

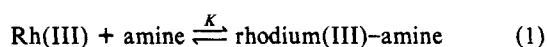
Table I. Binding Constants of Amines with Rhodium(III) Porphyrins in CHCl₃ at 15 °C^a

amine	<i>K</i> (M ⁻¹) Rh porphyrin	
	1c	1d
3	5 × 10 ⁶	1.6 × 10 ⁵
5b	2.9 × 10 ⁵	3.9 × 10 ⁵

^a [Rh porphyrin]_{total} = 4.30 × 10⁻⁵ M.

¹H NMR and IR spectra of adduct 1a-2 for CDCl₃ or CHCl₃ solutions showed nonequivalent OH proton resonances at δ 8.85 (1 H) and 6.00 (1 H) and ν_{OH} and ν_{CO} at 3430 and 1728 cm⁻¹, respectively. A large (~3 ppm) downfield shift of one OH proton and significant shifts to lower wavenumbers in ν_{OH} (~100 cm⁻¹) and ν_{CO} (14 cm⁻¹) as compared with those for reference compounds¹¹ indicate that the adducts of 1a and amino esters contain an intramolecular hydrogen bond between OH and CO₂CH₃ groups in addition to a common Rh-NH₂- coordination bond (refer to 6, R = CH₃ and X = CH₂C₆H₅, or CH₂CH(CH₃)₂).¹² A similar dual interaction has been observed for the C-bound acetone-rhodium derivatives of *trans*-bis(hydroxynaphthyl)-porphyrin (1c) and its *cis* isomer (1d).⁸ Compound 1a in CDCl₃ was also found to extract 1 mol of free amino acids such as phenylalanine and leucine in water at neutral pH to form similar two-point amino acid adducts (6, R = H and X = CH₂C₆H₅ or CH₂CH(CH₃)₂) irreversibly; ν_{OH} centered at 3400 cm⁻¹ and ν_{CO} 1717 cm⁻¹ for the phenylalanine adduct.¹³

Reversible amine coordination (eq 1) was achieved by using related Rh(III) porphyrins having an organic trans ligand in place of Cl. Amines 2-5 reversibly bind with 1c and 1d. In the latter



the acetone moiety is attached to Rh at the OH-containing side of the porphyrin plane.⁸ The binding constants (*K*) for 3 and 5b were determined by spectrophotometric titration with good isosbestic behaviors¹⁴ and are summarized in Table I. Although 1d whose open coordination site has no nearby OH groups (refer to 8) shows a slight preference for 5b over 3 (*K*_{1d}(3)/*K*_{1d}(5b) = 0.41), 1c binds 3 17 times more strongly than 5b (*K*_{1c}(3)/*K*_{1c}(5b) = 17). Although, in a different viewpoint, 5b is bound with 1d slightly more tightly than with 1c (*K*_{1c}(5b)/*K*_{1d}(5b) = 0.74), 3 prefers 1c to 1d by a factor of 31 (*K*_{1c}(3)/*K*_{1d}(3) = 31). These results indicate that the hydrogen bonding in the adduct 1c-3¹⁵ (7, R = CH₃ and X = CH₂CH(CH₃)₂) gives rise to a selectivity factor of 17/0.41 = 31/0.74 = 42, corresponding to a stabilization energy of *RT* ln 42 = 2.1 kcal/mol (15 °C). Reversible and highly selective amino ester binding with 1c was directly shown by the NMR spectrum for a 1:2:2 mixture of 1c, 3, and 5b in CDCl₃ ([1c] = 4.1 mM) affording two adducts 1c-3 and 1c-5b in a ratio of approximately 20:1.¹⁶ Reversible amino acid extraction from

neutral aqueous solutions was also achieved with 1c but practically not with 1d which lacks appropriate hydroxyl groups to assist ligand binding. Thus, vigorous stirring of a CDCl₃ solution of 1c (4.1 mM) and a saturated aqueous solution of phenylalanine gave adduct 7 (R = H and X = CH₂C₆H₅)¹⁷ (ν_{CO} for the CO₂H group at 1720 cm⁻¹)¹³ together with unbound 1c in a ratio of 1:2.4. Other amino acids such as tryptophan, leucine, and isoleucine were extracted similarly. Competitive extraction of phenylalanine and leucine demonstrated no significant difference in their extractabilities, indicating that π stacking interactions⁶ between an aromatic amino acid and the porphyrin plane are not important.

