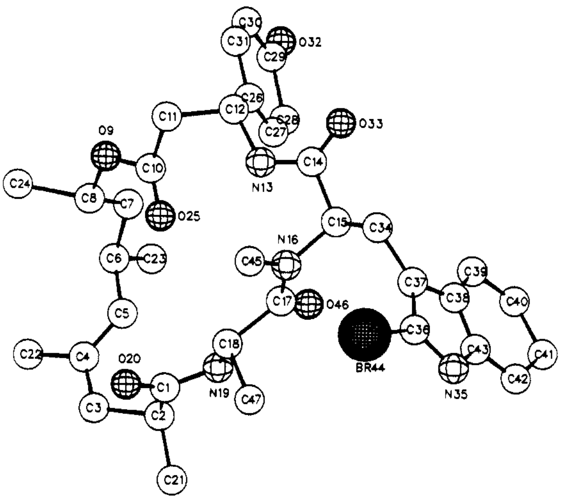
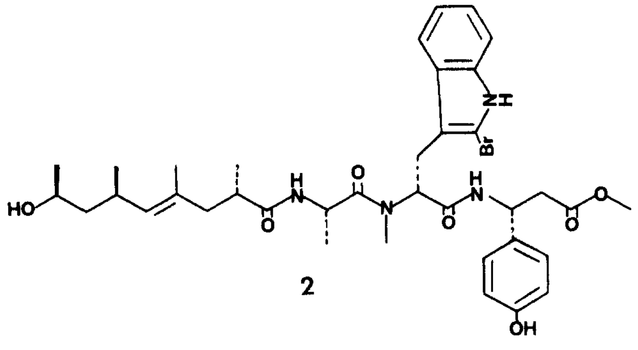


Figure 1. Computer-generated perspective drawing of the current X-ray model of jaspamide acetate. Hydrogens are omitted for clarity. The acetate at O32 is extensively disordered and not shown.

assigned on the basis of ^1H NMR data for a 2,3-disubstituted indole [δ 8.70 (br s, 1 H), 7.56 (br d, 1 H, J = 7.3 Hz), 7.24 (d, 1 H, J = 7.3 Hz), 7.13 (dd, 1 H, J = 7.3, 7.7 Hz), 7.10 (dd, 1 H, J = 7.3, 7.7 Hz)] and ^{13}C NMR data that correlated very closely with values recorded for the sodium salt of abrine.[5] The only notable difference observed was at the 2-position of the indole (C-36) which shows a 10 ppm upfield shift relative to abrine, consistent with a bromine at that position. The N-methyl was assigned to the bromoabrine unit because the α-proton at δ 5.85 (dd, J = 10.2, 6.4 Hz) did not show connectivity to an NH proton in the COSY spectrum. The remaining amino acid β-tyrosine is isomeric with tyrosine and exhibited ^1H and ^{13}C NMR data compatible with either structure, based on chemical shift analysis and proton decoupling studies. However, careful inspection of the COSY spectrum revealed allylic coupling between the methine proton H-12 and the ortho protons of the phenyl ring H-27 and H-31. The presence of this coupling is most consistent with a structure where the phenyl ring is attached directly to a methine carbon.

The fourth unit of jaspamide is an 11-carbon hydroxy acid containing four methyl groups on alternating carbons, characteristic of a polypropionate unit. The proton connectivities in this unit were defined as shown in Table I by a combination of proton decoupling and COSY data. The diastereotopic protons at C-3 (δ 2.38 and 1.89) both showed allylic coupling to the olefinic proton at C-5 allowing connection across the double bond. However, only one of the C-3 protons (downfield) showed coupling to the adjacent H-2, indicating there is some rigidity in the 19-membered ring.

