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CATALYTIC HYDROGENOLYSIS OF CYCLOPROPANES : METAL INSERTION INTO A SATURATED CARBON-CARBON BOND AS THE KEY STEP

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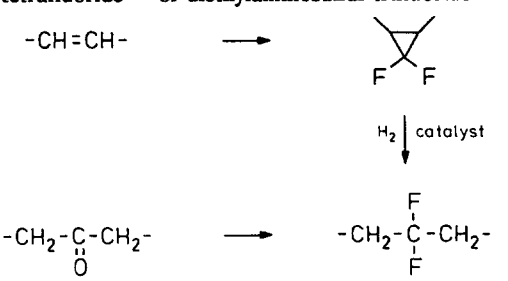
Summary : Hydrogenolytic ring cleavage of *gem*-difluorocyclopropanes occurs exclusively at the carbon-carbon bond opposite to the halogen-bearing center and affords mainly *gem*-difluoroalkanes. The intermediacy of catalyst/cyclopropane derived adducts (*e g*, palladacyclobutanes or 1,3-dipalladiopropanes) is postulated in order to rationalize the formation of monofluorinated and halogen-free by-products and, in addition, to explain specific substituent effects on the reaction rates.

Geminal difluorocyclopropanes are readily available by cycloaddition of difluorocarbene to alkenes. [1, 2] We wondered whether a hydrogenolytic ring opening could be selectively performed at the longer [3], hence weaker carbon-carbon bond opposite of the heterosubstituted center. If this could be accomplished, it would offer a new option for the introduction of a difluoromethylene group into an aliphatic chain This new method would be completely independent from the existing one which relies on the heteroatom exchange between a carbonyl compound and sulfur tetrafluoride [4] or diethylaminosulfur trifluoride [5]

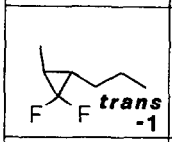
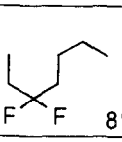
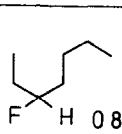
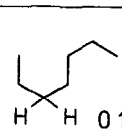
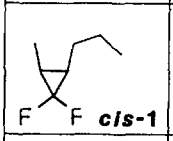
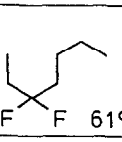
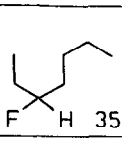
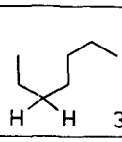
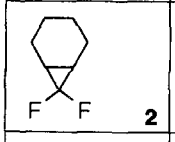
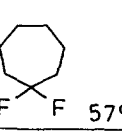
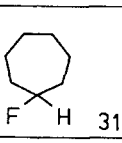
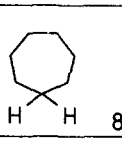
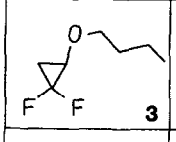
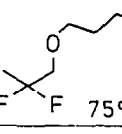
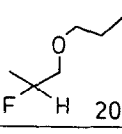
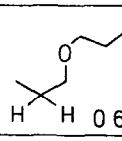
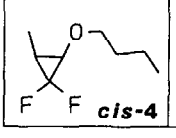
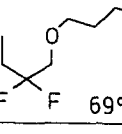
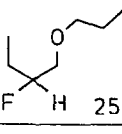
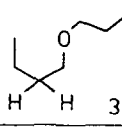


Up till now, only a few successful hydrogenation reactions with *gem*-difluorocyclopropanes have been reported Roth, Kirmse *et al* [6] were able to convert 2-vinyl-1,1-difluorocyclopropane and two closely related compounds almost quantitatively to the corresponding *gem*-difluoroalkanes (*e g.*, 2,2-difluoropentane)

The catalytic hydrogenation of 1,1-difluoro-2-phenylcyclopropane, studied by Isogai *et al* [7], afforded roughly equal amounts of 2,2-difluoro-1-phenylpropane, 2-fluoro-1-phenylpropane and 1-phenylpropane. In addition, small quantities of (*Z*)-2-fluoro-1-phenyl-1-propene were identified. Two structurally similar model compounds again produced mixtures of zero-, mono- and difluorinated ring opened derivatives

