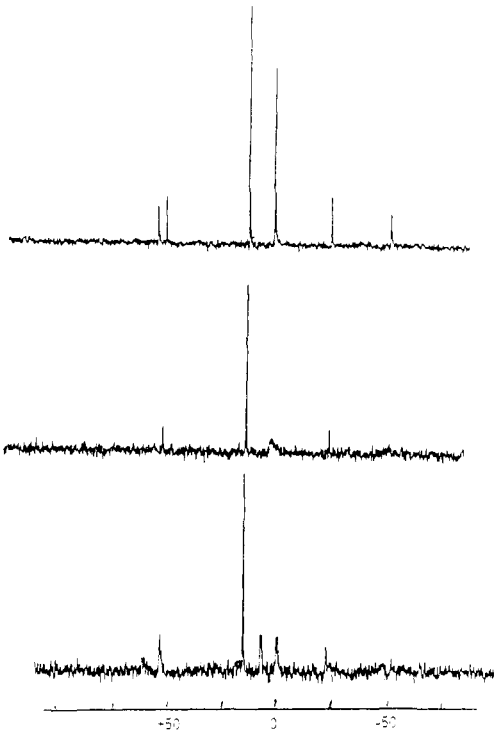
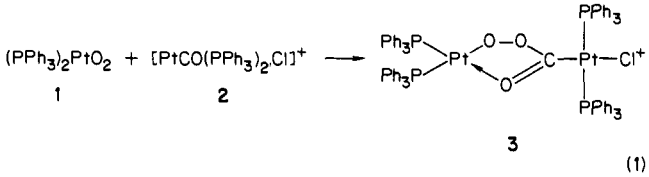


Figure 1. $^{31}P\{^1H\}$ NMR spectra of 3 in CH_2Cl_2 at (A) 298, (B) 233, and (C) 193 K (ppm vs. external 85% H_3PO_4).

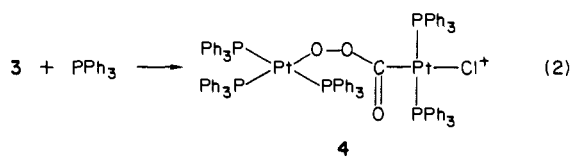
and Poropak Q columns indicated that no CO or CO_2 is given off. A colorless product **3** can be isolated and recrystallized from



(1)

CH_2Cl_2/Et_2O in 83% yield. Anal. Calcd for $C_{73}H_{60}O_3BClF_4P_4Pt_2$: C, 54.06, H, 3.73, P, 7.64. Found: C, 53.84; H, 4.00; P, 7.80, mp 180 °C dec.

The $^{31}P\{^1H\}$ NMR spectrum of **3** at 298 K has two singlet resonances (with ^{195}Pt satellites) at δ 16.22 $^1J(PtP)$ = 1918 Hz and δ 4.85 $^1J(PtP)$ = 1358 Hz. Cooling the sample to 258 K leads to collapse of the higher field singlet (Figure 1) and further cooling to 218 K leads to reappearance of the resonance as a doublet δ 8.21 and 1.21 $^2J(P,P)$ = 24.4 Hz. From these data, it may be deduced that compound **3** is a peroxy carbonyl complex in which the cis phosphorus atoms are equivalent on the NMR time scale. This may arise from dissociation of the Pt–carbonyl oxygen bond and rotation about the Pt–O bond. The singlet resonance at δ 16.2 for the trans P atoms in **3** remains sharp and unchanged at lower temperatures. Lithium chloride or phosphoric acid reacts with **3** to give CO_2. The addition of PPh_3 to **3** in CH_2Cl_2 leads to a substitution of the carbonyl oxygen ligand and formation of **4**.[4]



(2)

A preliminary survey to asses the generality of the MO_2 + MCO reaction indicated that the dioxygen metal complexes **1**, $Pd(PPh_3)_2O_2$, and $Ir(O_2)(PPh_3)_2(CO)Cl$ yield rapid CO_2 evolution when mixed with CH_2Cl_2 solutions of $Pt(PPh_3)(CO)Cl_2$, $[Fe(C_5H_5)(CO)_3]PF_6$, and $Pd(PPh_3)_2Cl_2$ first treated with CO. Intermediates analogous to **3** were not detected in these reactions. Reactions of the dioxygen complexes with $W(CO)_6$ and $Ru(PPh_3)_2(CO)_2Cl_2$ were very slow and reactions were not discernible with $Ir(PPh_3)_2(CO)Cl$, $Rh(PPh_3)_2(CO)Cl$, and $[Fe(C_5H_5)(CO)_2]_2$. The CO in acyl complexes such as $Pt(PR_3)_2Cl(COR)$, R = CH_3, C_6H_5, was not oxidized by the dioxygen complexes.

