decadiyne (45 μL) in acetone at 59 °C for 2 days. The product is isolated with a crude yield of ~90% by the addition of ether. It contains about 10% of other products, which presumably result from intermolecular cyclization. A singlet at δ 0.52 (6 H) in the ^{1}H NMR spectrum of **2** can only be assigned to the α-methyl groups. Therefore, the upfield singlet at δ 0.60 (6 H) observed in the ^{1}H NMR spectrum of **1** can be also attributed to the resonance of the α-methyl groups, and the singlet at δ 2.22 (6 H) then must be the resonance of the β-methyl groups. In the ^{13}C{^{1}H} NMR spectrum (acetone-d_6) of **2**, the bis-carbene carbon signals are found at δ 265.2.
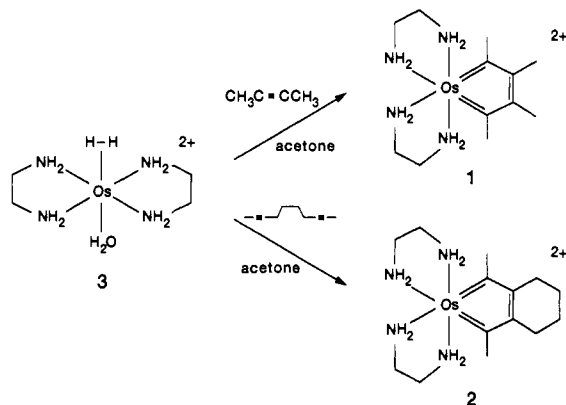
For further structural characterization, a single-crystal X-ray diffraction study was performed on **1** (Figure 1).[6] The OsC$_4$ unit is shown to be planar. The Os–C(5) and Os–C(8) bond distances of 1.940 (8) and 1.931 (8) Å are very close to the 1.90 Å Os–C bond distance observed in an osmium vinylidene complex.[7] The C(6)–C(7) bond distance of 1.357 (12) Å is a typical carbon–carbon double bond, and the C(5)–C(6) and C(7)–C(8) bond distances of 1.461 (13) and 1.448 (12) Å are typical carbon–carbon single bonds as observed in a butadiene structure (1.34 and 1.48 Å, respectively).[8] We conclude that the osmium metallacycle is a localized planar metallacyclopentatriene complex.[9]

A three-stage hydrogen–deuterium exchange is observed when complex **1** is dissolved into D$_2$O. A D$_2$O solution of **1** (7.3 × 10^{-3} mmol, 10.4 mM) kept under N$_2$ is followed by ^{1}H NMR spectroscopy.[10] In less than 2 min, the ^{1}H NMR spectrum shows that the two most downfield proton signals observed in acetone-d_6, corresponding to four amine protons, are now absent. After ~24 h, the peaks at δ 5.89 and 5.67 of the other four amine protons disappeared. Then, while the intensity of the singlet at δ 0.267, the α-methyl resonance, is decreasing, a broad triplet at δ 0.178 (J_{HD} = 1.9 Hz) is slowly growing. In 7 days, ~20% of the α-methyl is monodeuterated.[11] Here, we notice an unusually large

upfield isotope shift ($\Delta\delta$ = 0.089 ppm) from the singlet to the triplet.[12] The β-methyl resonance at δ 2.09 does not change during this period. The presence of acidic protons in the α-methyl groups demonstrated by the hydrogen–deuterium exchange experiment is an indication of the carbene character of the α-metallacycle carbons.[13]

A metallacyclopentatriene is composed of two cis carbene carbons in an unsaturated metallacycle. The study of this class of compounds can provide new insights on both carbene and metallacycle reactivity. An investigation of the chemistry is currently underway, the results of which will be reported later.

