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Fluorinated Bis(enyl) Ligands by Metal-Induced Dimerization of Fluorinated Allenes[**]

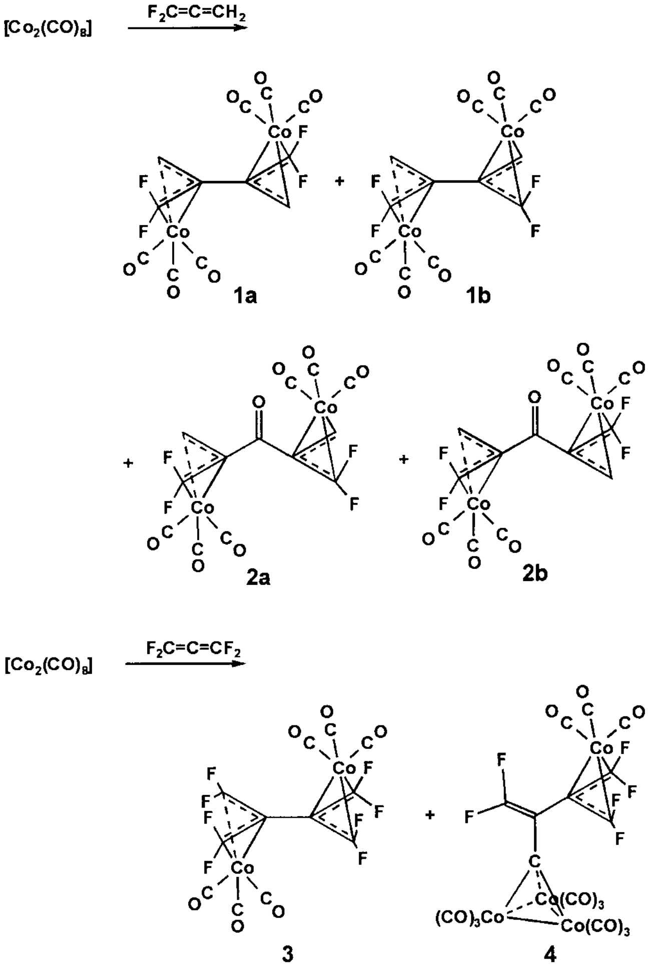
Dieter Lentz[*] and Stefan Willemsen

It is often extremely difficult to synthesize fluorinated analogues of ligands frequently used in organometallic chemistry,[1] such as cyclopentadienyl and propenyl (allyl) ligands. After many unsuccessful attempts pentafluorocyclopentadiene was synthesized and deprotonated;[2] however, no C_5F_5 complex could be prepared thereof. The synthesis of pentamethylcyclopentadienyl(pentafluorocyclopentadienyl)-ruthenium by vacuum pyrolysis of pentamethylcyclopentadienyl(pentafluorophenoxy)ruthenium with elimination of carbon monoxide at 750 °C demonstrates that fluorinated enyl complexes are not generally unstable,[3] but suitable synthetic methods are often missing. As the C–F bond is the strongest element–carbon bond (D(C–F) = 109 – 130 kcal mol^{-1}) and C–F activation is gaining increasing importance,[4] we are looking for methods to construct more complex ligands directly at metal complexes from simple, readily available fluoroorganic starting materials.

We started our investigations by studying the ligand properties of fluorinated allenes, which turned out to be very strong π-acceptor ligands; thus, stressing the importance of π backbonding as shown also by theoretical calculations.[6]

We expected to be able to construct new ligands by metal-induced dimerization of 1,1-difluoroallene and tetrafluoroallene on manganese and cobalt complex fragments, as reactions of allenes with decacarbonyldimanganese[7] and octacarbonyldicobalt[8] resulted in new ligand systems through C–C coupling. Furthermore the dimerization is the first step of a polymerization reaction which is not a metal-catalyzed process in the case of fluorinated alkenes. The polymerization of fluorinated alkenes to technically important products, such as polytetrafluoroethene (PTFE) and fluorinated ethylene propylene copolymer (FEP), is generally acheived by free radical polymerization.[9] In the presence of radical trapping agents, such as terpenes, fluorinated alkenes yield [2+2] cycloaddition products.[10] Tetrafluoroallene polymerizes to give a not fully characterized polymer and dimerizes in the presence of α-terpinene to give perfluoro-1,2-methylenecyclobutane.[11]

Reaction of 1,1-difluoroallene and tetrafluoroallene with octacarbonyldicobalt yielded the dinuclear cobalt complexes **1** and **3**, respectively (Scheme 1). The reaction with 1,1-



Scheme 1. Reactions of octacarbonyldicobalt with 1,1-difluoroallene and with tetrafluoroallene.

