

amide (entry 4), which is capable of such a process, underwent cleavage in the sense of $1 \rightarrow 2$.

Finally, the cleavage of tryptophan in the sense $1 \rightarrow 2$ is a property of the indole system. Other amino acids react with $C_6H_5I(OAc)_2$ via oxidative decarboxylation.¹⁴ For example, we have found that L-tyrosine yielded (*p*-hydroxyphenyl)acetonitrile in 70% yield under the standard reaction conditions. Similarly, Loudon et al. have obtained benzonitrile from α -phenylglycine using $C_6H_5I(OCOCF_3)_2$ in pyridine.^{8a} Subsequent oxidative decomposition, possible via a similar pathway, may account for the fate of the other portion of the peptide in the present system.¹⁵

The course of reaction of other amino acids and peptides with $C_6H_5I(OAc)_2/KOH/CH_3OH$ is currently being pursued.

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Registry No. 1, 73-22-3; 2, 78440-76-3; DL-tryptophan methyl ester, 78440-76-3; *N*-methyl-L-tryptophan, 526-31-8; DL-tryptophanamide, 7303-48-2; tryptamine, 61-54-1; tryptophol, 526-55-6; DL-indolelactic acid, 832-97-3; indole-3-acetic acid, 87-51-4; L-tryptophyl-L-alanine, 24046-71-7; L-tryptophyl-L-phenylalanine, 6686-02-8; L-tryptophyl-L-leucine, 13123-35-8; L-tryptophyl-L-tryptophan, 20696-60-0; iodine, 7553-56-2.

(13) Retro inverse peptides have been made via $C_6H_5I(OCOCF_3)$ -induced Hofmann rearrangement: Pessi, A.; Massimo, P.; Verdini, A. S.; Viscomi, G. C. *J. Chem. Soc., Chem. Commun.* **1983**, 195. Verdine, A. S.; Viscomi, G. C. *Brev. Ital.* **1981**, 25755. Pallai, P.; Goodman, M. *J. Chem. Soc., Chem. Commun.* **1982**, 280.

(14) Two mechanistically related reactions are the bromodecarboxylation reaction of amino acids upon treatment with *N*-bromosuccinimide (Konigsberg, N.; Stevenson, G.; Luck, J. M. *J. Biol. Chem.* **1960**, 235, 1341) and the photodecarboxylation of α -azido acids (Moriarty, R. M.; Rahman, M. *J. Am. Chem. Soc.* **1965**, 87, 2519).

(15) Cleavage of the dipeptides 11-14 according to eq 2 should yield $2 + NH=CHCONHCHR(COOH)$. Simple hydrolysis of this product would yield $OCHCONHCHR(COOH)$; however, no 2,4-DNP was obtained in the present study. Further oxidation yields $NC(=O)NHCHR(COOH)$ which would be expected to hydrolyze to $HO_2C-NHCHR(COOH)$ which, in turn, should decarboxylate to $NH_2CHR(COOH)$.

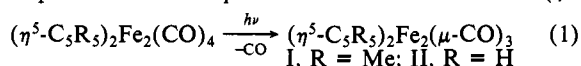
Dinuclear, 18-Electron Species Having a Triplet Ground State: Isolation, Characterization, and Crystal Structure of Photogenerated $(\eta^5-C_5Me_5)_2Fe_2(\mu-CO)_3$

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We wish to report the preparation and characterization of $(\eta^5-C_5Me_5)_2Fe_2(\mu-CO)_3$ (I), a 32- e^- molecule that can be formulated as having two 18- e^- Fe centers but by virtue of its symmetry has a triplet ground state. In some respects the electronic structure of I resembles that of ground-state O_2 in that for I and for O_2 the highest occupied molecular orbital (HOMO) is of π symmetry, antibonding, 2-fold degenerate, and doubly occupied. Compound I was previously shown by IR to be generated upon photolysis of $(\eta^5-C_5Me_5)_2Fe_2(CO)_4$ in a low-temperature organic glass,² eq 1. The IR spectrum of I or the related $(\eta^5-$



(1) (a) Department of Chemistry, MIT. (b) The Ohio State University. (c) Francis Bitter National Magnet Laboratory, MIT.