The addition of the dioxygen complex **1** to $[Fe(C_5H_5)(CO)_2(CS)]PF_6$ in CH_2Cl_2 results in rapid disappearance of ν(CS) at 1348 cm^{-1} and a slower decay of the ν(CO) centered at 2020 cm^{-1}. The formation of carbonyl sulfide (OCS) and CO_2 was confirmed by GLC and IR. The oxidation of the coordinated thiocarbonyl ligand has not previously been reported.[5]

The reactivity pattern that emerges from the observations described in this study is the reactions of the dioxygen complex $Pt(PPh_3)_2O_2$ as a nucleophile such as previously demonstrated in reactions with acids,[6] alkyl halides,[7] ketones, and aldehydes[8] which form the corresponding peroxides or ozonides. The dioxygen complexes thus react with metal carbonyl complexes which are susceptible to nucleophilic attack[9] to form a cycloperoxycarbonyl which subsequently decomposes to form CO_2. This new reactivity pattern thus provides new insights on a mechanism for the CO–O_2 reaction in which dioxygen is activated by a metal atom and CO is activated on a second metal atom.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also supported by the National Science Foundation (CHE-8410454). We thank the Perkin-Elmer Corporation for the Perkin-Elmer Model 983 infrared spectrophotometer and Douglas Meinhart for collecting the ^{31}P NMR spectra.

(4) IR 1680 cm^{-1}; $^{31}P\{^1H\}$ NMR δ 6.395 (J(Pt–P) = 1849 Hz), 11.51 (d, J(PP) = 11.51 Hz), 12.7 (t); Anal. Calcd for $Pt_2C_{91}H_{75}P_5O_2BF_4Cl \cdot 0.25CH_2Cl_2$: C, 58.0, H, 4.03, Cl, 2.82, P, 8.20. Found: C, 57.6; H, 4.17; Cl, 2.84; P, 8.35. mp 121 °C dec.

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Specific Side-Chain Cleavage of Tryptophan, Tryptophanyl Derivatives, and Tryptophanyl Dipeptides Using Hypervalent Iodine

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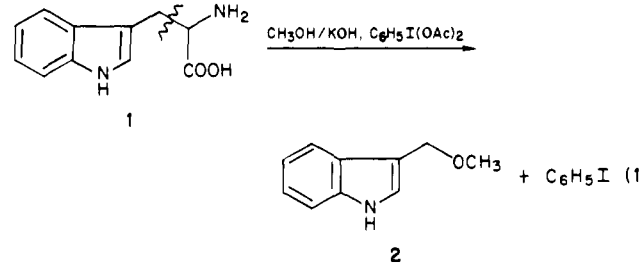
Received February 4, 1985

We wish to report a novel and specific cleavage reaction for L-tryptophan (**1**) and various derivatives (Table I) as exemplified by **1** → **2** (eq 1).



(1)

This process is a β-cleavage of the side chain and has not been observed, heretofore, in chemical systems; however, such a pathway

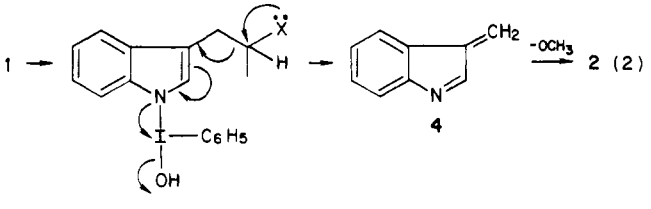
Table I. Cleavage of Tryptophan and Derivatives To Yield 3-(Methoxymethyl)-3*H*-indole (**2**) Using Hypervalent Iodine[a]

entry	compd[c]	3-(methoxymethyl)-3*H*-indole (**2**)[e] yield, %
1	L-tryptophan (**1**)	81
2	DL-tryptophan methyl ester	72
3	*N*-methyl-L-tryptophan	73
4	DL-tryptophanamide	52
5	1-methyl-DL-tryptophan	0
6	*N*-acetyl-DL-tryptophan	0
7	tryptamine	67
8	tryptophol	64
9	DL-indolelactic acid	78
10	indole-3-acetic acid	73
	dipeptides[b]	
11	L-tryptophyl-L-alanine	68
12	L-tryptophyl-L-phenylalanine	60
13	L-tryptophyl-L-leucine	63
14	L-tryptophyl-L-tryptophan	65
15	*N*-acetyl-L-tryptophyl-L-leucine[d]	0