(6) Crystal data for **1** (120 K): C$_{14}$H$_{16}$N$_4$OsF$_6$O$_6$S$_2$, orthorhombic, P_{ccn}; a = 14.208 (4) Å, b = 26.409 (7) Å, c = 12.723 (3) Å, V = 4774 (2) Å^3, Z = 8, D_{calcd} = 1.961 g cm^{-3}, μ = 5.597 mm^{-1}. A dark green hexagonal prism specimen (0.40 × 0.30 × 0.30 mm) was used for data collection (Siemens P3RA, 0.0° < 2θ < 55.0°, Mo Kα). Of 6126 reflections collected, 5524 were independent, and 3869 with F_o > 4.0σ(F) were considered observed and were empirically corrected for absorption by using the XABS program (this program generates an absorption correction tensor based on F_o and F_c differences. Hope, H.; Moezzi, B. Chemistry Department, University of California at Davis). The atoms were located by Patterson methods and refined by full-matrix least-squares. Hydrogen atoms were calculated and refined by riding model with fixed isotropic U: R = 4.43%, R_w = 5.20% (R = $\sum\|F_o\|$ – $\|F_c\|/\sum\|F_o\|$; R_w = $\sum\|F_o\|$ – $\|F_c\|w^{1/2}/\sum\|F_o\|w^{1/2}$), all data R = 7.06%, GOF = 0.72. All computer programs and sources of scattering factors are contained in SHELXTL PLUS (G. M. Sheldrick, a program for crystal-structure determination, version 4.0, 1989, Siemens Analytical X-ray Instruments, Madison, WI).

(7) Roper, W. R.; Waters, J. M.; Wright, L. J.; vanMeurs, F. *J. Organomet. Chem.* **1980**, *201*, C27.

(8) Stoicheff, B. P. *Advances in Spectroscopy*; Thompson, H. W., Ed.; Interscience Publishers: New York, 1959; Vol. 1, p 148.

(9) To compare the structure of **1** with its isoelectronic Ir(III) metalla-cyclopentadiene complexes, see: O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 6232.

(10) The ^{1}H NMR resonances of **1** in D$_2$O are shifted upfield by ca. 0.1–0.4 ppm from that in acetone-d_6.

(11) In the presence of base (e.g., propylamine), the α-methyl group is completely deuterated in minutes under similar conditions.

(12) (a) Substitution of a proton with a deuterium atom in a methyl group usually gives an upfield isotope shift of 0.01–0.02 ppm in the ^{1}H NMR spectrum: Batiz-Hernandez, H.; Bernheim, R. A. *Prog. Nucl. Magn. Reson. Spectrosc.* **1967**, *3*, 63. (b) An isotope shift as large as 0.05 ppm is observed in a bimetallic malonyl system: O'Connor, J. M.; Uhrhammer, R. *J. Am. Chem. Soc.* **1988**, *110*, 4448.

(13) Protons on the α-carbon of a Fischer carbene complex are acidic: ref 2a, p 128.

Modeling Fragments for the ab Initio Determination of Electron Density in Polypeptides. An Experimental and Theoretical Approach to the Electron Distribution in Leu-enkephalin Trihydrate

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The electron density of relatively large biomolecules is now accessible to X-ray diffraction techniques. The experience gathered in the last 20 years on smaller systems has shown that ab initio SCF calculations carried out with large, polarized basis sets could provide a near quantitative agreement with properly refined experimental maps.[1] Unfortunately, the dependence of

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(1) (a) Stevens, E. D.; Rys, J.; Coppens, P. *J. Am. Chem. Soc.* **1978**, *100*, 2324–2328. (b) Stevens, E. D.; Rys, J.; Coppens, P. *J. Am. Chem. Soc.* **1977**, *99*, 265–267. (c) Breitenstein, M.; Dannöhl, H.; Meyer, H.; Schweig, A.; Seeger, R.; Seeger, U.; Zittlau, W. *Int. Rev. Phys. Chem.* **1983**, *3*, 335–391. (d) Souhassou, M.; Lecomte, C.; Ghermani, N.-E.; Rohmer, M.-M.; Wiest, R.; Bénard, M.; Blessing, R. H. *J. Am. Chem. Soc.*, in press.
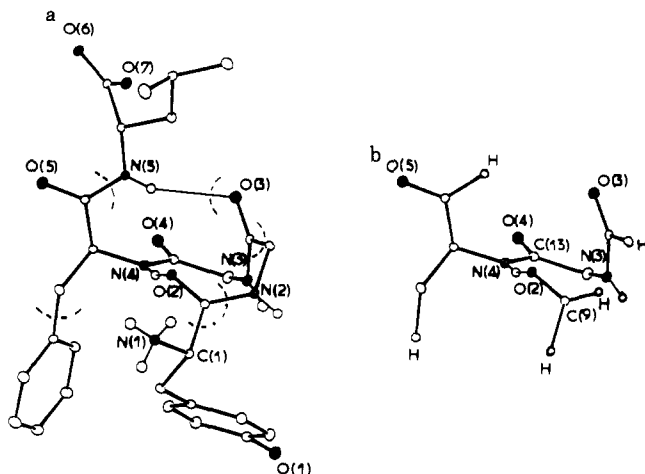
Figure 1. ORTEP view (a) Leu-enkephalin and (b) the molecular fragment used for the SCF calculation.