Since 1-alkenyl and aryl substituents are known to facilitate the hydrogenolysis of cyclopropane rings considerably [6 - 9], it was doubtful whether entirely saturated *gem*-difluorocyclopropanes would react at all. To our surprise, the hydrogenolytic ring scission was found to occur quite readily and with perfect regio- and reasonable typoselectivity, if palladium on charcoal was used as the catalyst. Geminal difluoro compounds were obtained as the main products contaminated with the corresponding monofluorinated derivatives (see Table). We wish to summarize our findings point by point

Table Products obtained by the palladium catalyzed hydrogenation of 1,1-difluoro-2-methyl-3-propylcyclopropane (**1**, *cis* or *trans* isomer), 7,7-difluoronorcarane (**2**), 2-butoxy-1,1-difluorocyclopropane (**3**) and *cis*-2-butoxy-1,1-difluoro-3-methylcyclopropane (**4**).

starting material	main product	side product	trace amount
 *trans*-**1**	 8%	 0.8%	 0.1%
 *cis*-**1**	 61%	 35%	 3%
 **2**	 57%	 31%	 8%
 **3**	 75%	 20%	 0.6%
 *cis*-**4**	 69%	 25%	 3%

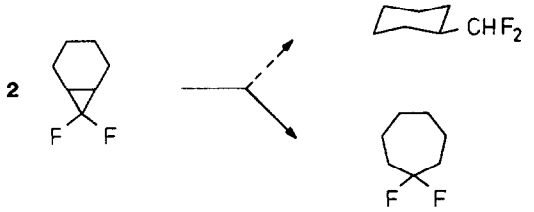
Fluorine Effect

The *gem*-difluorocyclopropanes undergo hydrogenolysis much faster than monofluorocyclopropanes [8, 10] not to speak of halogen-free cyclopropanes This rate enhancement reflects to some extent the destabilizing effect which the two fluorine atoms exert on the three-membered ring and which has been estimated to approximate 13 kcal/mol [6, 11] One may feel tempted to impute this destabilization to anti-bonding interactions between the substituents and the Walsh orbitals of the cyclopropane ring [12] This concept has provided an explanation for

substituent effects on the norcaradiene/cycloheptatriene equilibrium [13]. In the present case, however, simple geometrical factors ("hybridization" [14]) appear to be dominant. Due to the ring strain, cyclopropanes have severely compressed CCC angles and hence offer geminal substituents the comfort of expanding their exocyclic valence angles almost without restriction. Fluorine substituents cannot draw advantage of this opportunity since they prefer short angular distances to their nearest neighbors anyway (For example, 1,1,4,4-tetrafluorocyclohexane [15] < $C\text{-}CF_2\text{-}C$ 114.7°, < F-C-F 104.6°, < $C\text{-}CH_2\text{-}C$ 114.7°, < H-C-H ~ 109°, to be compared with cyclohexane [16] < C-C-C 111.3°, < H-C-H ~ 108° and propane [17] < C-C-C 112.4°, < H-C-H ~ 107°)

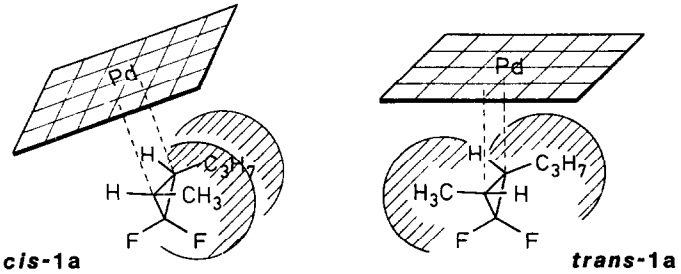
Regioselectivity

The hydrogenolytic scission affects practically exclusively the longest [3] carbon-carbon bond located across the ring in front of the geminal pair of fluorine atoms In a single case we were able to identify also a regioisomeric ring opening product 7,7-difluoronorcarane (**2**, 7,7-difluorobicyclo[4.1.0]heptane) gave just trace amounts (0.1 - 0.5%) of difluoromethylcyclohexane besides the main product 1,1-difluorocycloheptane



