is benzenethiol, even though attempts to locate the thiol hydrogen in electron density difference maps have been thus far unsuccessful.

Although no other structural data are available for transition metal complexes of benzenethiol, the parameters for the low-spin complex appear to be chemically reasonable. The two Fe-S distances of 2.27 (2) and 2.43 (2) Å are in the range of distances expected for iron to benzenethiolate and iron to benzenethiol, respectively. As in the case of the high-spin complex, electron density difference maps have not produced an unambiguous identification of the thiol hydrogen atom.

The structural interpretations above provide an important insight into the mechanism of the transformation in this material. Assuming that the shorter Fe-S bond in both forms corresponds to the coordinated thio*late*, S1 in the low-spin form appears to be protonated while S1* in the high spin form does not. This anomaly was initially attributed to a false minimum in the refinement caused by the pseudosymmetry of the complex, but numerous attempts to refine models in which the iron or axial ligand positions were interchanged resulted in convergence to the initial parameters. Thus it would appear that a proton transfer may accompany the structural transition. Speculation concerning the mechanism of such a transfer will be postponed until further studies of this complex are completed.

On the basis of the present information it is clear that the complex exists in the solid state as an equilibrium mixture of five and six-coordinate species. Crystallographic resolution of these two structural forms has produced a dynamic model for the transformation associated with the substrate binding in the catalytic cycle of P450 enzymes in which the low-spin, six-coordinate resting form is converted into a high-spin, five-coordinate species. Multiple-temperature x-ray and neutron investigations of this complex promise to provide further information related to the spin equilibria which have been observed for a number of hemoproteins and may yield, simultaneously, a detailed picture of a proton-transfer reaction.

Acknowledgments. Work at UCLA was supported by the UCLA Research Committee, the UCLA Campus Computing Network, and NSF Grant PCM76-10559; and work at Stanford by NIH Grant GM17880 (J.P.C.) and NSF Grant CHE 75017018 (J.P.C.). We thank Tom Eccles for assistance during the initial computing stages.

References and Notes

(1) The abbreviations used in this paper are as follows: P450$_{cam}$, cytochrome P450 camphor hydroxylase; TPP, tetraphenylporphyrin dianion; EPR, electron paramagnetic resonance.

(2) I. C. Gunsalus, J. R. Meeks, J. D. Lipscomb, P. Debrunner, and E. Munck in "Molecular Mechanisms of Oxygen Activation", O. Hayaishi, Ed., Academic Press, New York, N.Y., 1974, Chapter 14.

(3) For simple ferric porphyrin complexes thus far characterized, six coordination is associated with low-spin iron ($S = \frac{1}{2}$) while five coordination is indicative of a high-spin ($S = \frac{5}{2}$) configuration. For the most part this is true for the iron in hemoproteins as well; however, for very weak field ligands (F^-, H_2O), it now appears that certain six-coordinated complexes may also be high spin. See, for example, J. F. Deatherage, R. S. Loe, and K. Moffat, *J. Mol. Biol.*, **104**, 723 (1976).

(4) S. C. Tang, S. Koch, G. C. Papaefthymiou, S. Foner, R. B. Frankel, J. A. Ibers, and R. H. Holm, *J. Amer. Chem. Soc.*, **98**, 2414 (1976).

(5) (a) J. P. Collman, T. N. Sorrell, and B. M. Hoffman, *J. Amer. Chem. Soc.*, **97**, 913 (1975); (b) J. P. Collman and T. N. Sorrell in "Concepts in Drug Metabolism", D. M. Jerina, Ed., American Chemical Society Symposium Series, American Chemical Society, Washington, D.C., in press.

(6) Evidence has implicated a cysteine thiolate in the ferrous deoxy[7] and ferrous carbonyl[8] stages of the P450 cycle as well. A recent report disputes the possibility of thiolate ligation in the ferrous oxy form.[9] However, see ref 5b.

(7) J. P. Collman, T. N. Sorrell, J. H. Dawson, and H. H. Wickman, unpublished results.