the SCF algorithm on the fourth power of the contracted Gaussian basis set size makes it practically impossible to perform calculations at this level of accuracy on nonsymmetric systems with more than 20 non-hydrogen atoms. We think, however, that a comparison between theory and experiment at a high level of accuracy remains possible for large polypeptides. The reason is that the representation of the molecular density distribution by properly selected sets of planar maps restricts the global information to a series of snapshots limited each to the description of the bonds lying in the selected plane or in the near vicinity of it. Assuming that the deformation density associated with a localized bond is not affected by substituents beyond the α position, reliable theoretical maps of static deformation density could be obtained from SCF calculations performed on molecular fragments collecting all atoms separated from the reference plane by less than ~ 1.5 Å. The molecular ends located too far apart are then removed, and the dangling bonds are completed with hydrogen atoms with appropriate orientations and bond distances.[2]

This approach has been used for a joint experimental and theoretical study of leu-enkephalin (Tyr[1]-Gly[2]-Gly[3]-Phe[4]-Leu[5]) (Figure 1a), a natural substance that has some analogy with morphine. The crystals used for the low-temperature experiment were recrystallized from water (orthorhombic, $P2_12_12_1$, $Z = 4$, CAD4F, 100 K, Mo Kα radiation, $\sin \theta / \lambda < 1.36$ Å^{-1}). The 40844 measured reflections were reduced to 5444 unique reflections ($I > 2\sigma(I)$, $\sin \theta / \lambda < 1.15$ Å^{-1}). The initial parameters were taken from the room temperature structure of Aubry et al.[4] Then a Hansen–Coppens multipolar refinement[5] was performed. The present values of the agreement indices are as follows: $R(F) = 3.91\%$, $R_w(F) = 2.39\%$, GOF = 0.76. At this stage of refinement, each type of atom of all four peptide links shares the same multipole populations. This restriction limits the experimental study to nonlocal effects. Further work is in progress in order to see the influence of the side chain on the electron density of the peptide bonds.