Steric Hindrance

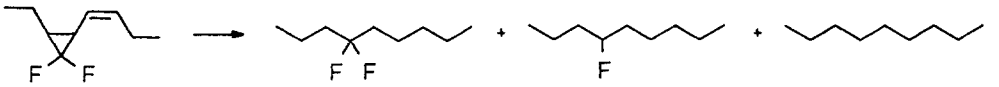
The rate of hydrogenolysis proved to be quite sensitive to steric effects. Even at a hydrogen pressure of 100 atm, *trans*-1,1-difluoro-2-methyl-3-propylcyclopropane (*trans*-**1**) reacted only sluggishly while the *cis* isomer (*cis*-**1**) as well as 7,7-difluoronorcarane (**2**) were rapidly consumed already at 25 atm Obviously the cyclopropane can much better approach the catalyst surface if at least one of its faces is not encumbered by bulky substituents (*cis*-**1a** *vs trans*-**1a**)



Geometrical Isomerization

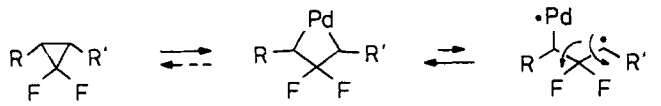
No mutual isomerization of *cis*- and *trans*-1,1-difluoro-2-methyl-3-propylcyclopropane (*cis*- and *trans*-**1**) was observed under the standard hydrogenation conditions. Furthermore, not even trace amounts of the *trans* isomer

were formed during the hydrogenation of *cis*-2-(*cis*-1-butenyl)-3-ethyl-1,1-difluorocyclopropane (*cis*-**5**). When the reaction was complete, 4,4-difluorononane (70%), 4-fluorononane (20%) and nonane (9,7%) were identified as the sole products



***cis*-5**

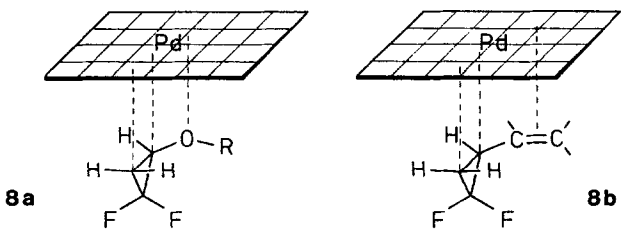
Apparently the reductive metal insertion [18] into the carbon-carbon bond of the three-membered ring, affording the metallacyclobutane [19] **6**, is an irreversible process In addition, no evidence was found for the intermediacy of a free radical species **7** in which free rotation would be restored [20]



6 **7**

Complexation Mediated Rate Enhancement

Alkoxy substituents facilitate significantly the hydrogenolytic ring opening Thus, *cis*-2-butoxy-1,1-difluoro-3-methylcyclopropane (*cis*-**4**) reacts roughly two orders of magnitudes faster than does its oxygen-free analog *cis*-1,1-difluoro-2-methyl-3-propylcyclopropane (*cis*-**1**) We ascribe this rate enhancement to the formation of a donor-metal complex **8a** which precedes the crucial reductive insertion into the ring carbon-carbon bond of the three-membered ring Olefinic and aromatic substituents presumably act in the same way (complex **8b**)