(8) J. P. Collman, T. N. Sorrell, J. H. Dawson, J. R. Trudell, E. Bunnenberg, and C. Djerassi, *Proc. Natl. Acad. Sci. U.S.*, **73**, 6 (1976).

(9) C. K. Chang and D. Dolphin, *J. Am. Chem. Soc.*, **98**, 1607 (1976).

(10) H. H. Wickman, S. W. McCann, T. N. Sorrell, and J. P. Collman, *Bull. Am. Phys. Soc.*, **22**, 337 (1977).

(11) I. Morishima and T. Iizuka, *J. Am. Chem. Soc.*, **96**, 5279 (1974), and references therein.

(12) A recent paper reports a highly purified liver microsomal P450 whose high-spin form is easily converted to a low-spin species simply by changing the concentration: D. A. Haugen and M. J. Coon, *J. Biol. Chem.*, **251**, 7929 (1976). The spin change is reversible, and it would appear that, in these systems, a very delicate balance exists which may be influenced by geometric constraints at the heme.

(13) C. E. Strouse, *Rev. Sci. Instr.*, **47**, 871 (1976).

(14) J. Strouse, S. W. Layten, and C. E. Strouse, *J. Am. Chem. Soc.*, **99**, 562 (1977).

(15) This complex is the *only* isolated and structurally characterized example of a six-coordinate ferric porphyrin having a thiolate ligand. Attempts to isolate such complexes by addition of a ligand to five-coordinate thiolate compounds usually result in reduction of the iron to the ferrous state, except at very low temperatures.[4,5]

(16) The Fe*–S2* distance in this form is 3.95 Å, consistent with the notion that the benzenethiol is best considered as a solvate molecule in the crystal lattice and probably exerts no influence on the electronic properties of the iron.

(17) Fellow of the Alfred P. Sloan Foundation.

James P. Collman,* Thomas N. Sorrell, Keith O. Hodgson[17]
Department of Chemistry, Stanford University
Stanford, California 94305

Ajaya K. Kulshrestha, Charles E. Strouse*
Contribution No. 3815 from the Department of Chemistry
University of California, Los Angeles
Los Angeles, California 90024

Received April 12, 1977

Pyramidal Dications. Introduction of Basal and Apical Substituents

Sir:

Recently the synthesis and the chemical behavior of $(CCH_3)_6^{2+}$, the first representative of the $(CH)_6^{2+}$ type of pyramidal dications, has been reported.[1] During our investigation on the preparation of other derivatives of this class of species we found a simple route to pyramidal dications[2] of general formula $(CCH_3)_5CR^{2+}$.

The philosophy followed to achieve this goal was to find a new precursor of $(CCH_3)_6^{2+}$ that could be synthesized by introduction of a methyl group into a starting material in which in a similar fashion other alkyl groups instead of the methyl one could easily be put. In principle the unsaturated ketone **1**,[3] easily available from the corresponding tricyclic diene, is one of the starting materials having the required characteristics.

In fact, when treated with MeLi, enone **1** provided allylic alcohol **2**,[4-6] a new precursor of dication **3**. Moreover different alkyl groups could be introduced using other Li reagents.[6]

A solution of dication $(CCH_3)_6^{2+}$ (**3**) was prepared by treating **2** with $HFSO_3/SbF_5$ (molar ratio 1:1) in SO_2ClF at −60 °C and characterized as previously reported (Scheme I).