[a] Cleavage procedure: KOH (30 mmol) was dissolved in MeOH (50 mL) and cooled to 0 °C. Tryptophan (6 mmol) was added to the stirred solution. With stirring at 0 °C, $C_6H_5I(OAc)_2$ was added portionwise over a period of 1.5 h. This resulting mixture was stirred an additional 1.5 h at 0 °C. Then most of the MeOH was removed in vacuo. The product was isolated by extraction with chloroform. After concentration of the extracts the crude product was washed with hexane to remove C_6H_5I and Et_2O was added to yield crystalline **2**. [b] The stability of the peptide bond under the condition used for the cleavage was demonstrated by subjecting L-tryptophyl-L-alanine to a blank reaction in the absence of $C_6H_5I(OAc)_2$. The resulting crude product was derivatized with BuOH/HCl and trifluoroacetic anhydride was analyzed by GC (2 m × 2 mm glass column packed with Tabsorb, 65–210 °C; injector 215 °C, detector 225 °C. Comparison was made with a known TAB standard of alanine. No peak corresponding to alanine TAB (with spiking) was observed under identical chromatographic parameters. [c] Compounds 1–14 are from Aldrich Chemical Co. or Sigma Chemical Co. [d] Shechter, Y.; Burnstein, Y.; Patchornik, A. *Biochemistry* **1975**, *14*, 4497.

has been invoked in biosynthetic schemes for the formation of gramine from tryptophan (**1**)[1] as well as in the enzymic decarboxylation of 3-indoleacetic acid.[2,3] In the present system the easily isolated and known 3-(methoxymethyl)-3*H*-indole (**2**)[4] is obtained in excellent yield (Table I).

In considering a mechanism for **1** → **2**, a priori, the indole system could provide a driving force for fragmentation by supplying electron density (in the sense of an enamine) toward an electron-deficient center formed by oxidation at NH_2 or CO_2^-. Alternatively, the electron-rich indole ring could serve as the site for reaction with C_6H_5IO and fragmentation could proceed by electron release from NH_2 or CO_2^-. Data in Table I favor the latter process as depicted in eq 2 (**1** → **3** → **4** → **2**).



There are five nucleophilic centers in **1** (N_1, C_2, C_3, NH_2, and CO_2^-) and by analogy with the reaction of α-methylene carbonyl systems, $C_6H_5I(OAc)_2/KOH/CH_3OH$, initial nucleophilic addition to C_6H_5IO or $C_6H_5I(OH)OAc$ is likely.[5] The carboxyl group is not a prerequisite for cleavage (entries 2, 3, 7, 8) nor is a free α-amino group (entry 3). Noncleavage in the sense of **1** → **2** for 1-methyltryptophan (entry 5) is a key observation since electron density at C_2 and C_3 should be increased by N_1-methyl substitution. Contrarily, an $-N_1-I(OH)C_6H_5$ intermediate cannot occur in this case, or, more specifically, intermediate **3** could not be formed. Fragmentation via **3** (eq 2) fits all the data in Table I. Noncleavage of α-*N*-acetyltryptophan (entry 6) is due to diminish electron density on nitrogen for the process depicted in eq 2 because of delocalization in amide-type resonance.

Examples of stable N–I(III) bonds as proposed in **3** are available in the cases of iminoiodanes[6] and 1,2-dichloro-1,2-benziodiazol-3(1*H*)-one.[7] Good analogy for nucleophilic addition of amido nitrogen to I(III) reagents comes from mechanistic studies of Loudon et al. on the bis(trifluoroacetoxy)iodobenzene oxidation of amides.[8]

Formation of 9-methoxy-9*H*-reserpine in the $C_6H_5I(OAc)_2/CH_3OH$ oxidation of reserpine has been rationalized on the basis of an intermediate similar to **3**[9] and 3-methyleneindolenine (**4**) has been detected in the indole-3-acetic acid oxidase catalyzed decarboxylation of that compound.[3]

Two items in the structural variations data presented in Table I indicated the potential of this cleavage process (eq 1) for specific NH_2-terminal tryptophanyl peptide cleavage. The first is the necessity for the free primary amino group of the tryptophan and the second is that acylation of the α-NH_2 (entry 6) prevents cleavage in the sense of formation of **2**.