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[**] This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft. We are indebted to the Hoechst AG (Frankfurt/Main) and DUPONT (Wilmington, DE) for some starting materials. We thank Dr. Dieter Zobel for the collection of X-ray data at 20 K.

difluoroallene additionally yields the dinuclear complex **2**, in which a CO unit is inserted between the two C_3 fragments, in the reaction with tetrafluoroallene small amounts of the cluster compound **4** were isolated. The NMR spectra of **1** exhibit two sets of signals, which are attributed to the presence of a C_i (**1a**) and a C_2-symmetrical isomer (**1b**). Crystals of both isomers were isolated and the structures of both were determined by X-ray crystallography[12] (Figure 1). The two isomeric cobalt complexes have very similar metal–carbon distances to the 2,3-dimethylenebuta-1,4-diyl ligands; the distances to the fluorine-substituted carbon atoms are about 0.1 Å shorter than those to the hydrogen-substituted ones. The distances to the central cabron atoms lie somewhere in between. Consequently the fluorine-substituted C−C bond is more elongated than the other one. Significant differences between the structures of the isomers **1a** and **1b** are observed for the C5−C5A distance (1.478(3) and 1.494(8) Å, respectively) and the torsion angles C4-C5-C5A-C4A (−180 and −96.8°, respectively). An isomerization of **1a** and **1b** would require that the [Co(CO)$_3$] fragment would migrate from one side of the allyl ligand to the other or that the coordination mode would change from η^3 to η^1. Both were not observed in the temperature range from −100 to 50 °C by NMR spectroscopy. Interestingly, the chemical shift values of one these isomers shows a strong temperature dependence not observed for the other one. Compound **3** crystallizes orthorhombic in the space group *Pcan* (no. 60, conventional *Pbcn*) with 1.5 molecules in the asymmetric unit. One of the molecules (molecule 2) possesses crystallographic C_2 symmetry (Figure 2), whereas the other (molecule 1) has only approximately C_2 symmetry. Major differences between the molecules are observed only for the torsion angles (C14-C15-C25-C26 −116.5°, C34-35-C35A-C36A −132.4°). The metal–carbon distances to the CF_2 groups lie between 1.955(3) and 1.971(3) Å and are slightly shorter than those to the central carbon atom. According to the C_2 symmetry the ^{19}F NMR spectrum of **3** should consist of two AB patterns for the four inequivalent fluorine atoms, as observed in the low-temperature spectrum at −60 °C. On raising the temperature the signals coalesce and only one AB pattern is found at ambient temperature, which can be explained by rapid rotation around the central C−C bond.