Scheme I

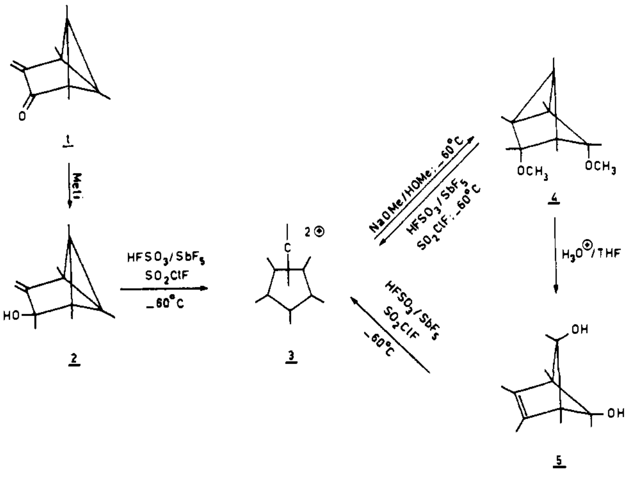


Table I

Dication	^{1}H NMR[a]	T, °C	Medium
3	2.14, 2.83	−25	$HFSO_3/CH_2Cl_2$
7	1.66 (t, J_{CH_2,CH_3} = 7.5 Hz, 3 H), 2.16 (s, 3 H), 2.84 (s, 6 H), 2.86 (s, 6 H), 3.10 (q, J_{CH_3,CH_2} = 7.5 Hz, 2 H)[b]	−25	$HFSO_3/CH_2Cl_2$
10	1.34 (t, J_{CH_2,CH_3} = 7.5 Hz, 3 H), 2.67 (q, J_{CH_3,CH_2} = 7.5 Hz, 2 H), 2.90 (s, 15 H)[b]	−25	$HFSO_3/CH_2Cl_2$
12	1.71 (d, J_{CH,CH_3} = 7.0 Hz, 6 H), 2.19 (s, 3 H), 2.79 (s, 6 H), 2.88 (s, 6 H), 3.74 (h, $J_{CH_3,CH}$ = 7.0 Hz, 1 H)[b]	−50	$HFSO_3/SbF_5$, SO_2ClF
13	1.42 (d, J_{CH,CH_3} = 7.0 Hz, 6 H), 2.95 (s, 15 H), 3.16 (h, $J_{CH_3,CH}$ = 7.0 Hz, 1 H)[b]	−50	$HFSO_3/SbF_5$, SO_2ClF
16	1.66 (t, J_{CH_2,CH_3} = 7.5 Hz, 6 H), 2.10 (s, 3 H), 2.82 (s, 3 H), 2.85 (s, 6 H), 3.08 (q, J_{CH_3,CH_2} = 7.5 Hz, 4 H)	−50	$HFSO_3/SbF_5$, SO_2ClF
17	1.70 (d, J_{CH,CH_3} = 7.0 Hz, 12 H), 2.13 (s, 3 H), 2.75 (s, 3 H), 2.87 (s, 6 H), 3.76 (h, $J_{CH_3,CH}$ = 7.0 Hz, 2 H)	−50	$HFSO_3/SbF_5$, SO_2ClF

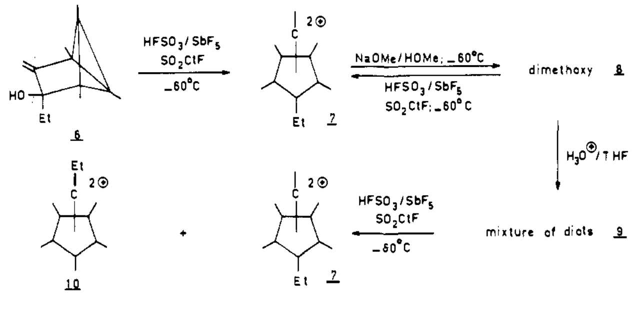
[a] Chemical shifts in parts per million from TMS using tetramethylammonium chloride as an internal reference (δ 3.20). See ref 4. [b] On irradiation at δ 1.66 (**7**), 1.34 (**10**), 1.71 (**12**), and 1.42 (**13**) singlets appeared at δ 3.10, 2.67, 3.74, and 3.16, respectively.

