

cause the relative intensity of the molecular ion in 9-bicyclo[3.3.1]nonanol is low (*ca.* 2%), the deuterium content in IV and V was calculated from the molecular ion in the low voltage mass spectra of the corresponding ketone⁵ to which the two alcohols were converted by Jones' oxidation.⁶

Under low voltage (nominal 12 eV) electron impact conditions the molecular ions of the deuterated 9-bicyclo[3.3.1]nonanols IV and V lost H₂O and HDO in the ratio of 100:0 and 10:90, respectively.⁷ This is in accord with the results obtained from previous studies of deuterated cyclohexanols,² that 1:4 *cis* and to a lesser extent 1:3 loss are the predominant modes of water elimination from six-membered rings in mass spectrometry. That the hydroxyl substituent retained its stereochemical identity in the mass spectral (M⁺ - water) decomposition of the two isomers rules out any appreciable α cleavage which is thought to precede 1:3 water elimination, and therefore we conclude that 1:4 *cis* loss is the major contributor (>80%).⁸ Use of this result to confirm the original *anti* and *syn* assignments to II and III, respectively, lead us to believe that this technique could be applied to deduce stereochemistry in similar bicyclic systems.

2-Bicyclo[4.3.1]decen-10-one (VI) is the product of the resin-catalyzed condensation and subsequent dehydration of 3-(2'-oxocycloheptyl)propanal, the method⁹ being a general one for the synthesis of bicyclo[*n*.3.1]alk-2-enones (*n* > 2). Reduction of the ketone using a variety of reagents gave a single alcohol as product (VIIa or b), the stereochemistry of which could not be definitely ascertained from its ir and pmr spectra, *in the absence of the other stereoisomer*. After carrying out the homogeneous catalytic deuteration of VII the mass spectrum of the product, 10-bicyclo[4.3.1]decanol-2,3-*d*₂ (VIIIa or b; 5% *d*₁, 88% *d*₂, 7% *d*₃) was recorded. This showed that the molecular ion predominantly lost H₂O (>96%) thereby ruling out structure VIIIb, a result that could only be interpreted¹⁰ as establishing an *anti* configuration VIIa for the parent 2-bicyclo[4.3.1]decen-10-ol. Oxidation of VIIIa by Jones' reagent⁶ to the saturated ketone VIIIc followed by lithium aluminum hydride reduction gave a product whose mass spectrum exhibited losses of H₂O (>96%) and HDO identical with those in the original alcohol,

(5) From a typical preparation the isotopic composition of IV was calculated to be 2% *d*₁, 78% *d*₂, 20% *d*₃; that of V, 5% *d*₁, 54% *d*₂, 41% *d*₃. Although reductions were carried out under conditions known to exclude or minimize scrambling in simple systems (R. L. Augustine and J. F. Van Peppen, *Chem. Commun.*, 495 (1970)) different preparations of the catalyst all produced similar deuteration results. Exchange has previously been observed in the reduction of some substituted cyclohexenes (A. S. Hussey and Y. Takeuchi, *J. Amer. Chem. Soc.*, **91**, 672 (1969)) and larger ring cycloalkenes (J. G. Atkinson and M. O. Luke, *Can. J. Chem.*, **48**, 3580 (1970)). From the pmr spectral study of V it was evident that the *d*₃ species was deuterated in the 2-, 3-, and 4-*exo* positions.

(6) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 142.

(7) From the mass spectra of different preparations of IV and V the reproducibility of results was $\pm 2\%$ for IV and $\pm 5\%$ for V. If the loss from V is calculated from the *d*₃ value, it is $5.95 \pm 2\%$; based on the *d*₂ isotopic species it is $12.88 \pm 2\%$.

(8) This is supported by the observed 86% HOD loss from *exo*-3-bicyclo[3.3.1]nonanol-9,9-*d*₂.³

(9) R. D. Allan and R. J. Wells, *Aust. J. Chem.*, **23**, 1625 (1970); R. D. Allan, B. G. Cordiner, and R. J. Wells, *Tetrahedron Lett.*, 6055 (1968).

(10) The possibility of a completely specific *endo* approach by the reducing agent to compound VII in the boat-cycloheptane ring conformation was considered to be untenable since models suggest that the cycloheptane chair conformation will be preferred when the carbon at C-10 is tetrahedral (see ref 11).

indicating that those factors responsible for a selective hydride attack on the ketone in VI were also acting in the reduction of VIIIc.

In a similar case, Marshall and Partridge¹¹ reported some difficulty in confirming the assignment of the stereochemistry at C-10 in a methyl substituted 2-bicyclo[4.3.1]decen-10-ol. Again, a single isomer was formed stereoselectively from reduction of the corresponding unsaturated ketone. The authors proposed that it was probably the *anti* isomer since trigonal hybridization at C-10 should favor the boat-cycloheptane ring conformation for the ketone and inhibit hydride attack from the 4-carbon tetramethylene face. This assignment was subsequently confirmed by chemical means. It appears obvious therefore that mass spectrometry coupled with deuterium labeling offers a simple and unequivocal alternative method of verifying such assignments in this bicyclic system.