Figure 2a displays the dynamic deformation model density in a plane defined by the C13–O4–N4 peptide group. The corresponding static theoretical map (Figure 2b) has been obtained from the molecular fragment defined by the dashed lines of Figure 1a and containing seven carbon, four oxygen, two nitrogen, and twelve hydrogen atoms. This fragment is represented in Figure 1b.[6] Atoms O2 and C9 are not bonded to the main part of the
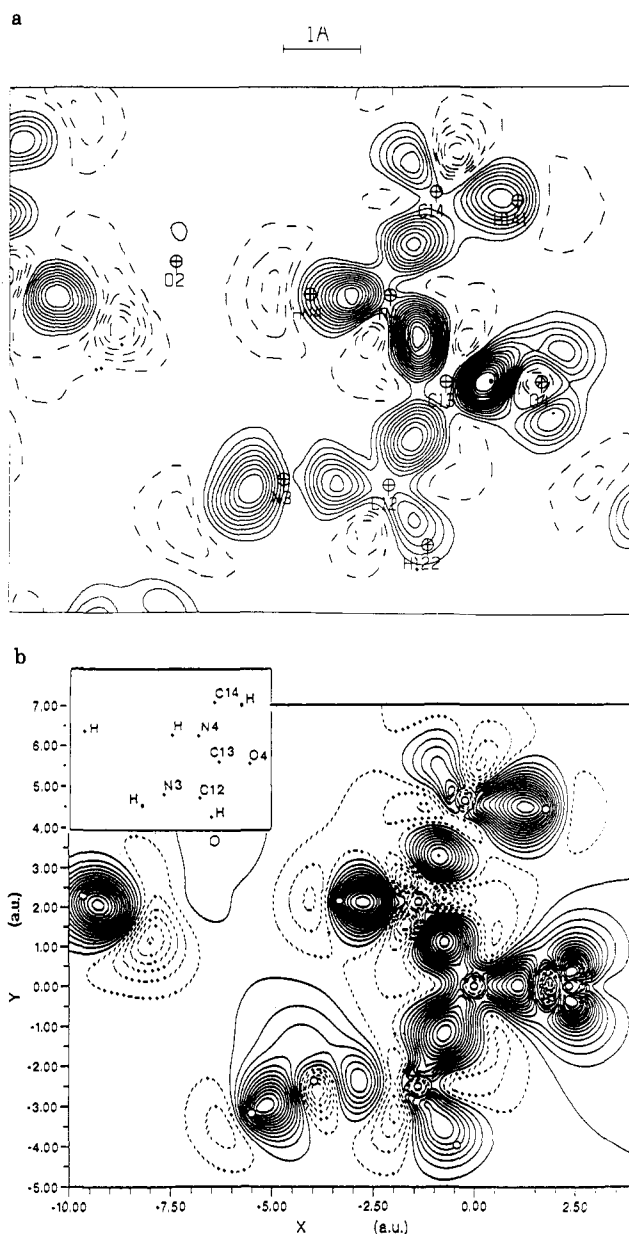

Figure 2. Deformation density in the plane of the N4–C13–O4 peptide group. (a) Experimental dynamic model map: contour interval, 0.05 e Å^{-3}; positive contours, solid; negative, dashed; zero contour omitted. (b) Theoretical map: contour interval, 0.05 e Å^{-3}; zero and positive contours, solid; negative, dashed.

fragment except for a close contact between O2 and H(N4) that has been attributed to an intramolecular hydrogen bond (β turn).[4] The agreement between theory and experiment is similar to what has been reported recently for *N*-acetyl-α,β-dehydrophenylalanine methylamide, a dipeptide for which the SCF calculation has been carried out on the complete molecule.[1d]

The intramolecular close contact which does exist between H(N4) and O2 (d(N4$\cdots$O2) = 2.918 Å; d(H$\cdots$O2) = 1.94 Å) has been attributed to a hydrogen bond.[4] Figure 3 displays the de-

(2) Addressing the general problem of the transferability of fragment properties, R. Bader has recently discussed the modeling of the total charge density of polypeptides from that of molecular fragments.[3]

(3) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893–928. See more specifically pp 926–927.

(4) Aubry, A.; Birlirakis, N.; Sakarellos-Daitsiotis, M.; Sakarellos, C.; Marraud, M. *Biopolymers* **1989**, *28*, 27–40.

(5) Hansen, N. K.; Coppens, P. *Acta Crystallogr.* **1978**, *A34*, 909–921.

(6) The SCF wave function has been computed using the ASTERIX system of programs.[7] Basis sets of triple-ζ + polarization quality have been used to describe all atoms directly contributing to the density contours of the maps (N3, N4, C12, C14 and the attached hydrogen atoms, C9, C13, O2, and O4). The other atoms (C11, C15, C22 and the attached hydrogens, O3, O5, H1(C9), and H2(C9)) are represented by split-valence basis sets. Details about those basis sets can be found in ref 1d.