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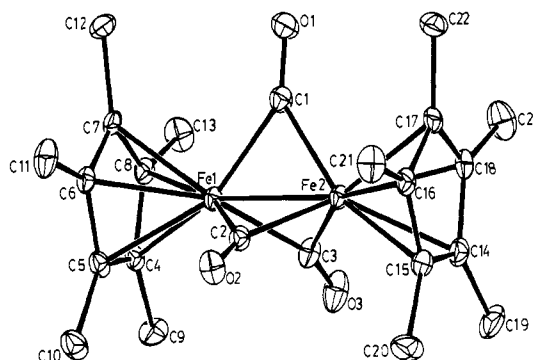


Figure 1. ORTEP diagram of $(\eta^5-C_5Me_5)_2Fe_2(\mu-CO)_3$ showing the atom labeling scheme and 30% probability ellipsoids. Selected bond distances and angles: Fe1-Fe2 = 2.265 (1); Fe1-C1 = 1.935 (6); Fe1-C2 = 1.920 (6); Fe1-C3 = 1.915 (6); Fe2-C1 = 1.928 (6); Fe2-C2 = 1.919 (6); Fe2-C3 = 1.927 (7); C1-O1 = 1.162 (7); C2-O2 = 1.167 (7); C3-O3 = 1.171 (7); C1...C2 = 2.713; C1...C3 = 2.653; C2...C3 = 2.715 Å; Fe1-C1-Fe2 = 71.8 (2)°; Fe1-C2-Fe2 = 72.3 (2)°; Fe1-C3-Fe2 = 72.2 (2)°. The three CO's and the two Fe atoms define three planes. Dihedral angles between the planes Fe1-Fe2-O1 (1), Fe1-Fe2-O2 (2), and Fe1-Fe2-O3 (3) are 1-2 = 115.2°, 1-3 = 121.4°, and 2-3 = 123.4°.

$C_5H_5)_2Fe_2(CO)_3$ (II)^{2,3} in the CO stretching region shows one absorption in the bridging CO region, consistent with a high symmetry structure now confirmed for I by an X-ray structure determination, Figure 1.

While thermal back reaction of I with CO occurs with a good rate at 298 K as is the case with II,⁴ a vigorously Ar purged alkane solution of $(\eta^5-C_5Me_5)_2Fe_2(CO)_4$ ⁵ gives isolable quantities of I upon 355-nm photolysis. A better synthesis of I results from photolysis of $(\eta^5-C_5Me_5)Fe(CO)_2H$ under the same conditions, because the hydride is more soluble than the dinuclear precursor and larger amounts of I can be prepared. Compound I is H_2O and O_2 sensitive and reacts rapidly with CO to generate $(\eta^5-C_5Me_5)_2Fe_2(CO)_4$ and with other 2- e^- donor ligands, L, to give substitution products $(\eta^5-C_5Me_5)_2Fe_2(CO)_3L$. The IR of I at 298 K in the CO stretching region exhibits one absorption at 1785 cm^{-1} , as reported for low temperature,² and the UV-vis in alkane exhibits absorption maxima at 880 nm (ϵ 3400 $M^{-1} cm^{-1}$) and 510 nm (ϵ 17000 $M^{-1} cm^{-1}$), again consistent with the low-temperature spectrum.² The X-ray structure,⁵ Figure 1, shows the highly symmetrical structure expected from the IR. In particular, the C_5Me_5 rings are pentahapto systems with planes perpendicular to, and centered on, the Fe-Fe bond, and the three CO's symmetrically bridge the two Fe centers.⁵ The molecule possesses no crystallographically imposed symmetry. I is isomorphous and isostructural with the Mn and Re $(\eta^5-C_5Me_5)_2M_2(\mu-CO)_3$,⁶ 30- e^- species.