This work presents a novel example of two-point fixation of amino acids and amino esters in nonionic forms. It is significant that the weaker interaction, hydrogen bonding, in fact brings about a sizable selectivity for amino esters in homogeneous solutions and also plays a crucial role in amino acid extraction from neutral aqueous solutions. Suitable modification of the present porphyrin may allow three-point interactions¹⁸ with amino acids. Tri-functional chiral metalloporphyrins have been prepared,¹⁹ and further work is now under way along this line.

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(16) Adducts 1c-3 and 1c-5b gave sharp NMR resonances in high field region at -30 °C: δ -5.26 and -5.60 (diastereotopic CH₃COCH₂-Rh), -4.69 and -5.50 (NH₂), -3.10 (CHNH₂), -2.10 (CH₃COCH₂-Rh), -1.23 (CH₂C-H(CH₃)₂), -0.71 (CH(CH₃)₂), and -0.14 and -0.91 (CH(CH₃)₂) for 1c-3; δ -5.74 (NH₂), -5.32 (CH₃COCH₂-Rh), -3.88 (CHNH₂), -2.10 (CH₃CO-CH₂-Rh), and -2.60, -1.40, -1.15, -0.96, and -0.10 (CH₂ and CH₃ in amine ligand) for 1c-5b. The selectivity (1c-3)/(1c-5b) is based on integration of these high field signals in the spectrum for a 1:2:2 mixture of 1c, 3, and 5b at -30 °C.

(17) Adduct 7 (R = H and X = CH₂C₆H₅) in the presence of unbound 1c gave sharp and characteristic NMR signals at -30 °C for the phenylalanine and acetone ligands and meso protons in a similar manner as adduct 1c-3 (7),¹⁶ but both hydroxyl (in the naphthol moiety) and carboxyl proton resonances could not be detected. This was also the case for adduct 6 (R = H and X = CH₂C₆H₅). It seems that the protons in the OH and CO₂H groups which are hydrogen bonded undergo extensive broadening due to rapid exchange.

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The C=C Double Bond of Tetrafluoroethylene

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Tetrafluoroethylene is an unusual olefin, with one of the weakest carbon-carbon double bonds known [*D*(C=C) ~ 60 kcal/mol]. Unfortunately, the experimental C=C bond energy for C₂F₄ remains quite uncertain, with values ranging from 53 to 76 kcal/mol.¹⁻³ In addition, the nature of the double bond in C₂F₄ has also been disputed: the importance of bent or "banana" bonds versus the conventional σ and π bonds has not been addressed quantitatively, although a recent paper has suggested that bent

(11) The corresponding absorptions for reference compounds are as follows: δ_{OH}, 6.15 (1 H) and 5.68 (1 H) for adduct 1a-4 and 5.23 (2 H) for the free base porphyrin of 1a; ν_{OH}, 3529 cm⁻¹ for 1a-4, 3524 cm⁻¹ for 1a, and 3520 cm⁻¹ for the free base porphyrin of 1a; ν_{CO}, 1742 cm⁻¹ for 1b-2.

(12) Other characteristic NMR signals for 1a-2 are as follows: δ -4.42 and -5.23 (both 1 H, m, diastereotopic NH₂), -3.20 (1 H, m, CHNH₂), 0.07 and 0.48 (both 1 H, m, diastereotopic CH₂C₆H₅), and 10.28 and 10.20 (both 1 H, s, meso-H).

(13) A shift to lower wavenumber by ~20 cm⁻¹ in ν_{CO} as compared with ν_{CO} at 1737 cm⁻¹ for adduct 1b-phenylalanine is consistent with an intramolecular hydrogen bonding between OH and CO₂H groups in 6 (R = H) and 7 (R = H).