(7) (a) Ernenwein, R.; Rohmer, M.-M.; Bénard, M. *Comput. Phys. Commun.* **1990**, *58*, 305–328. (b) Rohmer, M.-M.; Demuynck, J.; Bénard, M.; Wiest, R.; Bachmann, C.; Henriet, C.; Ernenwein, R. *Comput. Phys. Commun.* **1990**, *60*, 127–144.

a

b
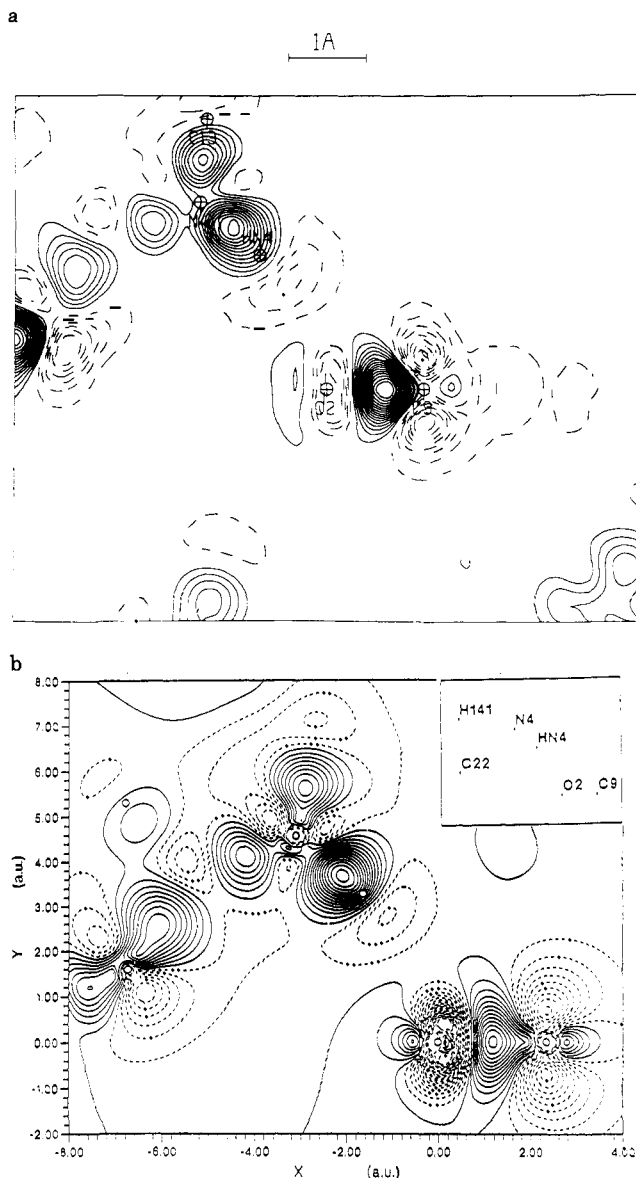
Figure 3. Deformation density in the plane defined by the C9–O2···N4 atoms (β turn). (a) Experimental dynamic model map; contours as in Figure 2a. (b) Theoretical map; contours as in Figure 2b.

formation density in the plane containing the N4, O2, and C9 atoms, respectively obtained from the enkephalin experimental model (Figure 3a) and from the SCF calculation on the fragment (Figure 3b). The O2 oxygen lone pairs do not show up on this map, due to the orientation of the C9–N2 and C9–C1 bonds (both represented by CH bonds in the model fragment) in a plane practically perpendicular to the figure. H(N4) is then faced to a region of density depopulation around O2, a situation which does not agree with the standard hydrogen-bond concept. An investigation of the electrostatic potential derived from the experimental charge distribution,[8a] however, suggests that an electrostatic interaction remains possible. As a matter of fact, the electrostatic potential around the O2 atom has not a "rabbit ear" shape[8] but rather an almost spherical "skull" shape (see Figure 6a,b in ref 8a). Calculations are now being carried out on other model fragments of the molecule in order to investigate, in connection with the experimental electron distribution, the various forms of hydrogen bonding between the enkephalin molecule and the three molecules of crystallization water. An investigation of

the topological properties of the Laplacian of the total charge density, either theoretical[9] or experimental,[10] could also help in locating the nonbonded charge concentrations responsible for the formation of hydrogen bonds.

(9) Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc.* **1984,** *106,* 1594–1605.