Compound I does not show a detectable 1H NMR in hydrocarbon solution in the temperature range ~ 196 to 298 K. This, initially confusing, finding is due to the fact that I is paramagnetic, and the broadened resonance that would be expected is not seen due to the low solubility. The diamagnetic $(\eta^5-C_5Me_5)_2Fe_2(CO)_4$ is quantitatively formed upon exposure of hydrocarbon solutions of I to CO, as monitored by growth of a singlet in the 1H NMR

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(5) After purification by chromatography on Al_2O_3 (eluted with hexane/toluene, 4:1), I can be crystallized from hexanes in the triclinic crystal system, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 9.744$ (2) Å, $b = 13.360$ (5) Å, $c = 8.752$ (2) Å, $\alpha = 93.98$ (3)°, $\beta = 101.44$ (2)°, $\gamma = 73.47$ (3)°, $V = 1070.44$ Å³. Data, in the range $3^\circ < 2\theta < 55^\circ$ and with general indices $(\pm h, \pm k, +l)$, were collected at $-50^\circ C$ by using Mo $K\alpha$ radiation on an Enraf-Nonius CAD4F-11 diffractometer. Data collection, reduction, and refinement procedures have been described in detail elsewhere (Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, 19, 3379). Hydrogen atoms were ignored and all other atoms were refined anisotropically. Final residual indices were $R_1 = 0.051$ and $R_2 = 0.067$ for 2997 observed reflections [$F_o > 6\sigma(F_o)$] and 253 variables.

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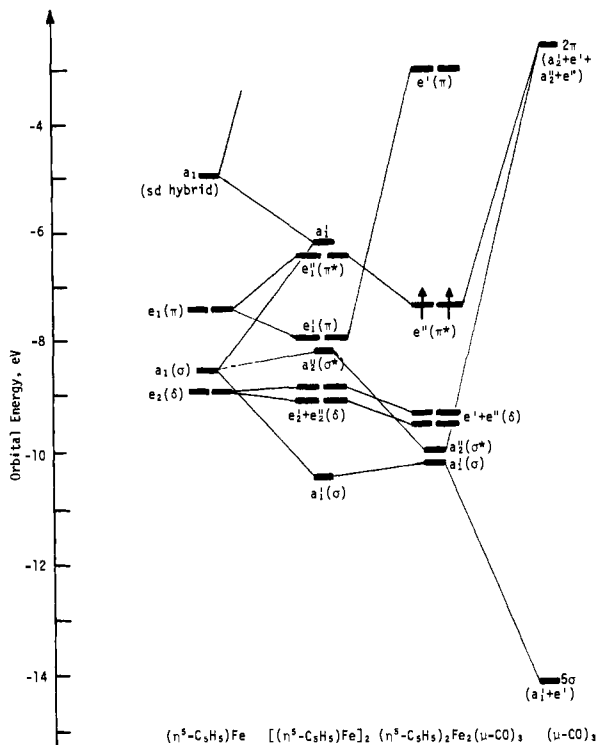


Figure 2. Molecular orbital diagram for II. The diagram for I is essentially the same except for the one-electron energies.

at 1.61 ppm in toluene- d_6 . The magnetic susceptibility of I (as a pure solid) has been determined for three independently prepared samples (including the sample from which the crystal for the structure determination was selected),⁷ and the data give an effective magnetic moment, μ_{eff} , of $2.5 \pm 0.1 \mu_B$, independent of temperature in the range 50–300 K. A consideration of the symmetry of the molecule leads to the expectation that I would have a triplet ground state due to a half-filled, doubly degenerate HOMO derived from overlap of the Fe (d_{xz} , d_{yz}) orbitals. A Fenske–Hall⁸ molecular orbital calculation for II gives the one-electron energy level diagram shown in Figure 2 where the HOMO is the π^* orbital derived principally from the interaction of the Fe (d_{xz} , d_{yz}) orbitals. A similar diagram would be expected for I,⁹ except the levels will be somewhat destabilized due to the extra electron density associated with 10 methyl groups. No EPR signal can be found for alkane solutions of I in the temperature range 100–300 K. The μ_{eff} declines somewhat below 50 K, $\mu_{\text{eff}} = 2.36$ at 10 K, indicating a zero field splitting of the triplet state. This is consistent with the absence of an EPR signal.