(11) J. A. Marshall and J. J. Partridge, *Tetrahedron*, **25**, 2159 (1969).

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Structure of the [HFe(CO)₄]⁻ Anion

Sir:

The geometry of HCo(CO)₄ has been the subject of one of the classic controversies in inorganic chemistry.¹ The issues in question were (i) whether the hydrogen atom occupied a "sterically active" position in the molecule (*i.e.*, whether the coordination about the metal was tetrahedral or trigonal bipyramidal) and (ii) whether the metal-hydrogen distance was "short" (1.2–1.4 Å) or "long" (~1.6 Å).

The structure of HCo(CO)₄ itself has never been solved by diffraction methods; this is probably due to the fact that the compound is quite unstable (it decomposes above -20°). We have, however, been able to isolate suitable single crystals of the isoelectronic anion [HFe(CO)₄]⁻, whose geometry is generally regarded to be closely related to that of HCo(CO)₄. In this communication we describe the structure determination of the [HFe(CO)₄]⁻ ion.

[HFe(CO)₄]⁻ was prepared by a standard method² and precipitated as its [(Ph₃P)₂N]⁺ salt by addition of a methanolic solution of [(Ph₃P)₂N]⁺Cl⁻.³ Recrystallization from a hot 1:1 ethanol-ethyl acetate mixture produced very pale yellow plate-like crystals of [(Ph₃P)₂N]⁺[HFe(CO)₄]⁻. *Crystal data*: space group *P*₂₁/*c* (monoclinic); *a* = 17.701 (9), *b* = 9.136 (4), and *c* = 22.251 (12) Å; β = 95.87 (4)°; *V* = 3579 Å³, *Z* = 4; *d*_{measd} = 1.29, *d*_{calcd} = 1.31. Two quadrants of data were collected on a fully automated Nonius CAD-3

(1) Accounts of this controversy have been given on several occasions: (a) J. A. Ibers, *Annu. Rev. Phys. Chem.*, **16**, 375 (1965); (b) A. P. Ginsberg, *Transition Metal Chem.*, **1**, 112 (1965); (c) B. A. Frenz and J. A. Ibers in "Transition Metal Hydrides," E. L. Muettterties, Ed., Marcel Dekker, New York, N. Y., 1971, p 33.

(2) R. B. King, "Organometallic Syntheses," Vol. I, Academic Press New York, N. Y., 1965, p 96.

(3) J. K. Ruff and W. J. Schlientz, *Inorg. Syn.*, in press.

Table I. Bond Distances and Angles in the $[\text{HFe}(\text{CO})_4]^-$ Anion

Bond Distances (in Ångströms)			
Fe-C ₁	1.72 (2)	C ₁ -O ₁	1.18 (2)
Fe-C ₂	1.76 (2)	C ₂ -O ₂	1.14 (2)
Fe-C ₃	1.78 (2)	C ₃ -O ₃	1.15 (3)
Fe-C ₄	1.71 (2)	C ₄ -O ₄	1.15 (3)
Fe-H	1.57 (12)		
Bond Angles (in degrees)			
Fe-C ₁ -O ₁	177.2 (14)	H-Fe-C ₁	175 (5)
Fe-C ₂ -O ₂	177.4 (16)	H-Fe-C ₂	84 (5)
Fe-C ₃ -O ₃	177.1 (14)	H-Fe-C ₃	82 (5)
Fe-C ₄ -O ₄	179.2 (18)	H-Fe-C ₄	78 (5)
C ₁ -Fe-C ₂	98.4 (7)	C ₂ -Fe-C ₃	115.3 (8)
C ₁ -Fe-C ₃	101.9 (7)	C ₃ -Fe-C ₄	115.1 (8)
C ₁ -Fe-C ₄	96.9 (8)	C ₄ -Fe-C ₂	122.4 (9)

diffractometer, corrected for absorption effects,⁴ and merged to give 1573 independent nonzero reflections. The Fe and P positions were located using direct methods and the rest of the atoms located through a series of difference Fourier maps. All the hydrogen atoms in the molecule were found without any difficulty. Least-squares refinement of all the atoms resulted in a final *R* factor of 7.6%. The fact that a fairly large number of low-angle reflections were available probably contributed to the successful refinement of the metal-bound hydrogen atom.

