single molybdenum and that the resting state MoFe protein contains two such centers.

Since the observed protons are not exchangeable, they are plausibly associated with carbon-bound hydrogens of amino acid residues which coordinate to the center and link it to the protein. It is probable that one or more of these linkages is supplied by the mercaptide sulfur atoms of a metal-coordinating cysteinyl residue. The observation of a large number of protons is clearly supportive of the conclusion, obtained from analysis of the Mössbauer data,[4,12] that the paramagnetism of this center arises from spin coupling among the component iron atoms, now with the added requirement that molybdenum is involved, as well.

If one next considers the magnitude of the ^{95}Mo hyperfine coupling, the ENDOR results suggest that the molybdenum is to be classified as a diamagnetic, even-electron ion with even formal valency and not as Mo(V) or Mo(III). Model studies show that hyperfine couplings for an isolated, sulfur-coordinated, $S = ^1/_2$ Mo(V) would be ca. 150 MHz[13] and that coupling constants for $S = ^3/_2$ Mo(III) would be comparable.[14] This is roughly 20-fold larger than we observe, and thus an isolated Mo ion having either of these two formal valences is ruled out, the former case doubly so because it has the wrong spin. If the $S = ^3/_2$ ground state of FeMo-co were achieved by spin coupling between an $S = ^1/_2$ Mo(V) and the net spin of the six iron atoms, the intrinsic molybdenum hyperfine coupling would be strongly reduced. The reduction would be maximal (fivefold) if the resultant $S = ^3/_2$ state of the center were achieved by antiferromagnetic couple of the $S = ^1/_2$ molybdenum with a net iron spin of $S = 2$, but this model still would predict a hyperfine interaction no less than ca. four-fold larger than observed. Spin coupling between an $S = ^3/_2$ Mo(III) and the net iron spin is even less favorable; a $S = ^3/_2$ state obtained by antiferromagnetic coupling between $S = ^3/_2$ molybdenum and a net $S = 3$ iron spin would reduce the ^{95}Mo hyperfine interaction of an isolated molybdenum by only 40%.

Consider next the indication that the ^{95}Mo quadrupole coupling is quite small. For an atom with an unfilled d shell, the coupling is primarily determined by any unbalance in the d-orbital populations; say, for the z direction, P^{Mo} is proportional to the total of the orbital populations of d_{z^2}, d_{xz}, and d_{yz} minus the populations of d_{xy} and $d_{x^2-y^2}$.[15] Molybdenum even-electron oxidation states in idealized geometries other than octahedral Mo(0), tetrahedral Mo(II), and Mo(VI) geometry would have a net unbalance of two d electrons. Although quadrupole data for molybdenum is scarce,[11] comparison with results for a variety of copper complexes,[9,16] taking proper notice of the difference in nuclear spins ($I(Cu) = ^3/_2$) and the greater radial expansion of the 4d orbitals,[9a] suggests[10] that such an unbalance would produce a quadrupole coupling constant of from two to tenfold larger than the upper bound estimated above. Thus oxidation state, geometry combinations other than those three are somewhat disfavored.

In summary, the magnetic resonance data here indicate that a single molybdenum atom is integrated into the $S = ^3/_2$ center of FeMo-co and that the molybdenum is best viewed as being in even-electron state, most plausibly as a nominally tetrahedral Mo(II) or a Mo(VI) ion.