Saponification and workup of jaspamide yielded a linear derivative **2**. The high-resolution FAB spectrum of **2** was consistent with the amino acid sequence shown, exhibiting intense ions corresponding to cleavage of the amide bond between β-tyrosine and 2-bromoabrine [m/z 546.1963, $C_{27}H_{37}N_3O_4Br$ (−0.6 mmu)] and cleavage of the amide bond between 2-bromoabrine and alanine [m/z 474.1031, $C_{22}H_{23}N_3O_4Br + 2H^+$ (0.1 mmu); 268.1925, $C_{15}H_{26}NO_3$ (1.1 mmu)].



2

Hydrolysis of jaspamide (**1**) with 4 N $MeSO_3H$, 0.2% 3-(2-aminoethyl)indole as catalyst, followed by derivatization with dansyl chloride and diazomethane yielded 1 equiv of (S)-alanine as determined by chiral HPLC [Pirkle type, (R)-N-(3,5-dinitrobenzoyl)phenylglycine, 75:25 hexane/EtOAc] but failed to give significant amounts of the other three expected products. Since these attempts to assign stereochemistry were largely unsuccessful and some question remained about the β-tyrosine unit, an x-ray analysis was performed on a crystalline acetate derivative **3**, mp 145-47 °C. A computer-generated perspective drawing is presented in Figure 1. The acetate group is extensively disordered. The absolute configuration was determined from the known configuration of alanine and is 2S,6R,8S, 12R,15R,18S. Efforts to improve the model are continuing and will be reported in a subsequent publication.

Jaspamide represents a new class of cyclic depsipeptides. It contains a propionate unit and two rare amino acids, β-tyrosine previously reported in the edeine peptides[6] and 2-bromoabrine which is apparently a new amino acid. Furthermore, both 2-bromoabrine and β-tyrosine have the unnatural D configuration.

Acknowledgment. We thank the National Institutes of Health (AI-11969, CA-24487, CA-36622), the National Science Foundation (INT14133), the Sea Grant Program of California and New York, and the Alfred P. Sloan Foundation for support of this research. Some NMR spectra were recorded on an IBM AF 200 spectrometer purchased with funds from the National Science Foundation (PCM 8400801). The collection of samples from Palau was made possible by a grant from Allergan Pharmaceutical.

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[5] ^{13}C NMR assignments for abrine Na salt recorded in D_2O: δ 182.1 (C-1′), 136.4 (C-7a), 127.5 (C-3a), 124.3 (C-5), 121.8 (C-6), 119.2 (C-4), 119.0 (C-2), 112.0 (C-7), 111.3 (C-3), 66.4 (C-2′), 33.6 (NCH_3), 28.8 (C-3′).

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Classical (M = Os) and Nonclassical (M = Fe, Ru) Polyhydride Structures for the Complexes $MH_4(PR_3)_3$

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Recent developments in the coordination chemistry of molecular hydrogen have been very rapid.[1-4] In particular we have described a method of detecting these species using the fact that $M(H_2)$ resonances for a dihydrogen complex have T_1's more than an order of magnitude shorter than those for classical hydrides containing only terminal M-H bonds.[4b,c] We have recently shown by this method that IrH_5L_2 ($L = P(C_6H_{11})_3$) has a classical structure but its protonation product $[IrH_2(H_2)_2L_2]^+$ is a nonclassical bis-dihydrogen dihydride.

The complexes $MH_4(PR_3)_3$ of the iron triad constitute one of the best known examples of polyhydride complexes and are often cited as examples of the M(IV) oxidation state. Recently, Morris

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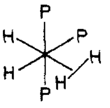
et al.[3] have shown that $[FeH(H_2)dpe_2]^+$ has a nonclassical structure. $[OsH_4(PMe_2Ph)_3]$ on the other hand has a classical structure[5] according to neutron diffraction work; although a nonclassical model was probably not considered, it would not be expected to have escaped detection. We therefore turned our attention to the problem of determining the true structure of the title complexes by the T_1 method.[4b]