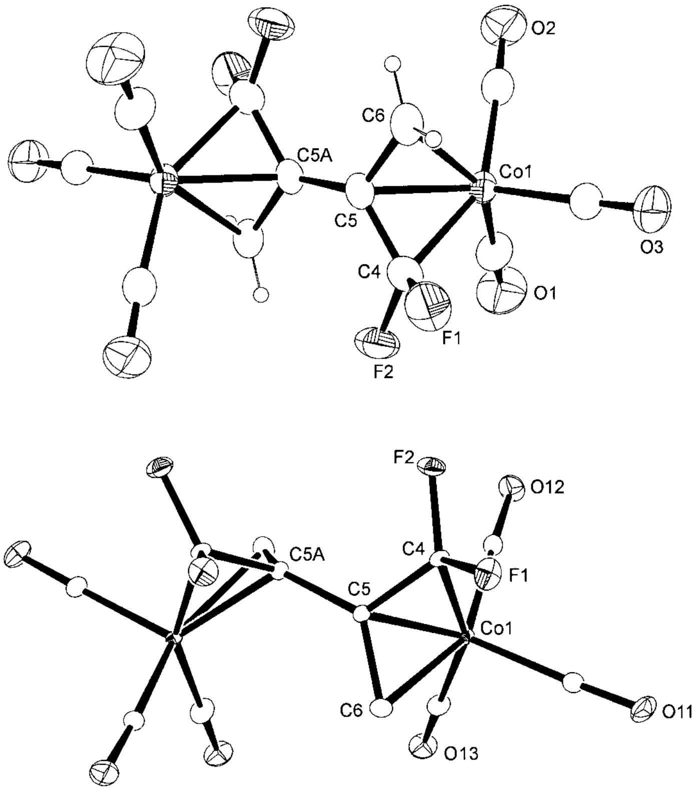


Figure 1. Molecular structures of **1a** (top, ORTEP[17]; 30 % ellipsoids) and **1b** (bottom, ORTEP[17]; 50 % ellipsoids; measurement temperature 20 K). Selected bond lengths [Å] and torsion angles [°] for **1a**/**1b**: Co1-C4 1.9632(19)/1.951(4), Co1-C5 2.0107(16)/1.996(4), Co1-C6 2.0706(18)/2.103(4), C4-C5 1.437(3)/1.446(5), C5-C6 1.419(2)/1.420(6), C5-C5A 1.478(3)/1.494(8); C4-C5-C5A-C4A −180.0(2)/−96.8(2).

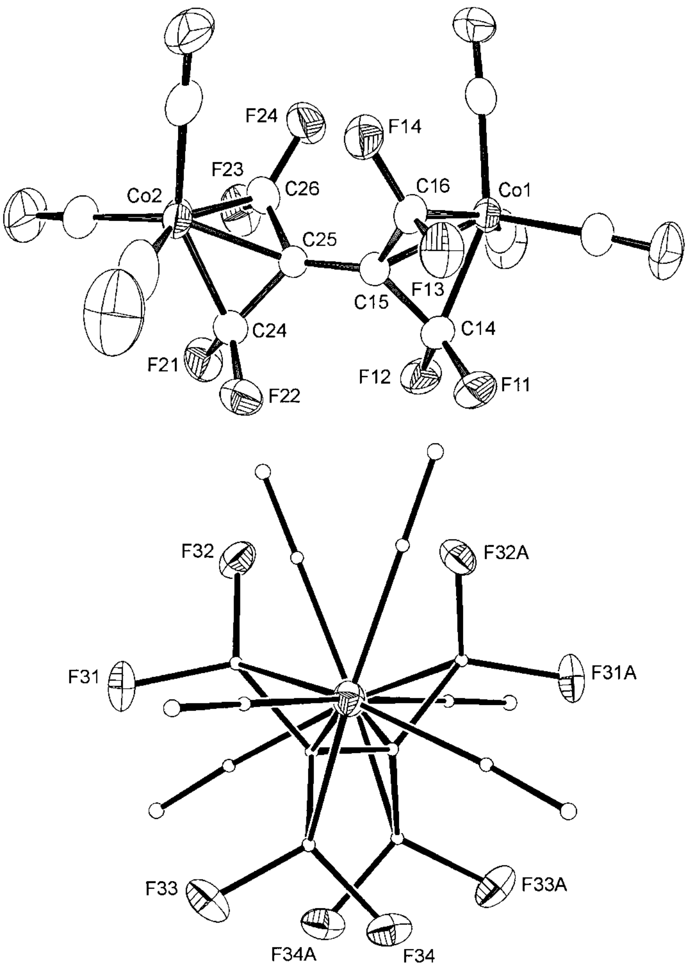


Figure 2. Molecular structures of **3** (ORTEP[17]). Top: molecule 2 (30 % ellipsoids), bottom: molecule 1 with view along the Co−Co axis to demonstrate the C_2 symmetry of the molecule. Selected bond lengths [Å] and torsion angles [°]. Co-CF$_2$ 1.955(3)–1.971(3), Co-C$_{\mathrm{central}}$ 1.988(3)–2.015(3), C-C$_{\mathrm{allyl}}$ 1.410(5)–1.425(5), C-C 1.483(4)–1.485(6); C14-C15-C25-C26 −116.5(3), C34-C35-C35A-C36A −132.4(3).