Accordingly, the reaction ($C_6H_5I(OAc)_2CH_3OH/KOH$) was carried out on the dipeptides L-tryptophyl-L-alanine, L-tryptophyl-L-phenylalanine, L-tryptophyl-L-leucine, L-tryptophyl-L-tryptophan, and *N*-acetyl-L-tryptophyl-leucine (entries 11–14, respectively).

In the cases of dipeptides 11–14 cleavage to **2** occurred in good yield (Table I). In agreement with prediction based on eq 2, *N*-acetyltryptophyl-L-leucine did not yield **2**. Control experiments established the stability of the peptides under the reaction conditions (Table I, footnote b). The identity of the other fragment from the dipeptide has not been determined (vide infra).

The cleavage of the tryptophanyl unit on the carboxyl side in proteins using *o*-iodosylbenzoic acid in 4 M quanidinium hydrochloride in 80% aqueous acetic acid has been claimed.[10] Subsequently, it was shown that *o*-iodosylbenzoic acid caused in situ oxidation of the chloride anion (of the buffer) and the reaction was actually an example of the familiar positive halogen cleavage method.[11] At any rate, this type cleavage is essentially different from the fragmentation process **1** → **2** in that in the former, oxindolylalanaine is formed.[12] Amides have been oxidized by using $(CF_3CO_2)_2IC_6H_5$ in CH_3CN-H_2O to yield the product of Hofmann rearrangement.[8,13] In the present work tryptophan-

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

Finally, the cleavage of tryptophan in the sense **1** → **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.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of research.

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 inverso 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 NCCONHCHR(COOH) which would be expected to hydrolyze to $HO_2CNHCHR(COOH)$ which, in turn, should decarboxylate to $NH_2CHRCOOH$.

Dinuclear, 18-Electron Species Having a Triplet Ground State: Isolation, Characterization, and Crystal Structure of Photogenerated $(\eta^2\text{-}C_5Me_5)_2Fe_2(\mu\text{-}CO)_3$

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Received January 8, 1985

We wish to report the preparation and characterization of $(\eta^5\text{-}C_5Me_5)_2Fe_2(\mu\text{-}CO)_3$ (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 $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$ in a low-temperature organic glass,[2] eq 1. The IR spectrum of I or the related $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3$ (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.

$$(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4 \xrightarrow[-CO]{h\nu} (\eta^5\text{-}C_5R_5)_2Fe_2(\mu\text{-}CO)_3 \quad (1)$$
I, R = Me; II, R = H

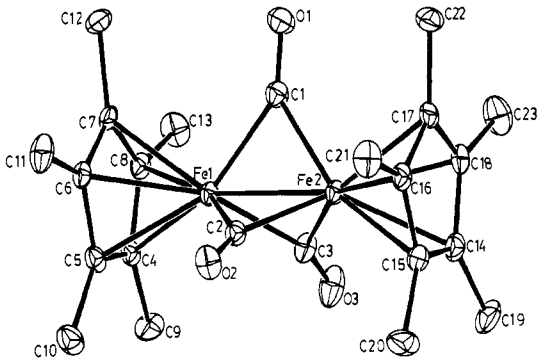

Figure 1. ORTEP diagram of $(\eta^5\text{-}C_5Me_5)Fe_2(\mu\text{-}CO)_3$ showing the atom labeling scheme and 30% probability ellipsoids. Selected bond distances and angles: Fe1-Fe2 = 2.265 (1); Fe1-C1 = 1.935 (6); Fe1-C2 = 1.920 (6); Fe1-C3 = 1.915 (6); Fe2-C1 = 1.928 (6); Fe2-C2 = 1.919 (6); Fe2-C3 = 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°.

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 $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$[5] gives isolable quantities of I upon 355-nm photolysis. A better synthesis of I results from photolysis of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$ 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 $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$ and with other 2-e⁻ donor ligands, L, to give substitution products $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_3L$. 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 17 000 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 $(\eta^5\text{-}C_5Me_5)_2M_2(\mu\text{-}CO)_3$,[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 $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$ 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)°, $V = 1070.44$ Å^3. Data, in the range $3° < 2\theta < 55°$ and with general indices $(\pm h,\pm k,+l)$, were collected at −50 °C by using Mo Kα 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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