2)···C(9)‖C(10) | 1.90 |
| Fe(1)–As(4) | 2.35 | | |
| Fe(2)···As(3) | 3.09 | | |
| Fe(2)···As(4) | 3.05 | | |
| Fe(1)–C(17) | 1.74 | C(17)–O(18) | 1.21 |
| Fe(1)–C(19) | 1.75 | C(19)–O(20) | 1.16 |
| Fe(1)–C(21) | 1.78 | C(21)–O(22) | 1.25 |
| Fe(2)–C(23) | 1.71 | C(23)–O(24) | 1.21 |
| Fe(2)–C(25) | 1.68 | C(25)–O(26) | 1.27 |
| Fe(2)–C(27) | 1.79 | C(27)–O(28) | 1.25 |
| Mean Fe–C | 1.74 | Mean C≡O | 1.23 |
| As(3)–Me(5) | 1.95 | As(3)–C(9) | 1.91 |
| As(3)–Me(6) | 1.93 | As(4)–C(10) | 1.91 |
| As(4)–Me(7) | 2.01 | | |
| As(4)–Me(8) | 1.89 | C(9)=C(10) | 1.51 |
| Mean As–Me | 1.95 | | |
| | | C(11)–F(13) | 1.37 |
| C(9)–C(12) | 1.52 | C(11)–F(14) | 1.38 |
| C(10)–C(11) | 1.57 | C(12)–F(15) | 1.41 |
| C(11)–C(12) | 1.53 | C(12)–F(16) | 1.31 |
| Mean C–C | 1.54 | Mean C–F | 1.37 |

| Angle | Deg | Angle | Deg |
|---|---|---|---|
| At Fe(1) | | At Fe(2) | |
| C(17)–Fe(1)–As(3) | 96 | Fe(1)–Fe(2)–C(9) | 80 |
| C(17)–Fe(1)–As(4) | 98 | Fe(1)–Fe(2)–C(10) | 78 |
| C(17)–Fe(1)–C(19) | 98 | Fe(1)–Fe(2)–mid-pt[a] | 78 |
| C(17)–Fe(1)–C(21) | 96 | Fe(1)–Fe(2)–C(25) | 92 |
| Fe(2)–Fe(1)–As(3) | 70 | Fe(1)–Fe(2)–C(27) | 89 |
| Fe(2)–Fe(1)–As(4) | 70 | C(23)–Fe(2)–C(9) | 97 |
| Fe(2)–Fe(1)–C(19) | 93 | C(23)–Fe(2)–C(10) | 99 |
| Fe(2)–Fe(1)–C(21) | 97 | C(23)–Fe(2)–mid-pt[a] | 99 |
| As(3)–Fe(1)–As(4) | 86 | C(23)–Fe(2)–C(25) | 91 |
| As(3)–Fe(1)–C(19) | 90 | C(23)–Fe(2)–C(27) | 93 |
| As(4)–Fe(1)–C(21) | 88 | C(25)–Fe(2)–C(27) | 103 |
| C(19)–Fe(1)–C(21) | 93 | C(25)–Fe(2)–mid-pt[a] | 127 |
| C(17)–Fe(1)–Fe(2) | 162 | C(27)–Fe(2)–mid-pt[a] | 128 |
| As(3)–Fe(1)–C(21) | 167 | C(25)–Fe(2)–C(9) | 106 |
| As(4)–Fe(1)–C(19) | 164 | C(25)–Fe–(2)–C(10) | 149 |
| | | C(27)–Fe(2)–C(9) | 149 |
| | | C(27)–Fe(2)–C(10) | 106 |
| | | C(9)–Fe(2)–C(10) | 43 |
| At As | | | |
| Fe(1)–As–Me | 119, 119, 119, 120 | | |
| Fe(1)–As–C(9,10) | 94.8, 94.2 | | |
| Me–As–Me | 102, 101 | | |
| Me–As–C(9,10) | 112, 110, 111, 111 | | |
| Fe–C–O | 168, 174, 177, 178, 178, 179 | | |
| As(3)–C(9)–C(10) | 116 | | |
| As(4)–C(9)–C(12) | 120 | | |
| As(3)–C(9)–C(12) | 136 | | |
| As(4)–C(10)–C(11) | 136 | | |
| In cyclobutene ring | 96, 85, 93, 86 | | |
| F–C–F | 103, 104 | | |

Displacement of Fe atoms

Fe(1) from plane As(3), As(4), C(19), C(21), O(20), O(22), 0.3 A away from Fe(2)

Fe(2) from plane C(9), C(10), C(25), C(27), O(26), O(28), 0.2 A away from Fe(1)

[a] Mid-pt = center of C(9)–C(10) bond.

Fe–Fe bonds[3–5] but is still short enough to indicate bonding, especially when viewed in conjunction with the over-all structure of the molecule. The bonding is most simply described in valence bond terms, the Fe–Fe bond involving overlap of an electron pair in a $d^2sp^3$ orbital of the octahedral iron atom with a $dsp^3$ orbital of the five-coordinate iron; each iron atom thus attains the krypton configuration. A description could also be given in terms of bonding between the second iron atom and a delocalized system in the five-membered ring of first iron, arsenic, and carbon atoms; however, the general arrangements around both iron atoms suggest that the valence bond description is more appropriate.

The compound probably arises from the addition of an $Fe(CO)_3$ fragment to the $LFe(CO)_3$ molecule.

(3) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).

(4) C.-H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966).

(5) A. A. Hock and O. S. Mills, *Acta Cryst.*, **14**, 139 (1961).

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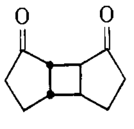
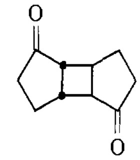
## On the Photodimerization of Cyclopentenone

*Sir:*

Eaton[1] has shown that on irradiation with wavelengths above 3000 A cyclopentenone, neat or in "a variety of solvents," produces the two dimer forms I and II in high yield and in approximately equal amounts.



I



II

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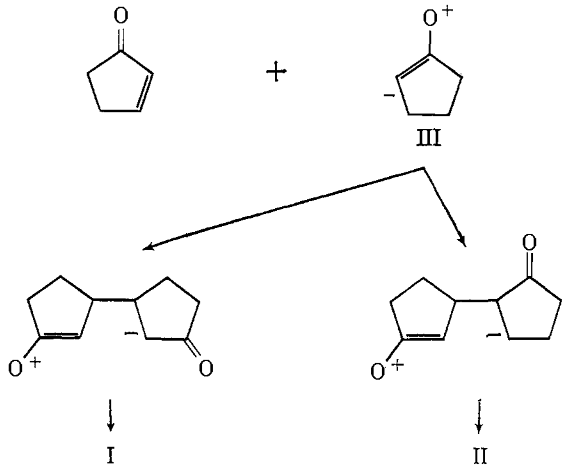
(1) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962).

(2) J. Calvert and J. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1965, p 407.

(3) To summarize earlier work Eaton[4] stated that although the initial excitation is presumably to the singlet state (n–π*) at 3080 A for neat solution, the charge distribution of the excited molecule taking part in the reaction is not known. However, taking the polarized form III as an adequate representation,[5] Eaton argued that *if* the dimerization takes place *via* a two-step mechanism, the reaction may be pictured as follows



Eaton then reasoned that this mechanism would result in a favoring of I due to the interaction of the adjacent carbonyl with the negative charge in the intermediate.

(4) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2454 (1962).

(5) Eaton[3] cites H. E. Zimmerman and D. I. Schuster, *ibid.*, **83**, 4486 (1961).