NMR studies of **2** show that this compound consists of a mixture of two isomers in the ratio 1:7; however, as above the spectrum does not allow an assignment of the signals to the specific isomers **2a** and **2b**. The bond lengths and angles of **2b** (Figure 3, top) do not differ significantly from those of **1** besides the presence of an additional carbonyl group between the two allyl groups.

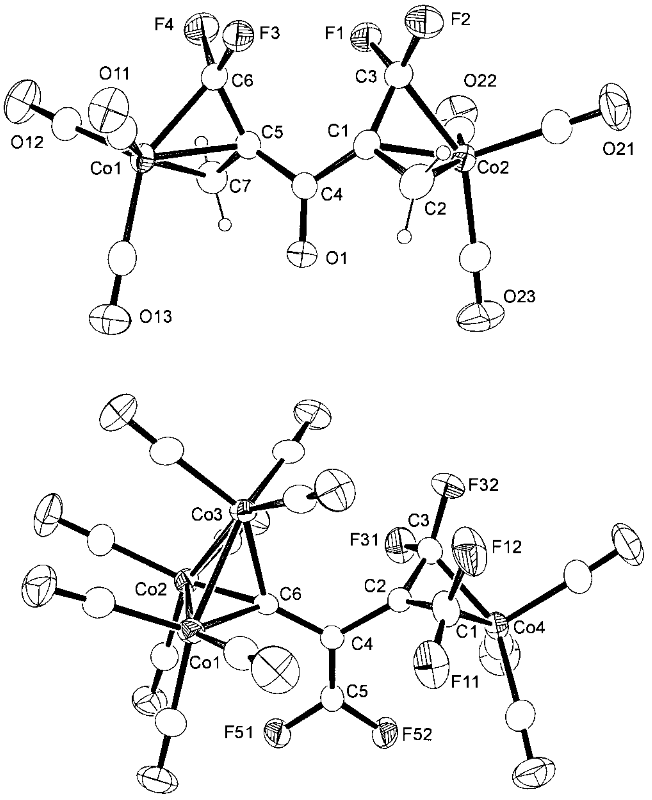
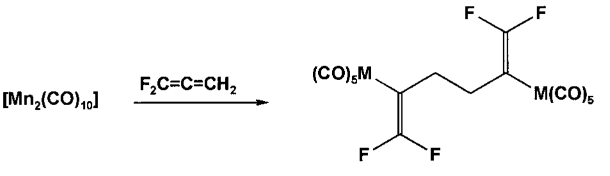


Figure 3. Molecular structures (ORTEP,[17] 30 % ellipsoids) of **2** (top) and **4** (bottom). Selected bond lengths [Å]: **2**: Co-CF_2 1.966(4) – 1.969(4), Co-$C_{central}$ 1.980(3) – 1.992(3), Co-CH_2 2.058(4) – 2.077(4), C-CF_2 1.422(5) – 1.433(5), C-CH_2 1.402(5) – 1.403(5); **4**: Co-C6 1.913(3) – 1.916(3), Co4-C1 1.966(3), Co4-C2 2.002(3), Co4-C3 1.964(3), C1-C2 1.418(4), C2-C3 1.417(4), C2-C4 1.500(4), C4-C6 1.466(4), C4-C5 1.320(4), C5-F 1.313(3) – 1.316(3), C3-F 1.347(4) – 1.348(4).

The cluster compound **4** results from a fluoride abstraction from one CF_2 group in the reaction with octacarbonyldicobalt under formation of a alkylidyne ligand. The tetrafluoroallyl cobalt unit (Figure 3, bottom) shows the same structural characteristics as already observed in **3**. The alkylidyne carbon atom C6 forms a μ_3 bridge to three tricarbonylcobalt fragments, as observed in numerous alkylidyne cluster compounds of cobalt.[13]