$FeH_4(PEtPh_2)_3$ (**1**) was prepared by the method of Aresta et al.[6] This complex shows a quartet at δ -11.5 (^2J(P,H) = 27 Hz) in the ^1H NMR (toluene-d_8) at 20 °C under H_2, but at low temperature, the multiplet collapses to a broad feature. At 205 K, the apparent T_1 for this resonance at 250 MHz is 24 ms.[4d] This is in the range previously identified as appropriate for a nonclassical structure.[4b,c] The short T_1's are not due to fast exchange between **1** and free H_2 because irradiation of the resonance for free H_2 seen at δ 4.56 did not affect the appearance of the metal hydride resonance.[4e] As shown by Aresta et al.,[6] the IR of **1** shows not only bands due ν(classical Fe–H) but also a band at 2380–2400 cm^{-1}, not present in $FeH_2(PEtPh_2)_3$. These bands could not be assigned by Aresta et al., but by analogy with similar bands in known dihydrogen complexes,[1,2] we can now assign them to ν-$(Fe(H_2))$. The fact that a simple quartet is observed at 25 °C in the ^1H NMR shows that exchange between the $Fe(H_2)$ and Fe–H groups is fast at this temperature but may begin to be frozen out on cooling.

$RuH_4(PPh_3)_3$ (**2**)[7] has a broad RuH resonance at 25 °C in the ^1H NMR (toluene-d_8) at δ -7.06. the T_1 of this resonance at 205 K is 38 ms, again suggesting a nonclassical structure. The IR spectrum shows classical Ru–H bands at 1942 cm^{-1}. The feature corresponding to $\nu(Ru(H_2))$ is probably buried under the C–H vibrations or is too weak to be seen. These results confirm the speculation by Ashworth and Singleton[7] that this complex might be better described as an H_2 complex.

$OsH_4(PPh_3)_3$[8] was too insoluble for the T_1 to be determined at 205 K. The more soluble derivative $OsH_4(Pp\text{-}tolyl_3)_3$ (**3**) gave the value 820 ms, appropriate to a classical structure. **3** is much less reactive than **1** and **2** and does not bind N_2 with release of H_2, facts that fall naturally into place given the difference in structure.

The stereochemistry shown in **4** is the most likely one for complexes **1** and **2**, because in all cases studied to date, an H_2 ligand has been trans to the ligand of highest trans effect in the molecule.



4

We can now see that MH_4L_3 complexes of the iron triad are really M(II) for Fe and Ru but **3** is genuinely Os(IV). The higher M–H bond energies of third-row metals may be responsible for the change in structure. A nonclassical dihydrogen complex can be seen as a way for a metal to gain the M–H_2 binding energy (ca. 3–10 kcal/mole in cases[4c] shere this has been measured) without losing much of the H–H binding energy. In other words we believe thermodynamics rather than kinetics decides the structural outcome. The rapid proton exchange between M(H) and $M(H_2)$, which lead to the fluxionality, may go via the classical tetrahydrides.

Acknowledgment. We thank ARO for funding and Dr. G. Hlatky for discussions.

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Stable Trifluoromethylated Allyl and Heteroallyl Anions: Structure and Dynamic Properties

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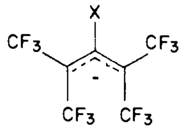
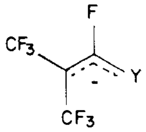
The tris(dimethylamino)sulfonium (TAS) cation uniquely stabilizes fluorinated anions. Unprecendented, isolable salts of perfluorinated tertiary carbanions[1a] and alkoxides[1b] have been described, and we report here the synthesis and characterization of isolable salts of fluorinated allyl and heteroallyl anions. The dynamic properties of these anions in solution are discussed and X-ray structural evidence for remarkably distorted 1,1,3,3-tetrakis(trifluoromethyl)allyl anion geometries (C_2 symmetry) is presented.