Table II

Dication	^{13}C NMR[a] (proton decoupled)	T, °C	Medium
3	126.4, 22.1, 10.2, −2.5	−50	$HFSO_3/CH_2Cl_2$
7	127.3, 126.6, 125.8, 22.2, 18.0, 10.0, 9.7, 9.1, −2.2	−50	$HFSO_3/CH_2Cl_2$
7 + **10**	127.6, 127.2, 126.6, 126.1, 22.6, 18.3, 10.5, 10.2, 10.0, 9.3, 8.1, −2.0	−50	$HFSO_3/CH_2Cl_2$
12	130.7, 128.3, 125.3, 28.2, 22.5, 17.4, 10.1, 9.7, −1.8	−50	$HFSO_3/SbF_5$, SO_2ClF/CH_2Cl_2
12 + **13**	130.4, 128.1, 126.3, 125.2, 28.1, 24.5, 22.3, 18.1, 17.3, 11.5, 10.5, 10.1, 9.6, −1.8	−50	$HFSO_3/SbF_5$, SO_2ClF/CH_2Cl_2

[a] Chemical shifts in parts per million from TMS using CH_2Cl_2 as internal reference (δ 54.02).

Scheme II



The ethyl-substituted allylic alcohol **6**[4,6,7] was converted to the new dication **7**[4] (^{1}H NMR spectrum, Figure 1) both by $HFSO_3/SbF_5$ (molar ratio 1:1) in SO_2ClF and $HFSO_3/CH_2Cl_2$ at −60 °C (Scheme II). Quenching of **7** with a 5% solution of NaOMe in HOMe at −60 °C provided in ~90 yield a nonsymmetrical dimethoxy derivative **8**[8] (which on basis of analogy is likely to have the same skeleton as **4**), which gave back dication **7** and protonated methanol[9] in $HFSO_3/SbF_5$ (molar ratio 1:1) and SO_2ClF at low temperature. Upon treatment with acid (H_3O^+/THF), **8** was transformed into a mixture of diols **9**[10] (which on basis of analogy are likely to have the same skeleton as **5**). The ^{1}H NMR and ^{13}C NMR spectra of a solution of a crystallized mixture of diols **9** in $HFSO_3/SbF_5$ (molar ratio 1:1) and SO_2ClF or $HFSO_3/CH_2Cl_2$ showed a mixture of dications **7** and **10**[4] (Tables I and II) in a ratio depending on the crop of crystallized material used. A representative ^{1}H NMR spectrum of this dication mixture is reported in Figure 2.

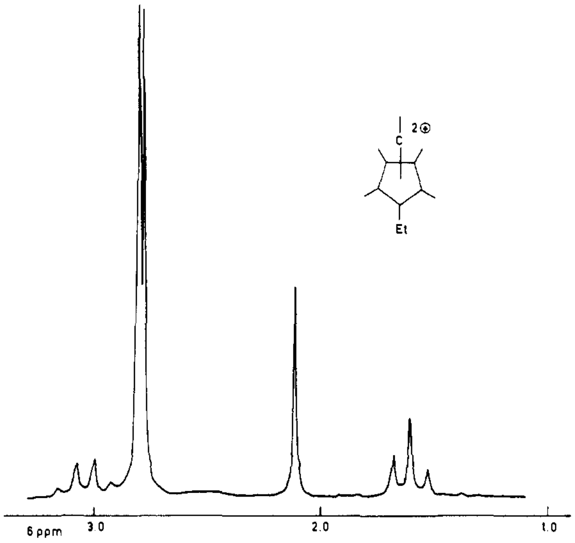


Figure 1.

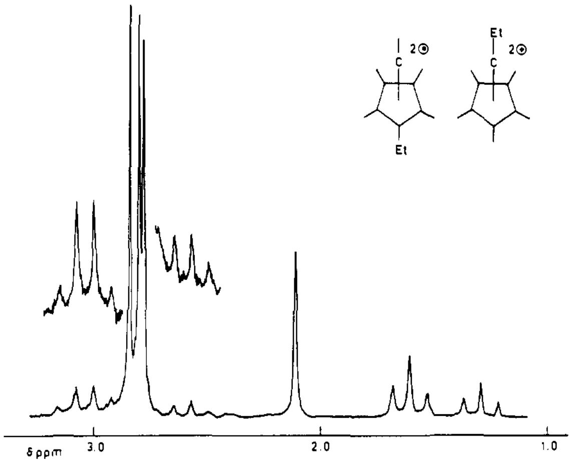
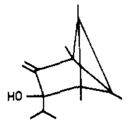


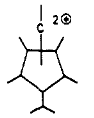
Figure 2.