The reaction of 1,1-difluoroallene with decacarbonyldimangenese yields the dimer **5**, in which the ligand bridges two pentacarbonyl manganese fragments (Scheme 2). During this C–C coupling reaction the new bond is formed between the two CH_2 groups instead of at the central carbon atom, and the 1,1,6,6-tetrafluoro-1,5-hexadiene-2,5-diyl ligand is η^1:η^1 coordinated to the pentacarbonyl manganese fragments. The centrosymmetric molecule crystallizes triclinic (space group $P\bar{1}$) with half a molecule within the asymmetric unit. The metal atoms are almost octahedrally coordinated by five carbonyl ligands and the carbon atoms C6 and C6A of the 1,1,6,6-tetrafluoro-1,5-hexadiene-2,5-diyl ligand (Figure 4). The metal – carbon distances to the *trans* carbonyl ligand is significantly shorter than those to the *cis* carbonyl ligands.



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Scheme 2. Reaction of decacarbonyldimanganese with 1,1-difluoroallene.

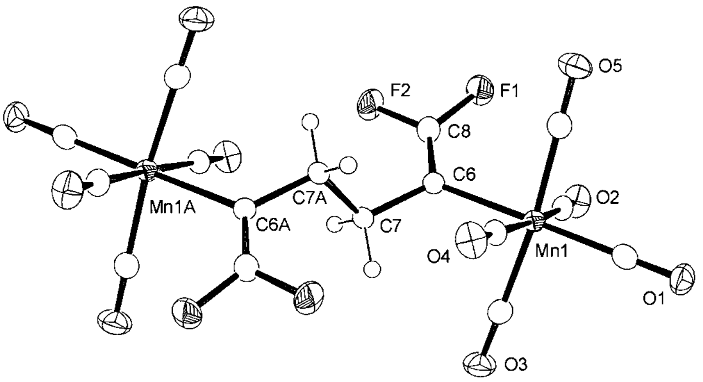

Figure 4. Molecular structure of **5** (ORTEP,[17] 50 % ellipsoids). Selected bond lengths [Å] of **5**. Mn-C1 1.847(2), Mn-C2-5 1.863(2), Mn-C6 2.108(2), C6-C7 1.524(2), C6-C8 1.309(2), C7-C7A 1.543(3), C-F 1.348(2) – 1.350(2).

The products of the metal-induced dimerization of flurorinated allenes strongly depends on the metal complex used and they are completely different to those obtained in a "metal-free" dimerization reaction.