(14) Compounds 1c and 1d undergo a considerable red-shift of their Soret absorption upon complex formation with amines; e.g., λ_{max} for 1c-3 (7, R = CH₃ and X = CH₂CH(CH₃)₂) (CHCl₃ solution) 421, 537, and 567 nm. Spectra in the region of 500-600 nm with varying amounts of amine were recorded, where isosbestic points were observed at 528, 548, and 566 nm in the case of titration of 1c with 3. Binding constants (*K*) were calculated from absorbance changes at 557 nm, a λ_{max} for 1c, according to *K* = [rhodium-amine]/[Rh][amine].

(15) Adduct 1c-3 (7) and 1d-3 (refer to 8) showed ν_{CO} for CO₂CH₃ groups respectively at 1728 and 1740 cm⁻¹, indicating a characteristic shift by 12 cm⁻¹ in ν_{CO} for 1c-3 due to hydrogen bonding.

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(1) An indirect determination of *D*(F₂C=CF₂) from the heat of formation of C₂F₄ (Δ*H*_{f,298}^o = -157.4 ± 0.7 kcal/mol) and a 1977 experimental value for Δ*H*_{f,298}^o(CF₂) = -52 kcal/mol (Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* 1984, 13, 695) yields *D*₂₉₈ = 53.4 ± 0.7 kcal/mol.

(2) Using another (more recent) determination of Δ*H*_{f,298}^o(CF₂) = -44.2 ± 1 kcal/mol (Berman, D.; Bomse, D. S.; Beauchamp, J. L. *Int. J. Mass Spec. Ion Phys.* 1981, 39, 263) yields *D*₂₉₈ = 69.0 ± 2.7 kcal/mol.

(3) This value constitutes the only directly determined bond energy (*D*₂₉₈ = 76.3 ± 3 kcal/mol) for C₂F₄ in a Knudsen cell equilibrium study at high temperature (~1200 K) by Zmbov et al. (Zmbov, K. F.; Uy, O. M.; Margrave, J. L. *J. Am. Chem. Soc.* 1968, 90, 5090).

Table I. C=C Bond Energies (D_e) in kcal/mol for $F_2C=CF_2^a$

calculation	total energies (hartrees)		$D_e^{diab}(F_2C=CF_2)^c$	$D_e(H_2C=CH_2)^d$	$D_e^{diab}(F_2C=CF_2)$	
	$F_2C=CF_2 (^1A_1)$	$CF_2 (^3B_1)^b$			direct ^e	using ΔE_{ST}^f
HF	-473.49255 (1/1)	-236.64724 (1/1)	124.3	122.2	59.4	9.3
HF*S*D	-474.07613 (18772/34184)	-236.92980 (3155/16053)	135.9	153.7	39.1	20.9
GVB-RCI	-473.54868 (5/6)	-236.92980 (3155/16053)	159.5	154.6		44.5
CCCI ^g	-473.59909 (1719/2728)	-236.65739 (63/157)	178.4	174.1		63.4
$D_e^{diab} + \Delta_{corr}$						68.3 ± 2.5 ^h
D_{298}						64.5 ± 2.5 ⁱ
expt (D_e)				179.0 ± 2.5 ^j		
expt (D_{298})				172.2 ± 2.1 ^k	53.4 ± 0.7, ^l 69.0 ± 2.7, ^m 76.3 ± 3 ⁿ	