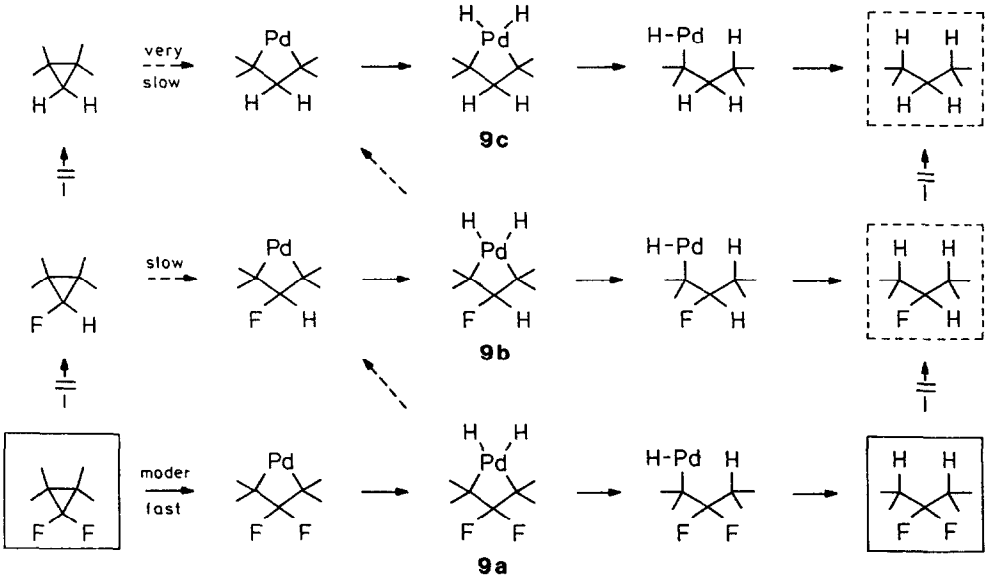


8a **8b**

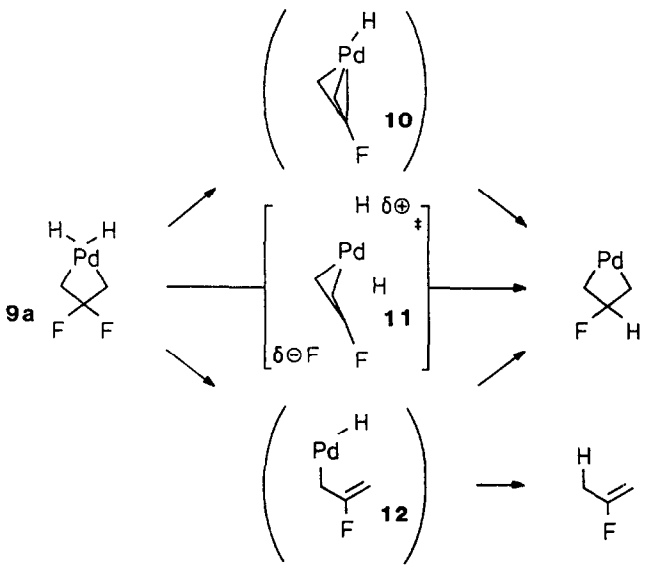
Loss of Fluorine

As already recognized previously [6 - 8], the hydrogenolytic ring opening of *gem*-difluorocyclopropanes is accompanied by partial replacement of fluorine by hydrogen atoms This reduction must occur at some transient stage since *gem*-difluoroalkanes prove to be completely inert towards hydrogenation Tentatively we suggest a reaction sequence involving the dihydropalladacyclobutane **9a** as a turntable. It may emerge from direct insertion of palladium hydride into the carbon-carbon bond of the *gem*-difluorocyclopropane or, much more probably, be generated by consecutive insertion of a Pd(0) species and hydrogen addition Its principal mode of reaction is ring opening and simultaneous or subsequent hydride transfer from the palladium to one of the adjacent carbon atoms, giving rise to an alkylpalladium hydride which immediately undergoes stabilization by reductive elimination of zero-valent palladium In a competitive process, however, the hydride may instead be delivered to the β-carbon atom where it ejects a fluoride ion which then picks up the second metal-attached hydrogen atoms Thus,

after hydrogen addition a monofluorinated hydridopalladacyclobutane **9b** is obtained which again has the choice to proceed by hydrogenolysis towards a monofluoroalkane or to loose also the second fluorine atom before it passes through the intermediate **9c** and ends up as a halogen-free hydrocarbon.