Experimental Section

Hexacarbonyl-μ-(η^3:η^3-1,1,5,5-tetrafluoro-2,3-dimethylenebuta-1,4-diyl)dicobalt (**1**) and hexacarbonyl-μ-(η^3:η^3-1,1,5,5-tetrafluoro-2,4-dimethylene-3-oxopenta-1,5-diyl)dicobalt (**2**): Octacarbonyldicobalt (2 g, 5.86 mmol) was dissolved in *n*-pentane (60 mL). 1,1-Difluorallene (18.3 mmol) was condensed onto the solution by using a glass vacuum system. The reaction mixture was stirred for 48 h. The solvent was removed under vacuum and the residue was purified by column chromatography (*n*-pentane/silica, 45 × 3 cm^2). The first fraction contained compound **2**, which, after removal of the solvent, was sublimed under vacuum at 40 °C/10^{-3} mbar onto a receiver cooled to – 25 °C. Compound **2** (1172 mg, 43 %) was obtained as yellow crystals as a mixture of two isomers in the ration 1:7 (isomer 2: isomer 1). M.p. 77 – 78 °C. ^1H NMR ($CDCl_3$, – 50 °C): $\delta = 2.17$ (s, 1 H; CH_2, isomer 2), 2.21 (s, 1 H; CH_2, isomer 1), 2.58 (s, 1 H; CH_2, isomer 2), 2.99 (s, 1 H; CH_2, isomer 1); ^{19}F NMR ($CDCl_3$): $\delta = -77.55$ (d, $^2J_{F,F} = 84.0$ Hz, 1 F; CF_2, isomer 2), – 79.30 (d, $^2J_{F,F} = 89$ Hz, 1 F; CF_2, isomer 1), – 90.80 (d, $^2J_{F,F} = 89.5$ Hz, 1 F; CF_2, isomer 1), – 91.10 (d, $^2J_{F,F} = 84$ Hz, 1 F; CF_2, isomer 2); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 197.7$ (s; CO), 190.5 (s; CO), 142.0 (dd, $^1J_{C,F} = 318, 335$ Hz; CF_2), 63.9 (s; *C*-CF_2), 45.5 (s; CH_2); $^{13}C\{^{19}F\}$ NMR ($CDCl_3$): isomer 1: $\delta = 197.7$ (s; CO), 190.5 (s; CO), 142.0 (s; CF_2), 63.9 (s; *C*-CF_2), 45.6 (t, $^1J_{HC} = 167$ Hz; CH_2); isomer 2: $\delta = 197.8$, 189.1, 143.0, 65.6 and 44.0. IR (KBr): $\tilde{\nu} = 3098$ w, 3074 w, 2321 w, 2093 vs (CO), 2053 vs (CO), 2031 vs (CO), 1997 s (CO), 1666 s (CO), 1491 w, 1452 m, 1400 s, 1346 s, 1162 s, 1099 s, 1017 s, 962 w, 884 m, 827 m, 808 w, 749 w, 712 m, 668 s, 610 m, 551 s, 534 s, 500 s, 490 s, 477 m, 454 m, 440 w, 419 m, 368 w, 345 m, 302 w cm^{-1}; IR (*n*-pentane): $\tilde{\nu} = 2094$ vs (CO), 2045 vs cm^{-1}; MS (70 eV): *m*/*z* (%): 466 (1) [M^+], 438 (15) [$M^+ - CO$], 410 (70) [$M^+ - 2CO$], 382 (20) [$M^+ - 3CO$], 354 (17), [$M^+ - 4CO$], 326 (10) [$M^+ - 5CO$], 298 (100) [$M^+ - 6CO$]; elemental analysis calcd (%) for $C_{13}H_4F_4O_7Co_2$ (466.03): C 33.50, H 0.87; found: C 33.40, H 1.29. Compound **1** (386 mg, 15 %) was isolated from the second fraction after sublimation under vacuum (40 °C/10^{-3} mbar) as yellow crystals which consist of two isomers in the ratio 4:5. M.p. 66 °C (decomp); ^{1}H NMR ($CDCl_3$): $\delta = 2.87$ (s, 2H; CH_2, isomer 1), 2.95 (s, 2H; CH_2, isomer 2), 3.10 (s, 2H; CH_2, isomer 2), 3.35 (s, 2H; CH_2, isomer 1); ^{19}F NMR ($CDCl_3$): $\delta = -82.42$ (d, $^{2}J_{F,F} = 94$ Hz, 2F; CF_2, isomer 1), -84.17 (d, $^{2}J_{F,F} = 88$ Hz, 2F; CF_2, isomer 2), -86.01 (d, $^{2}J_{F,F} = 88$ Hz, 2F; CF_2, isomer 2), -91.51 (d, $^{2}J_{F,F} = 94$ Hz, 2F; CF_2, isomer 1); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 198.6$ (s; CO), 143.1 (dd, $^{1}J_{C,F} = 318$, 349 Hz; CF_2), 142.3 (dd, $^{1}J_{C,F} = 318$, 345 Hz; CF_2), 68.9 (s; *C*-CF_2 isomer 2), 65.2 (s; *C*-CF_2, isomer 1), 46.2 (s; CH_2, isomer 2), 45.1 (s; CH_2, isomer 1); ^{13}C{^{19}F} NMR ($CDCl_3$): $\delta = 198.6$ (s; CO), 143.1 (s; CF_2, isomer 1), 142.4 (s; CF_2, isomer 2), 68.9 (s; *C*-CF_2, isomer 2), 65.2 (s; *C*-CF_2, isomer 1), 46.2 (dd, $^{1}J_{C,H} = 166$ Hz; CH_2, isomer 2), 45.7 (dd, $^{1}J_{C,H} = 166$ Hz; CH_2, isomer 1); IR (KBr): $\tilde{\nu} = 3120$ w, 2512 w, 2340 w, 2319 w, 2082 vs (CO), 2024 vs (CO), 1943 s (CO), 1464 w, 1409 w, 1387 w, 1339 s, 1232 w, 1146 s, 1053 s, 961 w, 824 m, 801 m, 757 w, 721 w, 664 m, 592 s, 540 s, 519 m, 510 m, 491 m, 475 m, 445 m, 415 m, 366 w, 317 w cm^{-1}; IR (*n*-pentane): $\tilde{\nu} = 2097$ s (CO), 2083 vs (CO), 2034 vs (CO), 2002 w (CO) cm^{-1}; MS (70 eV): *m*/*z* (%): 438 (1) [M^+], 410 (24) [$M^+ - CO$], 382 (53) [$M^+ - 2CO$], 354 (7) [$M^+ - 3CO$], 326 (20) [$M^+ - 4CO$], 298 (21) [$M^+ - 5CO$], 270 (100) [$M^+ - 6CO$]; elemental analysis calcd (%) for $C_{12}H_4F_4O_6Co_2$ (438.02): C 32.90, H 0.92; found: C 32.82, H 1.41. If the reaction was carried out under a carbon monoxide atmosphere the yields of both compounds increased: **1** 19.7 %, **2** 53.5 %. Unexpectedly under these conditions the ratio of the products **1** and **2** does not change in favor to product **2**.