^aVDZD basis on C and VDZ basis on F. See ref 5 for details of the calculations. The corresponding number of spatial configurations/spin eigenfunctions for each wave function are given beneath each total energy. ^bTotal energies for CF_2 are for the appropriate limit at $R(C-C) = \infty$, i.e., HF or HF*S_{val}. ^c $D_e^{diab}(F_2C=CF_2) = 2 \times E(^3B_1 CF_2) - E(C_2F_4)$. ^dIncluded for comparison to $D_e^{diab}(F_2C=CF_2)$ to indicate convergence [$D_e^{expt}(H_2C=CH_2) = 179.0 \pm 2.5$ kcal/mol; ref 5]. ^eDirect $D_e(F_2C=CF_2)$ from $2 \times E(^1A_1 CF_2) - E(C_2F_4)$ where the HF and HF*S*D total energies of $^1A_1 CF_2$ are -236.698 98 and -237.006 93 hartrees (2633 spatial configurations/4399 spin eigenfunctions). ^f $D_e^{diab}(F_2C=CF_2) = D_e^{diab}(F_2C=CF_2) - 2 \times \Delta E_{ST}$, where $\Delta E_{ST} = 57.5$ kcal/mol (ref 7). ^gRCI*[SD_σ + SD_π + S_{val}]. ^h $\Delta_{corr} = 4.9$ kcal/mol is the correlation error inherent to the CCCI method for double bonds (obtained from $D_e^{expt} - D_e^{calc} = 179.0 \pm 2.5 - 174.1 = 4.9 \pm 2.5$ kcal/mol for C_2H_4). ⁱThe predicted D_e is converted to D_{298} by using the temperature and zero-point energy corrections for C_2F_4 from ref 9 and 10. ^j D_{298} and D_e are derived from $\Delta H_{f,298}^\circ$ and $\Delta H_{f,0}^\circ$ (from ref 10a and *J. Phys. Chem. Ref. Data* 1975, 4, 1) with zero-point energy corrections from ref 9a and 12 (Bunker et al.). ^kReference 1. ^lReference 2. ^mReference 3.

bonds may be preferred in C_2F_4 .⁴ In order to settle these issues, we carried out ab initio generalized valence bond with configuration interaction (GVB-CI) calculations, utilizing a new approach in the CI expansion which systematically includes all correlations likely to change appreciably in the bond cleavage process. This correlation-consistent CI (CCCI), so named to indicate that no biases are built into the wave functions of either reactant or product, truncates much more rapidly than traditional singles and doubles CI approaches yet gives much more accurate results.⁵

Table I shows the C_2F_4 bond strength as a function of electron correlation.⁶ Hartree-Fock (variational MO) theory predicts a direct bond energy of 59.4 kcal/mol, by using $\Delta E^{HF} = 2 \times E^{HF}(^1A_1 CF_2) - E^{HF}(C_2F_4)$. This is close to our best estimate of 68.3 kcal/mol but only as an artifact of the incapability of HF theory to properly describe the singlet states of carbenes [e.g., $\Delta E_{ST}(CF_2) = 32.5$ kcal/mol for HF, whereas the CCCI value is 57.5 kcal/mol⁷ and the experimental value is 56.6 kcal/mol⁸], leading to an artificially destabilized dissociation limit.

Including singles and doubles CI (HF*S*D) leads to a bond 20 kcal/mol weaker than HF because it leads to a good description of singlet CF_2 but cannot remove all problems in the HF description of C_2F_4 , even though 34 184 spin eigenfunctions are included in the CI calculation. The problem with HF*S*D is that the triple and quadruple excitations required to properly describe the two fragments are not accounted for in the molecule, resulting in a low bond energy.

The GVB-CCCI method yields much more accurate bond energies (despite using only one-tenth of the configurations), due to its correlation-consistent nature and emphasis on including the dominant correlations important for describing bond rupture. Briefly, the GVB-CCCI method begins with the generalized valence bond wave function, which allows the electrons in the breaking bond to each occupy their own orbital (rather than doubly-occupied as in restricted HF theory) and which results in unique, localized orbitals describing the various bonds. Two sets

of correlations are included in the CCCI: (i) full correlation of the electrons in the breaking bond (i.e., all single and double excitations to all orbitals of the full basis) and (ii) all single excitations from all valence orbitals to allow for orbital shape changes which accompany higher order correlations.⁵ The CCCI result for the C=C bond energy of C_2F_4 is $D_e = 63.4$ kcal/mol.