In the left-most column of Figure 2, the $e_2(\delta\delta)$, $a_1(d\sigma)$, $e_1(d\pi)$, and $a_1(sd\sigma)$ hybrid metal-based frontier orbitals of the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$ fragment are shown. These are combined into frontier orbitals of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}]_2$ resulting most notably in $a_1'(\sigma)$, $a_2''(\sigma^*)$, $e_1'(\pi)$, $e_1''(\pi^*)$, and four essentially nonbonding δ levels. When these orbitals are allowed to interact with three CO molecules symmetrically disposed about the Fe–Fe bond, the σ and π orbitals are destabilized through interaction with the CO 5σ orbitals; the σ^* and π^* orbitals are stabilized via donation into the empty 2π orbitals of the CO ligands. The resulting occupied MO's of II,

labeled according to the D_{3h} symmetry of the $\text{Fe}_2(\mu\text{-CO})_3$ core, are $a_1'(\sigma)$, $a_2''(\sigma^*)$, $e' + e''$ (δ nonbonding), and $e''(\pi^*)$ orbitals, the last of which being half-occupied with two electrons results in a triplet ground state. Thus, the HOMO is π^* with respect to the Fe–Fe interaction. The isostructural analogue of I, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\mu\text{-CO})_3$,⁶ which has $30 e^-$, is diamagnetic.

The electronic structure of I and II closely resembles that of the diamagnetic triplet-decker Fe sandwiches $\text{Fe}_2(\text{CO})_9$ and $(\eta^4\text{-C}_4\text{R}_4)_2\text{Fe}_2(\mu\text{-CO})_3$ ¹¹ which have been analyzed by Hoffmann and co-workers.^{11,12} It is notable that these latter two systems are 34- and 30- e^- systems, respectively, whereas I and II are 32- e^- systems formally isovalent with $\text{Fe}_2(\text{CO})_9$.²⁺ The removal of two weakly Fe–Fe antibonding electrons together with a higher formal Fe oxidation state most likely account for the appreciably shorter ($\sim 0.26 \text{ \AA}$) Fe–Fe bond in I compared to $\text{Fe}_2(\text{CO})_9$.¹³ It is noteworthy that $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-NO})_2$ is reportedly diamagnetic;¹⁴ though isoelectronic with I with II the symmetry¹⁵ of the $\text{Fe}_2(\mu\text{-NO})_2$ core is such that the HOMO is not expected to be 2-fold degenerate.

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Registry No. I, 87985-71-5; II, 87985-70-4; $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\text{CO})_4$, 35344-11-7; $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}(\text{CO})_2\text{H}$, 80409-91-2.

Supplementary Material Available: Tables I and II giving final positional and thermal parameters and final observed and calculated structure factors for $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\mu\text{-CO})_3$ (14 pages). Ordering information is given on any current masthead page.

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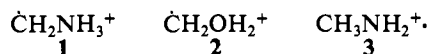
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Reactions of Cyclic Cation Radicals with Nucleophiles: A New Route to Distonic Ions

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Distonic ions¹ such as those represented as **1** and **2** are intriguing



species because often they have no stable neutral counterpart. Ions adopting the distonic form, **1**, have been predicted to be surprisingly more stable than the corresponding conventional isomer, e.g., **3**.² The predicted existence of distonic ions has been confirmed recently in a number of experimental studies.^{3,4}

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(7) The magnetic susceptibility was recorded from 10 to 298 K with pure I loaded in the sample container under an inert atmosphere. After the measurement, the sample was recovered, dissolved in O_2 -, H_2O -free hydrocarbon and reacted with CO to generate $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\text{CO})_4$. The solvent was removed, the solid was isolated, and the magnetic susceptibility was recorded as a control for possible paramagnetic impurity in I and to establish the diamagnetic correction.

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