Hexacarbonyl-*μ*-(η^3:η^3-1,1,4,4-tetrafluoro-2,3-bisdifluoromethylenebuta-1,4-diyl)dicobalt (**3**): Octacarbonyldicobalt (2 g, 5.86 mmol) was dissolved in *n*-pentane (60 mL). Tetrafluoroallene (18.3 mmol) was condensed onto the solution using a glass vacuum line. The reaction mixture was stirred for 48 h at ambient temperature. The solvent was removed under vacuum and the residue was purified by column chromatography (*n*-pentane/silica, 45 × 3 cm^2). The first fraction was sublimed under vacuum at 40 °C/10^{-3} mbar to yield **3** (670 mg, 22 %) as yellow crystals. M.p. 53–54 °C; ^{19}F NMR ([D$_8$]toluene, 20 °C): $\delta = -78.59$ (d, $^{2}J_{F,F} = 90$ Hz, 4F; CF_2), -80.47 (d, $^{2}J_{F,F} = 90$ Hz, 4F; CF_2); ^{19}F NMR ([D$_8$]toluene, -60 °C): $\delta = -77.34$ (d, $^{2}J_{F,F} = 94$ Hz, 2F; CF_2), -79.75 ($^{2}J_{F,F} = 90$ Hz, 2F; CF_2), -81.02 (d, 2F; CF_2), -81.25 (d, 2F; CF_2), the coupling constants cannot be determined due to overlap of two signals; ^{13}C NMR ($CDCl_3$): $\delta = 194.3$ (s; CO), 136.3 (dd, $^{1}J_{C,F} = 307$, 350 Hz; CF_2), 30.9 (s; *C*-CF_2); IR (KBr): $\tilde{\nu} = 2126$ s (CO), 2111 vs (CO), 2065 vs (CO), 1772 w, 1695 w, 1635 w, 1358 s, 1208 m, 1192 s, 1183 s, 1117 m, 974 m, 930 s, 918 m, 893 s, 774 m, 768 m, 707 m, 668 w, 649 m, 623 m, 595 m, 569 s, 534 m, 502 m, 478 m, 463 m, 420 w, 398 w, 351 w, 337 w, 281 w cm^{-1}; IR (*n*-pentane): $\tilde{\nu} = 2121$ (CO), 2108 (CO), 2067 (CO) cm^{-1}; MS (70 eV): *m*/*z* (%): 510 (4) [M^+], 482 (29) [$M^+ - CO$], 454 (34) [$M^+ - 2CO$], 426 (68) [$M^+ - 3CO$], 398 (29) [$M^+ - 4CO$], 370 (27) [$M^+ - 5CO$], 342 (100) [$M^+ - 6CO$], 186 (18) [$CoC_3F_5^+$], 59 (24) [Co^+]; elemental analysis calcd (%) for $C_{12}F_8O_6Co_2$ (509.98): C 28.26; found: C 27.61. Compound **4** (40 mg, 0.9 %) was obtained from the second fraction by crystallization at -30 °C as black crystals. ^{19}F NMR ($CDCl_3$): $\delta = -78.3$ (d, $^{2}J_{F,F} = 92$ Hz, 1F; CF_2), -77.05 (d, $^{2}J_{F,F} = 93$ Hz, 2F; allyl CF_2), -78.92 (d, $^{2}J_{F,F} = 92$ Hz, 2F; allyl CF_2), -79.9 (d, $^{2}J_{F,F} = 93$ Hz, 1F; CF_2). MS (70 eV): *m*/*z* (%): 758 (1) [$M^+ - CO$], 730 (1) [$M^+ - 2CO$], 702 (3) [$M^+ - 3CO$], 673 (2), 646 [$M^+ - 5CO$], 617 (1), 571 (47), 543 (47), 515 (10), 488 (8), 460 (46) [$CFCo_3(CO)_9^+$], 432 (100) [$CFCo_3(CO)_8^+$], 404 (34) [$CFCo_3(CO)_7^+$], 376 (28) [$CFCo_3(CO)_6^+$], 348 (27) [$CFCo_3(CO)_5^+$] and smaller fragment ions.