CCCI calculations on ethylene⁵ lead to a C=C bond energy of $D_e = 174.1$ kcal/mol, which is just 4.9 ± 2.5 kcal/mol weaker than the experimental value (Table I). Assuming the same residual correlation error for C_2F_4 yields a final prediction of $D_e(F_2C=CF_2) = 68.3 \pm 2.5$ kcal/mol. Using experimental values for the zero-point energies of C_2F_4 (13.4 kcal/mol) and CF_2 (4.3 kcal/mol),⁹ along with the temperature correction (1.0 kcal/mol) to the bond energy of C_2F_4 ,¹⁰ we calculate $D_{298}(C_2F_4) = 64.5 \pm 2.5$ kcal/mol.

Of the three experimental values for $D_{298}(C_2F_4)$ listed in Table I, we can rule out the lowest value of 53.4 ± 0.7 kcal/mol, since the CCCI method provides a lower bound on the bond energy (electron correlation error is larger in the molecule than in the fragments). Our theoretical prediction agrees most closely to the intermediate value of 69.0 ± 2.7 kcal/mol.² From our prediction of $D_{298}(C_2F_4)$ plus the experimental $\Delta H_{f,298}^\circ(C_2F_4) = -157.4 \pm 0.7$ kcal/mol, we derive $\Delta H_{f,298}^\circ(CF_2) = -46.5 \pm 1.6$ kcal/mol, in good agreement with the most recent (1981) experimental value² of -44.2 ± 1 kcal/mol. This suggests that the 1977 value¹ of -52 kcal/mol for the heat of formation of CF_2 is in error and that the 1981 value is correct.

Recently there has been some concern whether the CC double bond in C_2F_4 is better described as a σ bond plus a π bond or as two "banana" or bent bonds.⁴ To address this issue, we calculated the relative energies of three C=C bonding configurations: (i) σ and π C-C bonds, (ii) skewed σ and π bonds with no symmetry restrictions, and (iii) symmetric bent bonds. The one-electron GVB orbitals for (i)-(iii) are shown in Figure 1. At the self-consistent GVB-PP level, all three descriptions are within 0.1 kcal/mol in energy, with the unsymmetrical wave function (ii) lowest. When the four electrons involved in the C=C bond are allowed any occupation of the four bonding orbitals (GVB-CI), the three descriptions remain very close in energy (within 0.3 kcal/mol), but the σ and π bond wave function prevails as the lowest energy structure. Thus we believe that the double bond is best thought

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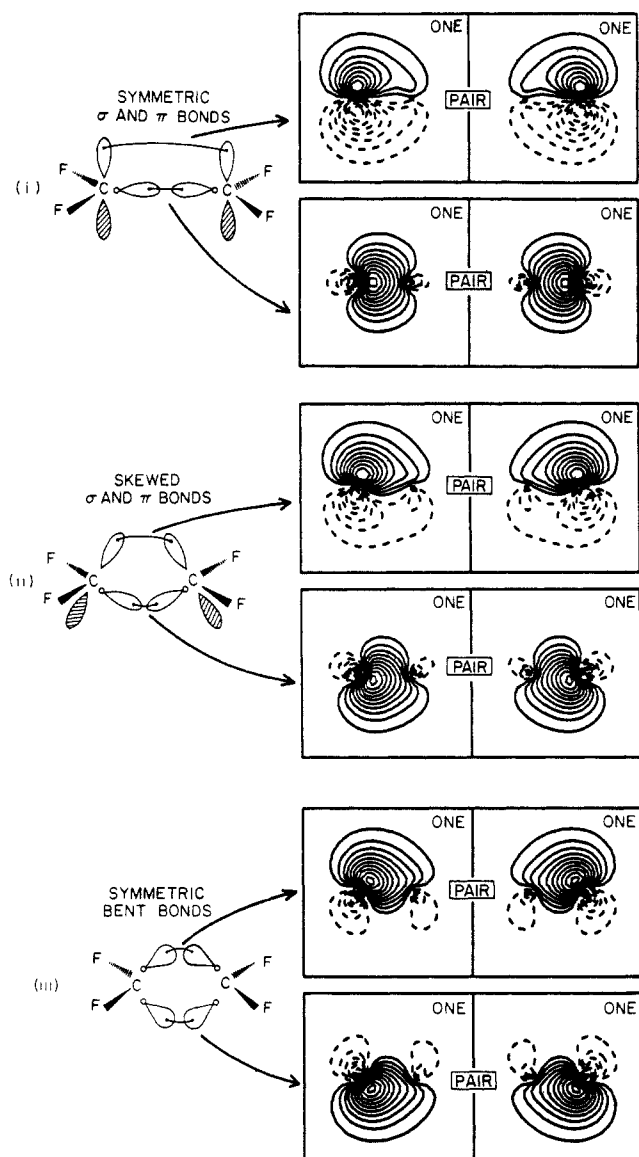