(10) (a) Stewart, R. F. In *Application of Charge Density Research to Chemistry and Drug Design*; Jeffrey, G. A., Piniella, J. F., Eds.; NATO ASI Series, Physics; Plenum: New York, 1991; Vol. 250, pp 63–101. (b) Bianchi, R.; Destro, R.; Gatti, C.; Merati, F. *Ibid.*; p 339. (c) Bianchi, R.; Destro, R.; Merati, F. *Ibid.*; p 340. (d) Souhassou, M.; Li, N. American Crystallographic Meeting, Toledo, OH, July 1991.

Boron–Boron Double Bonding in the Species [B₂R₄]²⁻: Synthesis and Structure of [{(Et₂O)Li}₂{Mes₂BB(Mes)Ph}], a Diborane(4) Dianion Analogue of a Substituted Ethylene

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Compounds of boron are characterized by an enormous range of structural types that often possess features rarely found among derivatives of other elements. Accordingly, research on their chemical properties has been prominent for more than three decades.[1] Nonetheless, there remain numerous classes of boron compounds that are, at present, either unknown or only partially understood. For example, there is relatively little structural information available for compounds that have bonds of multiple character between two boron centers,[2–4] nor have compounds of the general formula $(MBR_2)_n$ (M = alkali metal, R = organo group, n = 1, 2, 3...) been well characterized experimentally.[5] In

(1) (a) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, England, 1984. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980.

(2) Structural data appears to be confined to transition metal complexes of heterocycles that incorporate B_2 or B_3 units. B–B distances as low as 1.563 Å have been observed in such complexes. See in the following references: Robinson, W. T.; Grimes, R. N. *Inorg. Chem.* **1975,** *14,* 3056. Herberich, G. E.; Hessner, B.; Hostalek, M. *Angew. Chem., Int. Ed. Engl.* **1986,** *25,* 642. Herberich, G. E.; Hessner, B.; Hostalek, M. *J. Organomet. Chem.* **1988,** *355,* 473. Davis, J. H.; Sinn, E.; Grimes, R. M. *J. Am. Chem. Soc.* **1989,** *111,* 4784. A series of uncomplexed three-membered rings with B–B distances as low as 1.58 Å have been reported: Dirschl, F.; Hanecker, E.; Nöth, H.; Rattay, W.; Wagner, W. Z. *Naturforsch.* **1986,** *41b,* 32. van Bonn, K.-H.; Schreyer, P.; Paetzold, P.; Boese, R. *Chem. Ber.* **1988,** *121,* 1045. Meyer, H.; Schmidt-Lukasch, G.; Baum, G.; Massa, W.; Berndt, A. Z. *Naturforsch.* **1988,** *43b,* 801.

(3) Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1981,** *20,* 870. Berndt, A.; Klusik, H.; Schlüter, K. *J. Organomet. Chem.* **1981,** *222,* C25. These papers describe the preparation and the solution EPR spectra of the tetraalkyldiborane(4) radical anions [B₂R₄]•⁻, e.g., (R = CH₂(t-Bu), which presumably have multiple B–B character. A two-electron reduction of B₂R₄ was not reported.

(4) The existence in solution of species of the type [B₂Ar₄]•⁻ (Ar = C₆H₄(4-NMe₂)) has been postulated in the following reference: Leffler, J. E.; Watts, G. B.; Tanigaki, T.; Dolan, E.; Miller, D. S. *J. Am. Chem. Soc.* **1970,** *92,* 6825.

(5) Compounds of formula MB(C₄H₉)₂ (M = alkali metal) have been implicated in the reduction of ClB(C₄H₉)₂ by Na/K alloy: Auten, R. W.; Kraus, C. A. *J. Am. Chem. Soc.* **1952,** *74,* 3398. For further information on the reduction of diorganoboron halides by Li, Na/K, or Mg, see the following references: Köster, R.; Benedikt, G. *Angew. Chem., Int. Ed. Engl.* **1964,** *3,* 515. Köster, R.; Benedikt, G.; Grassberger, M. A. *Justus Liebigs Ann. Chem.* **1968,** *719,* 187.

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