The geometry of the $[\text{HFe}(\text{CO})_4]^-$ anion is shown in Figure 1. Bond lengths and angles of the anion are given in Table I. Bond lengths and angles associated with the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation (Table II) and a complete listing of positional and thermal parameters of all the atoms in the molecule (Table III) are available elsewhere.⁵ The configuration of the anion is that of a distorted trigonal bipyramid, with the hydrogen in an axial position. The Fe-H distance of 1.57 (12) Å compares favorably with other M-H bond lengths, such as 1.51 (4) Å found in $\text{H}_2\text{Fe}[\text{PPh}(\text{OEt})_2]_4$,⁶ 1.601 (16) Å in $\text{HMn}(\text{CO})_5$,⁷ and 1.60 (12) Å in $\text{HRh}(\text{CO})(\text{PPh}_3)_3$.⁸ As in $\text{HMn}(\text{CO})_5$, the equatorial carbonyl groups are bent toward the hydrogen atom, the average C(ax)-Fe-C(eq) angle being 99.1° (the corresponding angle in $\text{HMn}(\text{CO})_5$ is 97.1°). The $\text{Fe}(\text{CO})_4$ part of the anion may thus be described as half-way between tetrahedral and trigonal bipyramidal. The Fe atom is displaced 0.27 Å from the plane of the three equatorial carbons.

Because of the close similarities between the vibrational spectra⁹ of $\text{HCo}(\text{CO})_4$ and $[\text{HFe}(\text{CO})_4]^-$, our

(4) Programs used in this work: absorption correction, GONOR (by W. C. Hamilton); direct methods, REL (by R. E. Long); Fourier maps, CRYGIS (by G. N. Reeke); least-squares refinements, CRYM (by R. E. Marsh); molecular diagram, ORTEP (by C. K. Johnson).

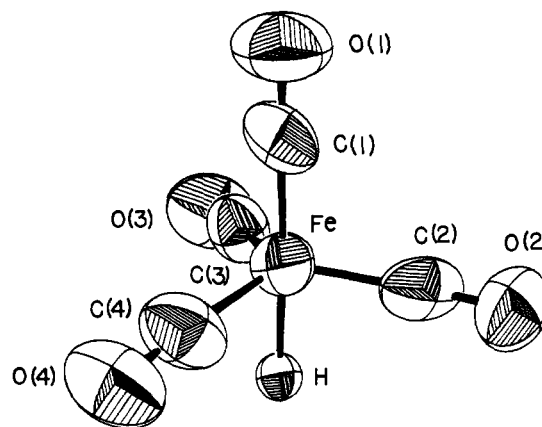
(5) Listings of the bond lengths and angles of the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation (Table II) and the final atomic parameters of the molecule (Table III) will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to code number JACS-73-2388. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

(6) L. J. Guggenberger, D. D. Titus, M. T. Flood, R. E. Marsh, A. A. Orto, and H. B. Gray, *J. Amer. Chem. Soc.*, **94**, 1135 (1972).

(7) S. J. La Placa, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, **8**, 1928 (1969).

(8) S. J. La Placa and J. A. Ibers, *Acta. Crystallogr.*, **18**, 511 (1965).

(9) (a) R. A. Friedel, I. Wender, S. L. Shufler, and H. W. Sternberg, *J. Amer. Chem. Soc.*, **77**, 3951 (1955); (b) W. F. Edgell, C. Magee, and G. Gallup, *ibid.*, **78**, 4185 (1956); (c) W. F. Edgell, J. Huff, J. Thomas, H. Lehman, C. Angell, and G. Asato, *ibid.*, **82**, 1254 (1960); (d) H. Stammrich, K. Kawai, Y. Tavares, P. Krumholz, J. Behmoiras, and S. Brill, *J. Chem. Phys.*, **32**, 1482 (1960); (e) K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. A*, 2339 (1969).

Figure 1. The geometry of the $[\text{HFe}(\text{CO})_4]^-$ anion.

result strongly implies that the geometry of $\text{HCo}(\text{CO})_4$ is very similar to the one described here. The finding that the H atom in $[\text{HFe}(\text{CO})_4]^-$ occupies a discrete coordination position is gratifying. Although the question of "sterically active" vs. "sterically inactive" hydride ligands seemed to have been settled in favor of the former some years ago, recent structure determinations have shown that there are cases (mainly involving pentacoordinated species such as $\text{HRh}(\text{PPh}_3)_4$,¹⁰ $\text{HRh}(\text{AsPh}_3)(\text{PPh}_3)_3$,¹¹ and $\text{HCo}(\text{PF}_3)_4$ ¹²) in which the hydride ligand appears to exert very little influence on the geometry of the rest of the molecule. The difference between the geometries of $[\text{HFe}(\text{CO})_4]^-$ and $\text{HCo}(\text{PF}_3)_4$ (which can also be considered isoelectronic with $\text{HCo}(\text{CO})_4$) might be attributed to the difference in steric bulk between the CO and PF_3 ligands.

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(12) B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, **9**, 2403 (1970).

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Synthesis and Reactions of Anionic Phosphide and Arsenide Complexes Derived from Disodium Tetracarbonylferrate(-II)

Sir:

We have shown $\text{Na}_2\text{Fe}(\text{CO})_4$ to be an inexpensive reagent for selective organic syntheses.¹⁻⁴ Here we report its use in the preparation of isolable anionic

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(2) J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, **94**, 1788 (1972).

(3) J. P. Collman, S. R. Winter, and R. G. Komoto, *ibid.*, **95**, 249 (1973).

(4) J. P. Collman and W. O. Siegl, *ibid.*, **94**, 2516 (1972).