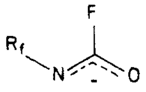
The salts **1a**, **2a**, **2b**, and **3** were prepared in nearly quantitative yields by simply adding the unsaturated fluoride acceptors $(CF_3)_2C{=}C{=}C(CF_3)_2$,[2] $(CF_3)_2C{=}C{=}O$,[3] $(CF_3)_2C{=}C{=}S$,[4] and $R_fN{=}C{=}O$,[5] respectively, to $TAS^+(CH_3)_3SiF_2^-$ in THF at low temperatures. Similarly, $(C_2H_5)_4N^+$ CN^- and 4-(dimethylamino)pyridine (DMAP) with $(CF_3)_2C{=}C{=}C(CF_3)_2$ gave **1b** and **1c**, respectively. Although some of these anions have been reported previously,[6] the cations employed here provide well-characterized, analytically pure solids of high stability that are suitable for spectroscopic and structural analyses[7,8] (Table I).



1a, X = F
b, X = CN
c, X = DMAP⁺



2a, Y = O
b, Y = S



3a, R_f = CF_3
b, R_f = n-C_3F_7

The single-crystal X-ray diffraction analysis of zwitterion **1c** reveals an unusual twisted structure[9] (Figure 1). Features of this

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(7) Except for **1c**, these salts are sensitive to water. Their preparation and manipulation were routinely carried out in a drybox.

(8) ^{19}F NMR (solvent, T, °C): **1a** (THF-d_8, 24) δ −52.50 (d, 12F, J = 18.5 Hz), −74.02 (13-line m, 1 F, J = 18.5 Hz); **1b** (THF-d_8, −20) δ −49.75 (m), −55.91 (m); **1c** (o-xylene-d_{10}/EtCN, 24) δ −50.11 (m), −56.66 (m); **2a** (DMF-d_7, 50) δ 5.03 (qq, 1 F, J = 19.5, 11.8 Hz), −47.92 (dq, 3 F, J = 19.5, 11.8 Hz), −49.41 (dq (quintet), 3 F, J = 11.8, 11.8 Hz); **2b** (CD_3CN, 25) δ 4.41 (qq, 1 F, J = 15, 23 Hz), −52.9 (dq, 3 F, J = 23, 10 Hz), −54.0 (dq, 3 F, J = 15, 10 Hz); **3a** (DMF-d_7, −50) major isomer δ 1.00 (q, 1 F, J = 11.3 Hz), −45.30 (d, 3 F, J = 11.3 Hz); minor isomer δ 11.4 (q, 1 F, J = 11 Hz), −40.7 (d, 3 F, J = 11 Hz); **3a** (DMF-d_7, 50) δ 1.55 (s, 1 F, $w_{1/2}$ = 105 Hz), −45.75 (s, 3 F, $w_{1/2}$ = 14 Hz); **3b** (THF, −50 °C) major isomer δ 5.5 (br s, 1 F), −79.04 (t, J = 7.6 Hz, 3 F), −79.4 (br s, 2 F), −127.53 (t, J = 10 Hz, 2 F); **3b** (DMF-d_7, 23 °C) δ 7.05 (br s, $w_{1/2}$ = 30 Hz, 1 F), −77.75 (br s, $w_{1/2}$ = 30 Hz, 2 F), −79.48 (t, J = 7.5 Hz, 3 F), −127.06 (t, J = 10 Hz, 2 F). UV (CH_3CN) λ_{max} (nm): **1a** 270 (ϵ 25 900); **1b** 352 (ϵ 15 200), 224 (ϵ 5400); **1c** 298 (ϵ 29 600), 216 (ϵ 7600).

(9) Crystal structure information for **1c**: orthorhombic; space group *Pbca* (No. 61); a = 11.262 (1) Å, b = 17.022 (2) Å, c = 17.167 (2) Å, V = 3291 $Å^3$, Z = 8; T = −100 °C. Data collected on Syntex R3 diffractometer, graphite monochromator, Mo Kα, λ = 0.710 69 Å; 3787 reflections, 4.0 < 2θ < 55.0°; 1653 unique reflections with $I > 3.0\sigma(I)$. Structure solved by direct methods (MULTAN); full-matrix, least-squares refinement. All hydrogens refined isotropically; other atoms, anisotropically. Final R = 0.043, R_w = 0.042 for 293 independent variables.

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