Details of the fluoride-by-hydride replacement are unknown. It may imply an intramolecular substitution with palladium as the nucleophile (producing the metallabicyclic intermediate **10**), a direct intramolecular nucleophilic substitution by hydrogen (transition state **11**) and finally a combined Pd-centered α-elimination and a CC-centered β-elimination (generating a σ-2-fluoroallylpalladium species **12**). The latter route may also lead to fluoroalkenes which indeed are occasionally observed as final products [7, 8]



Of course, the concomitant formation of mono- and zero-fluorinated by-products impairs the practical utility of the new synthetic entry to *gem*-difluoroalkanes. Suitable modifications of the experimental conditions, however, should allow to minimize the side reactions. Actually, with rhodium (5% on charcoal) rather than palladium as the hydrogenation catalyst, *cis*-2-butoxy-1,1-difluoro-3-methylcyclopropane (*cis*-4) afforded 87% of butyl 2,2-difluorobutyl ether and only 3% of the monofluoro analog besides 2% of dibutyl ether

EXPERIMENTAL PART

1 General

Starting materials have been purchased from Fluka AG, Buchs, Aldrich-Chemie, Steinheim, or Merck-Schuchardt, Darmstadt, unless literature sources or details for the preparation are given. All commercial reagents were used without further purification

Anhydrous *tetrahydrofuran* and *glycol dimethyl ether* (1,2-dimethoxyethane) were obtained by distillation from sodium wire after the characteristic blue color of *in situ* generated sodium diphenylketyl [21] was found to persist In case of poor quality of the crude material, the latter solvent was pretreated with cuprous chloride [22] and potassium hydroxide pellets *Dichloromethane* was distilled from phosphorus pentoxide after having been stirred 4 h in the presence of the drying agent

Ethereal extracts were dried with sodium sulfate. Before distillation of compounds prone to radical polymerisation or sensitive to acids a spatula tip of *hydroquinone* or, respectively, *potassium carbonate* was added.

The temperature of dry ice-methanol baths is consistently indicated as -75 °C, "room temperature" (22 - 26 °C) as 25 °C If no reduced pressure is specified, *boiling ranges* were determined under ordinary atmospheric conditions (720 ± 25 mmHg) All products were liquids and attempts to crystallize them have failed even at temperatures as low as -75 °C

Whenever reaction products were not isolated, their yields were determined by *gas chromatography* comparing their peak areas with that of an internal standard and correcting the ratios by response factors The purity of distilled compounds was checked on at least two columns loaded with stationary phases of different polarity. Chromosorb G-AW of 80 - 100 and, respectively, 60 - 80 mesh particle size were chosen as the support for packed analytical or preparative columns (2 or 3 m long, 2 mm inner diameter and 3 or 6 m long, 1 cm inner diameter, respectively) All packed columns were made of glass, while quartz was the material for coated, Grob-type capillary columns (≥ 10 m long)

Nuclear magnetic resonance spectra of hydrogen nuclei were recorded at 360 MHz and of fluorine-19 nuclei at 188 MHz Deuterochloroform was used as the solvent. Chemical shifts refer to the signal of tetramethylsilane (δ = 0 ppm), which served as an internal standard in the case of ^{1}H spectra, and of α,α,α-trifluorotoluene for ^{19}F spectra Coupling constants (J) are measured in Hz Coupling patterns are described by abbreviations . s singulet), d (doublet), t (triplet), q (quadruplet), pent (pentuplet), hex (hexuplet), td (triplet of a doublet) and m (multiplet)

In general, *mass spectra* under electron impact were obtained at a 70 eV ionization potential and at 200 °C source temperature The intensities of fragments relative to the base peak are given in parentheses after their molecular weight (m/e) M^+ means the peak of the intact molecule in form of its radical-cation When no molecular peak was observed under standard conditions, chemical ionization ("c i ") in an ammonia atmosphere at 95 3 eV ionization potential and at 100 °C source temperature was applied

2. Starting Materials and Products for Comparison

a) *1,1-Difluorocyclopropanes* : Most compounds have already been described previously. [1] Using the same procedure [1], *cis,cis*-3,5-octadiene [23] was converted to ***cis*-2-(*cis*-1-butenyl)-3-ethyl-1,1-difluorocyclopropane** (5), 86%, bp 55 - 56 °C/30 mmHg; n_D^{20} 1 4138. - ^{1}H-NMR : 5.65 (1 H, dtd, *J* 10.7, 7.3, 0.7), 5.14 (1 H, symm. m), 2 32 (1 H, symm m), 2 12 (2 H, pent, *J* 7.5), 1.5 (3 H, m), 1 01 (3 H, t, *J* 7.4), 0.98 (3 H, t, *J* 7.4). - ^{19}F-NMR . -89 2 (d, *J* 154), -60.9 (dt, *J* 154, 13). - MS : 160 (11%, M^+), 131 (17%), 118 (70%), 103 (100%). - Analysis : calc for $C_9H_{14}F_2$(160 20) C 67 48, H 8 80, found C 67 10, H 8.58%.