A solution of dication **12**[4] was prepared by dissolving isopropyl derivative **11**[4,6,12] in $HFSO_3/SbF_5$ (molar ratio 1:1) and SO_2ClF at −60 °C. After quenching at −60 °C of **12** with a 5% solution of NaOMe in HOMe followed by acidic treatment (H_3O^+/THF), a mixture of diols was obtained. This mixture of diols was converted as described above into a mixture of two dications **12** and **13**. Several ^{1}H NMR spectra of the mixture of dications **12** and **13**[4] at temperatures between −40 and −45 °C were run during 48 h. While **12** appeared to be stable, dication **13** turned out to decompose completely within this period. No evidence for decomposition of either **7** or **10** was obtained under similar conditions. The *tert*-butyl homologue **14** behaves differently and is at present being investigated.

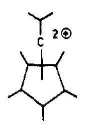
Finally precursors containing two ethyl[13] or two isopropyl[14]



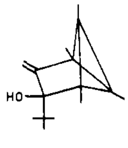
11



12

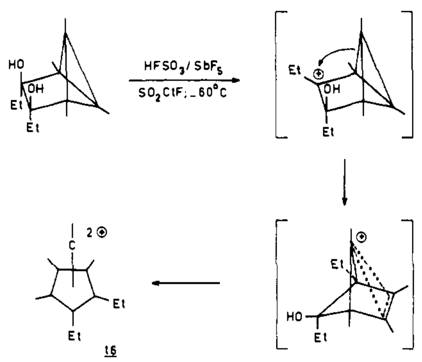


13

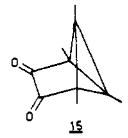


14

Scheme III

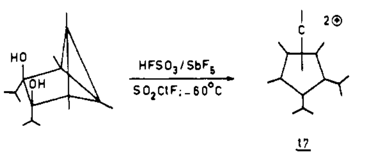


groups were obtained in an analogous way when diketone **15** was allowed to react with the appropriate lithium reagent



15

followed by addition of water. Both ethyl and isopropyl groups were found to be in *basal* positions in the corresponding dications **16** and **17**, respectively, which is rationalized in Scheme III.



Acknowledgment. C.G wishes to thank Montedison S.p.A. Dipartimento di Chimica Organica (Novara-Italia) for a leave of absence.

References and Notes

(1) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 1665 (1973); *J. Am. Chem. Soc.*, **96**, 2208 (1974); *Acc. Chem. Res.*, **8**, 413 (1975).

(2) For reasons of simplicity we have used a representation of the pyramidal dications in the way indicated (the similarity with organometallic chemistry is clear). The positions of the substituents may be indicated as basal (at the five-membered ring) and apical (at the top).

(3) R. F. Heldeweg and H. Hogeveen, *Tetrahedron Lett.*, 1517 (1975).

(4) Reported melting points were determined by the Kofler method and were not corrected. Satisfactory analytical data have been obtained for compounds **2**, **6**, and **11**. NMR spectra were recorded with a Varian XL-100 (^{1}H, 100.1 MHz; ^{13}C, 25.2 MHz) in the case of **7**, **8**, 9, **10**, **11**, and **13** and with a JEOL C-60 HL.

(5) Mp 53–54 °C (pentane, − 40 °C); IR (Nujol) 3330 (OH stretch), 1655 cm^{-1} (C=C stretch); ^{1}H NMR (CDCl$_3$) δ 4.92 (s, 1 H), 4.66 (s, 1 H), 1.40 (s, 3 H), 1.32 (s, 3 H), 1.20 (s, 3 H), 1.10 (s, 3 H), 1.06 (s, 3 H).