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^{13}C–^{13}C Coupling Constants in Bicyclic Hydrocarbons

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One of the more controversial aspects of carbon–carbon coupling[1] concerns the relative importance of the various interactions which are responsible for one-bond coupling, $^1J(CC)$. On the one hand, a view shared by some is that spin–spin coupling between directly bonded carbon nuclei is determined predominantly by Fermi contact and, as such, is a measure of the state of hybridization of the atoms concerned.[2] Alternatively, attention has been drawn by others to the effect of the noncontact terms, and it has been suggested that such interactions frequently contribute significantly to the magnitude of $^1J(CC)$, particularly in the case of multiply bonded carbons or where the atoms form part of a strained system.[2]

In order to provide further experimental data of coupling involving directly bonded carbons, we have synthesised for NMR analysis the bicyclic systems **1–5** (R = $^{13}CH_3$)[3] as part of a projected series of caged compounds substituted with ^{13}C-labeled methyl at the bridgehead. At the same time we were interested in evaluating the vicinal coupling constants involving methyl and the appropriate bridgehead carbon in **2–5** (R = $^{13}CH_3$). Barfield and his colleagues[4] have recently demonstrated the importance of the effect of nonbonded interactions on $^3J(CC)$ in these kinds of molecules.

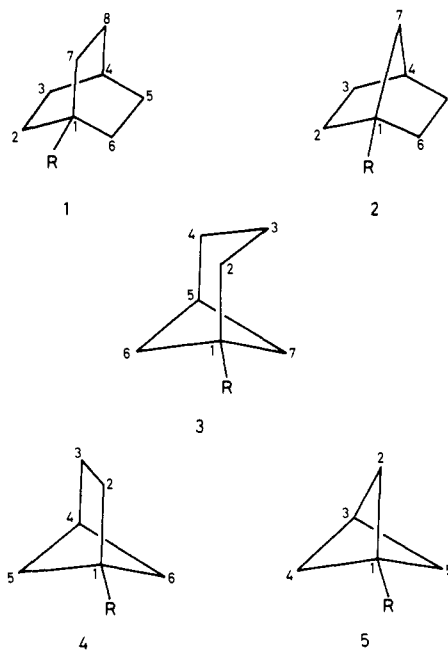Table I contains the ^{13}C chemical shifts and Table II the various carbon–carbon coupling constants of the substrates **1–5** (R = $^{13}CH_3$). As anticipated, the features of most interest are $^1J(CC)$ and $^3J(CC)$. For coupling between directly bonded carbons the data demonstrate that in these systems there is little correlation

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(2) For leading references, see (a) H. Egli and W. von Philipsborn, *Tetrahedron Letters*, 4265 (1979); (b) T. Khin and G. A. Webb, *Org. Magn. Reson.*, *12*, 103 (1979).

(3) The syntheses and relevant properties of these hydrocarbons will be reported fully in the main paper.

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Table I. Chemical Shifts^a of the Hydrocarbons 1-5 (R = $^{13}CH_3$)

compd	carbon atom								
	1	2	3	4	5	6	7	8	CH_3
1	27.14	33.20	26.61	24.44	26.61	33.20	33.20	26.61	28.78
2	43.72	36.74	31.22	37.76	31.22	36.74	45.23		21.00
3	39.74	36.41	16.86	28.47	30.08	38.75	38.75		28.00
4	48.47	32.98	29.16	36.74	43.77	43.77			19.78
5	42.17	52.18	27.39	52.18	52.18				19.07

^{a} ± 0.02 ppm.

Table II. Carbon–Carbon Coupling Constants, $^nJ(^{13}C-^{13}CH_3)$,^{a} in the Hydrocarbons 1-5 (R = $^{13}CH_3$)

compd	$^1J^b$	^2J	^3J	^4J
1	38.09 (134.3)	0.34 (C2,6,7)	3.39 (C3,5,8)	0.31 (C4)
2	39.45 (140.1)	1.56 (C2,6)	3.36 (C3,5)	-
		1.07 (C7)	3.96 (C4)	
3	37.90 (144.9)	1.10 (C2)	2.91 (C3)	0.27 (C4)
		0.66 (C6,7)	5.82 (C5)	
4	39.65 (150.5)	2.44 (C2)	2.77 (C3)	-
		ncd (C5,6)	7.50 (C4)	
5	37.62 (167.5)	ncd (C2,4,5)	9.71 (C3)	-