b) gem-*Difluoro(cyclo)alkanes* 3,3-Difluoroheptane [27], (difluoromethyl)cyclohexane [24] and 1,1-difluorocycloheptane [28] as well as two new compounds were prepared in the usual manner [25] by treatment of the corresponding carbonyl compound with diethylaminosulfur trifluoride - **4,4-Difluorononane** . 44%; bp 158 - 159 °C, n_D^{20} 1 3868 - ^{1}H-NMR 1.78 (4 H, symm m), 1 5 (4 H, m), 1 31 (4 H, symm m), 0.96 (3 H, t, *J* 7.3), 0.90 (3 H, t, *J* 7 0) - ^{19}F-NMR . -35 0 (pent, *J* 16) - MS : 182 (0 7%, $M^+ + NH_4$), 144 (8%, M^+ - HF), 124 (50%), 81 (100%) - Analysis calc. for $C_9H_{18}F_2$ (164 24) C 65 82, H 11 05, found C 66 01, H 10.95%. - **Butyl 2,2-difluoropropyl ether** (from 1-butoxy-2-propanone [29]) 50%, bp 123 -124 °C; n_D^{20} 1 3675 - ^{1}H-NMR : 3 57 (2 H, t, *J* 12 0), 3 54 (2 H, t, *J* 6 6), 1.64 (3 H, t, *J* 18 7), 1 59 (2 H, pent-like m, *J* ~ 7), 1 40 (2 H, hex, *J* 7 4), 0.93 (3 H, t, *J* 7 4) - ^{19}F-NMR : -35 2 (qt, *J* 18, 12) - MS 152 (0 1%, M^+), 109 (9%), 87 (24%), 57 (100%) - Analysis . calc for $C_7H_{14}F_2O$ (152.18) C 55 25, H 9 27, found C 55 10, H 9.35%

c) *Fluoro(cyclo)alkanes* Fluorocycloheptane [24] and three new compounds were prepared by treating the corresponding alcohol with diethylaminosulfur trifluoride according to the standard literature procedure [25] - **3-Fluoroheptane** : 29%, bp 110 - 111 °C, n_D^{20} 1 3848 - ^{1}H-NMR 4 41 (1 H, dm, *J* 49.6), 1 5 (8 H, m), 0 97 (3 H, t, *J* 7 5), 0.90 (3 H, t, *J* 7 3) - ^{19}F-NMR -118 6 (symm m). - MS [c.i] 136 (2%, $M^+ + NH_4$), 98 (19%), 83 (30%), 70 (100%) - Analysis calc for $C_7H_{15}F$ (118 19) C 71 13, H 12.79; found C 70 98, H 12 87% - **4-Fluorononane** 63%, bp 160 - 162 °C, n_D^{20} 1 4002 - ^{1}H-NMR · 4 49 (1 H, dm, *J* 49 0), 1.5 (12 H, m), 0 94 (3 H, t, *J* 7 2), 0 90 (3 H, t, *J* 7 0) - ^{19}F-NMR -117 8 (symm m). - MS 126 (4%, M^+ - HF), 97 (32%), 55 (100%) - Analysis calc for $C_9H_{19}F$ (146 25) C 73 91, H 13 09; found C 73.89, H 13 08%. - **Butyl 2-fluoropropyl ether** (from 1-butoxy-2-propanol [26]) . 9%, bp 129 - 130 °C; n_D^{20} 1.3863 - ^{1}H-NMR · 4 83 (1 H, dm, *J* 48 8), 3.5 (4 H, m), 1 60 (2 H, pent-like m, *J* ~ 7), 1.40 (2 H, hex-like m, *J* 7.5), 1.35 (3 H, dd, *J* 23 8, 6 4), 0.93 (3 H, t, *J* 7.4) - ^{19}F-NMR -116.5 (symm m) - MS 134 (1%, M^+), 91 (8%), 87 (11%), 57 (100%) - Analysis calc for $C_7H_{15}FO$ (134 19) C 62.65, H 11.27, found C 62 78, H 10 98%.