Figure 1. The GVB(2/4)PP one-electron orbitals of the C=C bond in C_2F_4 are shown for (i) (symmetry-constrained) σ and π bonds, $E_{PP(2/4)} = -473.53219$ hartrees, $E_{GVB-CI(2/4)} = -473.54944$ hartrees; (ii) skewed σ and π bonds (no symmetry constraints), $E_{PP(2/4)} = -473.53242$ hartrees, $E_{GVB-CI(2/4)} = -473.54899$ hartrees; and (iii) symmetric bent or "banana" bonds, $E_{PP(2/4)} = -473.53226$ hartrees, $E_{GVB-CI(2/4)} = -473.54924$ hartrees. Contours are plotted from -0.5 to $+0.5$ au, with increments every 0.05 au.

of in terms of the σ and π bond description.¹¹

In conclusion, we report an accurate ab initio theoretical prediction of the bond energy of C_2F_4 [$D_{298}(C=C) = 64.5 \pm 2.5$ kcal/mol] and of the heat of formation of CF_2 ($\Delta H_{f,298}^\circ = -46.5 \pm 1.6$ kcal/mol), by using the newly-developed CCCI methods. The predicted bond energy helps distinguish between the large discrepancies in existing experimental values for $D_{298}(C_2F_4)$, ruling out one estimate (53.4 kcal/mol) and strongly supporting the 69.0 kcal/mol value. In addition, we find that the traditional picture of multiple bonds (σ and π bonds) is correct for C_2F_4 .

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(11) The calculations on $FC\equiv CF$ (ref 4), which find bent bonds ~ 2 kcal/mol lower than $\sigma\pi$ bonds, did not go beyond the GVB-PP description.

(12) Zero-point energies for CF_2 were taken from ref 9b (4.3 kcal/mol) for the 1A_1 state, while the zero-point motion of the 3B_1 state was estimated (4.1 \pm 0.1 kcal/mol) from the frequency shifts in C_2D_2 going to CD_2 (Bunker, P. R.; Jensen, P.; Kraemer, W. P.; Beardsworth, R. *J. Chem. Phys.* **1986**, *85*, 3724) and the frequencies in C_2F_4 . This leads to $T_0(CF_2) = 57.3 \pm 0.1$ kcal/mol [$\Delta E_{ST} = T_0(CF_2) = 57.5$ kcal/mol].

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The Synthesis, Characterization, and Reactivity of a Novel Nitroruthenium(III) Complex

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Transition-metal nitro complexes have attracted much attention due to their ability to act as oxygen atom transfer agents and also because of the potential these reagents have as catalysts for the air oxidation of organic substrates.^{1,2} These complexes have been shown to oxidize a number of organic³⁻¹⁰ and inorganic substrates,¹¹⁻¹⁶ where the corresponding transition-metal nitrosyl complexes are formed along with the oxidized substrates. The metal nitrosyl species which is produced can be oxidized back to the original metal nitro complex by a symmetric cleavage of dioxygen.^{5,6,17-21} While a variety of transition-metal nitro complexes have been studied, only one example of an isolable nitroruthenium(III) complex has appeared in the literature, with no

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