(6) All the precursors were prepared starting from crude enone **1** and the corresponding Li reagents. Methyl derivative **2** was purified by crystallization (pentane, −40 °C) and isolated as pure compound in 40% yield. Ethyl derivative **6** was obtained in 20% yield by distillation (60–70 °C (0.9 mmHg)) and subsequent crystallization (pentane, −20 °C). Compound **11** was purified by distillation (20% yield).

(7) Mp 52–53 °C (pentane, −20 °C); IR (Nujol) 3350 (OH stretch), 1655 cm^{-1} (C=C stretch); ^{1}H NMR (CDCl$_3$) δ 4.78 (s, 1 H), 4.60 (s, 1 H), 1.65 (q, J_{CH_3,CH_2} = 7.0 Hz, 2 H), 1.37 (s, 3 H), 1.27 (s, 3 H), 1.07 (s, 3 H), 1.00 (s, 3 H), 0.68 (t, J_{CH_2,CH_3} = 7.0 Hz, 3 H).

(8) ^{1}H NMR (CDCl$_3$) δ 3.32 (s, OCH$_3$), 3.12 (s, OCH$_3$), 1.28 (s), 1.24 (s), 1.16 (s), 1.01 (s), 0.99 (s) (owing to overlapping signals, the ethyl absorptions could not be assigned unambiguously); ^{13}C NMR (CDCl$_3$, proton decoupled) δ 81.3, 80.5, 57.4, 52.1 (OCH$_3$), 51.6 (OCH$_3$), 43.6, 36.9, 31.4, 18.7, 17.2, 15.5, 12.1, 7.9, 6.9, 2.7.

(9) G. A. Olah and E. Namanworth, *J. Am. Chem. Soc.*, **88**, 5328 (1966).

(10) The elemental analysis corresponds to the formula $C_{13}H_{22}O_2$. The following spectroscopic data are in agreement with the proposed mixture: IR (Nujol) 3200 cm^{-1} (OH stretch); ^{1}H NMR (CDCl$_3$) shows three groups of absorptions centered on δ 4.9 (four peaks disappearing on treatment with D_3O^+), 1.7, 0.9 (the ratio of the relative area of the downfield group and the combined integral of the latter groups was found to be 1:10); ^{13}C NMR revealing 27 peaks in a proton-decoupled spectrum (CDCl$_3$) δ 143.1, 139.4, 138.1, 104.3, 101.6, 101.4, 101.0, 65.0, 60.9, 60.6, 60.1, 25.2, 18.9, 18.1, 17.1, 16.5, 14.2, 12.7, 11.2, 10.7, 10.5, 10.2, 9.3, 4.7, 3.7, 3.6, 3.0; mass spectrum *m/e* 192 ($M^+ - H_2O$). The IR of mixture **9** on heating[11] at 150 °C showed the following absorptions: 1690, 1650, 1355, 1190, 1090, 1070 cm^{-1} in agreement with those as reported for the cyclopentadienyl ketone by H. N. Junter, W. Schäfer, and H. Niedenbrück, *Chem. Ber.*, **100**, 2508 (1967).

(11) L. A. Paquette, S. A. Lang Jr., S. K. Porter, and J. Clardy, *Tetrahedron Lett.*, 3137 (1972).

(12) Bp 54–56 °C (0.6 mmHg); IR 3500 (OH stretch), 1650 cm^{-1} (C=C stretch); ^{1}H NMR (CDCl$_3$) δ 4.89 (s, 1 H), 4.65 (s, 1 H), 2.00 (h, $J_{CH_3,CH}$ = 7.0 Hz, 1 H), 1.39 (s, 3 H), 1.29 (s, 3 H), 1.05 (s, 3 H), 1.01 (s, 3 H), 0.97 (d, J_{CH,CH_3} = 7.0 Hz, 3 H), and 0.86 (d, J_{CH,CH_3} = 7.0 Hz, 3 H).