d) *Halogen-free products* Butyl propyl ether was prepared from propyl bromide and potassium butoxide in tetrahydrofuran, following a literature procedure [30], 46%, bp 115 - 116 °C, n_D^{20} 1 3909

3 Hydrogenation Reactions

a) *General method* If the reaction was carried out on an analytical scale, the 1,1-difluorocyclopropane (1 0 mmol) was dissolved in pentane (5 0 mL), 10% palladium on charcoal (0 10 g) was added and a hydrogen pressure of 25 atm was applied during 30 min at 25 °C Tenfold quantities were used for preparative reactions

b) *Evaluation of products* Yields (see Table) were determined by gas chromatography (GC) relative to an internal standard and were corrected by calibration factors Whenever possible, products were identified by gas chromatographic comparison with authentic samples (see Section 2) and by GC-coupled mass spectrometry The two principal products resulting from the hydrogenolysis of *cis*-2-butoxy-1,1-difluoro-3-methylcyclopropane (*cis*-4) were isolated by means of preparative GC (3 m, 8% Carbowax 20 M, 65 °C) from the hydrogenation mixture **Butyl (2,2-difluorobutyl) ether** bp 146 - 147 °C, n_D^{20} 1.3784 - ^{1}H-NMR 3.59 (2 H, t, *J* 12 5) 3.53 (2 H, t, *J* 6 5), 1 94 (2 H, qt, *J* 17 0, 7 5), 1 58 (2 H, pent-like m, *J* ~ 7), 1.39 (2 H, hex, *J* 7 5), 1.03 (3 H, t, *J* 7 5), 0 93 (3 H, t, *J* 7 4) - ^{19}F-NMR -44 3 (tt, *J* 17, 13) - MS 166 (0 1%, M^+), 87 (22%), 73 (6%), 57 (100%) - Analysis calc for $C_8H_{16}F_2O$ (166 21) C 57 81, H 9 70, found C 57 97, H 9 69%. - **Butyl (2-fluorobutyl) ether** bp 154 - 155 °C, n_D^{20} 1 3949 - ^{1}H-NMR 4 57 (1 H, ddtd, *J* 49 3, 10 8, 5 5, 4 0), 3 5 (2 H, m), 3 49 (2 H, t, *J* 6 7), 1 6 (4 H, m), 1 39 (2 H, hex, *J* 7 5), 1 00 (3 H, t, *J* 7 2), 0 93 (3 H, t, *J* 7 4) - ^{19}F-NMR · -124 0 (symm m) - MS 148 (0 5%, M^+), 87 (24%), 75 (4%), 57 (100%) - Analysis calc for $C_8H_{17}FO$ (148 22) C 64 83, H 11 56, found C 65 22, H 11 22%