^{a} In Hz (± 0.05); ncd = no coupling detected and thus presumably ⩽0.2 Hz. ^{b} Numbers in parentheses refer to the values of $^1J(^{13}C-H)$ of the bridgehead carbon in the unsubstituted hydrocarbon 1-5 (R = H) (data of Della and associates, ref 5).

between $^1J(CC)$ and the corresponding parameter $^1J(CH)$ in the unsubstituted hydrocarbon 1-5 (R = H).[5] One-bond carbon–hydrogen coupling is generally assumed to be governed by Fermi contact and hence to reflect the s electron density at the bridgehead carbon. Clearly, in the case of the hydrocarbons 1-5 (R = $^{13}CH_3$) the spin dipolar and orbital interactions exert an obvious and substantial influence on $^1J(CC)$. This behavior is in sharp contrast with observations[6] on the analogous bridgehead fluorides 1-5 (R = F). We found $^1J(CF)$ in the latter to be linearly related to $^1J(CH)$ in 1-5 (R = H), and this was attributed to the fact that while the contribution from the noncontact terms is undoubtedly important in the series of fluorides, it presumably does not vary significantly within that range of compounds.

As far as vicinal coupling is concerned, the ring carbons fall into one of two categories: (i) the C3 methylene carbons in 1-4 (R = $^{13}CH_3$) and (ii) the nonsubstituted bridgehead carbons in 2-5 (R = $^{13}CH_3$). Interestingly, three-bond coupling between methyl and C3 in 1-4 (R = $^{13}CH_3$) (in which the dihedral angle is relatively constant) decreases as the strain in the ring system increases. On the other hand, the magnitude of ^3J-($^{13}CH_3-^{13}C_{bridgehead}$) increases markedly along the series 2-5 (R = $^{13}CH_3$), ranging from 3.96 Hz in 1-methylbicyclo[2.2.1]heptane to 9.70 Hz in 1-methylbicyclo[1.1.1]pentane. Although this parameter would have been expected to become progressively larger from 2 → 3, 4 → 5 in accordance with the greater number of three-bond pathways through which coupling could be transmitted, nevertheless the increments are not as large as anticipated. It has been suggested[4] that this suppressed enhancement is a reflection of the negative contribution of nonbonded interactions to the coupling. Significant also is the large discrepancy between the values of $^3J(^{13}CH_3-^{13}C_{bridgehead})$ in the [3.1.1] and [2.1.1] hydrocarbons. In these systems the number of three-bond pathways is the same, and, because the interbridgehead carbon distances are not appreciably different,[7] through-space interactions were expected to be similar. One notable difference in the geometry of 3 and 4 is the size of the dihedral angle between the

coupled nuclei.[8] We suggest that, other things being equal, the difference in vicinal coupling between 3 and 4 arises as a result of the variation in dihedral angle.[9]

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Registry No. 1 (R = $^{13}CH_3$), 80326-44-9; 2 (R = $^{13}CH_3$), 76450-98-1; 3 (R = $^{13}CH_3$), 80326-45-0; 4 (R = $^{13}CH_3$), 80326-46-1; 5 (R = $^{13}CH_3$), 80326-47-2.

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Phospholipids Chiral at Phosphorus. 1. Stereochemistry of Transphosphatidylation Catalyzed by Phospholipase D[1]

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The recent research activity concerning the stereochemistry of biological processes at phosphorus features the following: introduction of phosphorothioates;[2] synthesis and application of chiral [$^{16}O,^{17}O,^{18}O$]phosphate monoesters,[3] chiral inorganic [$^{16}O,^{17}O,^{18}O$]thiophosphates,[4] and ATP chirally labeled at all positions;[5] preparation of "substitution-inert" metal–nucleotide complexes of known stereochemical structures;[6] use of metal ion dependence in stereospecificity to assess binding stereochemistry;[7] the development of ^{31}P NMR methods based on an ^{18}O isotope effect[8] and an ^{17}O quadrupolar effect[9] for configurational analysis.

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