(13) Mp 83.0–84.0 °C (pentane, −20 °C); IR (Nujol) 3600–3500 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.52 (q, J_{CH_3,CH_2} = 7.0 Hz, 4 H), 1.32 (s, 3 H), 1.20 (s, 3 H), 1.08 (t, J_{CH_2,CH_3} = 7.0 Hz, 6 H), 1.00 (s, 6 H); mass spectrum exact mass M$^+$ peak calculated at *m/e* 224.178, found *m/e* 224.181.

(14) Mp 83.0–83.5 °C (pentane, −20 °C); IR (Nujol) 3600–3500 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.10 (h, $J_{CH_3,CH}$ = 7.0 Hz, 2 H), 1.32 (s, 3 H), 1.22 (s, 3 H), 1.12 (d, J_{CH,CH_3} = 7.0 Hz, 6 H), 1.05 (s, 6 H), 1.04 (d, J_{CH,CH_3} = 7.0 Hz, 6 H); mass spectrum exact mass M$^+$ peak calculated at *m/e* 252.209, found *m/e* 252.211.

Claudio Giordano, Rudi F. Heldeweg, Hepke Hogeveen*
Department of Organic Chemistry,
The University of Groningen
Zernikelaan, Groningen, The Netherlands

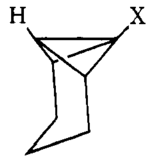
Received December 10, 1976

Organolithium Substitution at a Bicyclo[1.1.0]butane Bridgehead Position. Evidence for a Bicyclo[1.1.0]but-1(3)-ene as a Reaction Intermediate

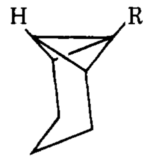
Sir:

The intriguing molecule bicyclo[1.1.0]but-1(3)-ene has so far only been known to theorists; calculations[1] suggest that it represents a local minimum on the C_4H_4 potential energy hypersurface. We now wish to report preliminary experimental evidence for the fleeting existence of a species containing such a skeletal unit in the reaction of 1-chlorotricyclo-[4.1.0.0^{2,7}]heptane (**1a**)[2] with organolithium derivatives.

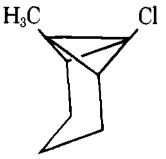
Addition of **1a** to an ether solution of 3 equiv of *n*-butyllithium at room temperature produced, after aqueous workup, an 87% isolated yield of 1-*n*-butyltricyclo[4.1.0.0^{2,7}]heptane (**2a**) in a practically instantaneous reaction. Structure proof for **2a** rests on its mass spectrum and its ^{1}H NMR, the latter showing, in addition to the expected signals for the side chain, the same pattern for the framework protons as the parent hydrocarbon tricyclo[4.1.0.0^{2,7}]heptane (**1c**).[3]



1



2



3

	X	R
a	Cl	$CH_2(CH_2)_2CH_3$
b	Br	$CH(CH_3)C_2H_5$
c	H	$C(CH_3)_3$
d	Li	C_6H_5

The derivatives **2b**–**2d** were prepared under similar conditions;[4] the NMR spectra of **2c**[5] and **2d**[6] were identical with those reported in the literature.

We consider three mechanistic pathways as possible routes to the products: (I) direct coupling between the organolithium compound and **1a**; (II) halogen-metal exchange between **1a** and the organolithium derivative forming **1d** and the corresponding chloride, followed by a coupling reaction between these components (in the case of **2d** dehydrobenzene could be involved); (III) elimination of hydrogen chloride from **1a** by the organometallic reagent with the formation of a bicyclo[1.1.0]but-1(3)-ene derivative and addition of the organolithium compound to the strained double bond. The following observations provide arguments against the mechanisms I and II. (a) When 1-chloro-7-methyltricyclo[4.1.0.0^{2,7}]heptane (**3**)[2] was added to a threefold excess of *n*-butyllithium in ether and kept for 15 h at 20 °C, on aqueous workup, **3** was