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REFERENCES

[1] Y. Bessard, U Müller, M. Schlosser, *Tetrahedron* **46** (1990), in press.
[2] D.J. Burton, D.G Naae, *J. Am Chem. Soc* **95** (1973), 8467
[3] A.T. Perretta, V W Laurie, *J Chem. Phys* **62** (1970), 2469; see also . J E Boggs, K.-n. Fan, *A Scand.* **A42** (1988), 595
[4] G.A. Boswell, W.C Ripka, R.M Scribner, C W Tullock, *Org React* **21** (1974), 1.
[5] M. Hudlicky, *Org React.* **35** (1987), 513
[6] W.R. Roth, W. Kirmse, W. Hoffmann, H.W. Lennartz, *Chem Ber* **115** (1982), 2508
[7] K. Isogai, N Nishizawa, T. Saito, J. Sakai, *Bull Chem. Soc Japan* **56** (1983), 1555
[8] K. Isogai, J. Sakai, K. Kosugi, *Bull Chem Soc. Japan* **59** (1986), 1349
[9] C. Gröger, H Musso, I. Roßnagel, *Chem. Ber.* **113** (1980), 3621.
[10] M. Schlosser, G. Heinz, *Angew Chem.* **79** (1967), 617, *Angew Chem Int Ed. Engl.* **6** (1 M. Schlosser, G Heinz, Le Van Chau, *Chem Ber.* **104** (1971), 1921
[11] H.E O'Neal, S W Benson, *J. Phys. Chem* **72** (1968), 1866
[12] R Hoffmann, W.D Stohrer, *J Am Chem Soc* **93** (1971), 6941
[13] H Gunther, *Tetrahedron Lett* **11** (1970), 5173.
[14] See also in this context M E Jason, J.A Ibers, *J Am Chem. Soc* **99** (1977), 6012, W.A *J Org Chem.* **34** (1969), 1772, S Y. Wang, W T Borden, *J Am. Chem Soc* **111** (1989), 7282
[15] J D Dunitz, W.B Schweizer, B Seiler, *Helv Chim Acta* **66** (1983), 134
[16] M Davis, O. Hassel, *Acta Chem Scand.* **17** (1963), 1181
[17] R.A. Bonham, L.S Bartell, D.A Kohl, *J Am Chem Soc.* **81** (1959), 4765.
[18] For comparison, see the addition of Pd(0) to methylenecyclopropane [P Binger, U Schuchai *Ber* **113** (1980), 3334; see also R Noyori, T. Odagi, H. Takaya, *J Am Chem Soc.* **92** (1970 Binger, *Synthesis* **1973**, 427] and 1-alkenylcyclopropanes [I Shimizu, Y Ohashi, J. Tsuji, *Ti Lett* **26** (1985), 3825, see also Y Morizawa, K. Oshima, H Nozaki, *Isr J Chem* **24** (1984) addition of $PdCl_2$ [M.F Rettig, D E. Wilcox, R S Fleischer, *J. Organomet Chem* **214** (1981), Ahmad, J.E. Backvall, R.E Nordberg, T. Norin, S. Stromberg, *J Chem Soc, Chem Comn* 321] or $PtCl_2$ [R.J Puddephatt, *Coord Chem. Rev.* **33** (1980), 149] to mono- or bicyclic der cyclopropanes as well as the Ir(I)-promoted isomerization reaction of cyclopropanes to prope Campbell, P.W. Jennings, *Organometallics* **1** (1982), 1071]
[19] We write metallacyclobutane structures for simplicity, although we are aware that we may r with surface attached 1,3-diradicals, in other words with 1,3-dimetal compounds
[20] According to a very crude thermochemical evaluation, the oxidative addition of Pd(0) to a ty difluorocyclopropane should be *exothermal* by approximately 10 kcal/mol [partial relief o enhanced ring strain 20, C-C, Pd-Pd and C-Pd bond strength 85, 20 and, respectively, 50 l while the homolytic scission of the metallacyclobutane should be *endothermal* by some 25 [relief of fluorine enhanced ring strain · 20, radical stabilization 5, P-C bond strength 50 kcal/
[21] W. Schlenk, E. Bergmann, *Liebigs Ann Chem* **464** (1928), 22
[22] W. Bunge, in *Houben-Weyl Methoden der organischen Chemie*, Vol **1/2**, p 814, G Thiem Stuttgart 1959
[23] J F Normant, G. Cahiez, M Bourgain, C. Chuit, J Villieras, *Bull Soc Chim Fr* **1974**, 1656
[24] G.A Olah, N Najima, I Kerekes, *Synthesis* **1973**, 779
[25] W.J Middleton, *J Org Chem* **40** (1975), 574
[26] H C. Chitwood, B.T Freure, *J Am Chem Soc* **68** (1946), 680
[27] F. Mathey, J. Bensoam, *Tetrahedron* **27** (1971), 3965
[28] D R. Strobach, G.A Boswell, *J Org Chem* **36** (1971), 818
[29] By the oxidation of 1-butoxy-2-propanol with pyridinium chlorochromate
[30] R.A Spurr, H Zeitlin, *J Am Chem Soc* **72** (1950), 4832