Decacarbonyl-*μ*-(η^1:η^1-1,1,6,6-tetrafluoro-1,5-hexadien-2,5-diyl)dimanganese (**5**): Decacarbonyldimanganese (430 mg, 1.1 mmol) was dissolved in *n*-pentane in a photo reactor. 1,1-Difluoroallene (9.2 mmol) was condensed onto the solution using a glass vacuum line. The reaction mixture was irradiated for 4 h resulting in an orange solution containing a pale yellow precipitate. The precipitate was collected by filtration and dried under vacuum. Concentration of the filtrate under vacuum yielded additional substance. Column chromatography (silica, 45 × 3 cm^2) using *n*-pentane/dichloromethane in the ratio 2:1 as eluent yielded **5** in the fraction with the largest R_f value. Compound **5** (85 mg, 14 %) was isolated by crystallization at -30 °C as pale yellow crystals. M.p. 110–111 °C (decomp); ^{1}H NMR ($CDCl_3$): $\delta = 2.31$ (s, 4H; CH_2); ^{19}F NMR ($CDCl_3$): $\delta = -69.23$ (d, $^{2}J_{F,F} = 66$ Hz, 2F; CF_2), -77.48 (d, $^{2}J_{F,F} = 66$ Hz, 2F; CF_2); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 209.5$ (s; CO_{cis}), 207.2 (s; CO_{trans}), 150.9 (dd, $^{1}J_{C,F} = 266$, 304 Hz; CF_2), 76.3 (dd, $^{2}J_{C,F} = 46$, 10 Hz; *C*-CF_2), 37.3 (s; CH_2); ^{13}C{^{19}F} NMR (CD_2Cl_2): $\delta = 209.5$ (s; CO_{cis}), 209.1 (s; CO_{trans}), 150.8 (s; CF_2), 76.3 (s; *C*-CF_2), 37.3 (t, $^{1}J_{C,H} = 130$ Hz; CH_2); IR (KBr): $\tilde{\nu} = 2968$ w, 2925 w, 2873 w, 2122 m (CO), 2040 s (CO), 2003 vs (CO), 1668 m (C=CF_2), 1460 w, 1262 w, 1196 w, 1155 m, 1072 w, 906 m, 805 w, 747 w, 646 s, 582 w, 527 w, 458 w, 438 w, 408 w, 325 w cm^{-1}; IR (*n*-pentane): $\tilde{\nu} = 2122$ m (CO), 2030 vs (CO), 1999 m (CO) cm^{-1}; MS (70 eV): *m*/*z* (%): 402 (5) [$M^+ - 5CO$], 346 (3) [$M^+ - 7CO$], 318 (4) [$M^+ - 8CO$], 290 (34) [$M^+ - 9CO$], 262 (100) [$M^+ - 10CO$]; elemental analysis calcd (%) for $C_{16}H_4F_4O_{10}Mn_2$ (542.07): C 35.45, H 0.74; found: C 35.16, H 1.32.

Received: January 26, 2001 [Z 16514]

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[12] Crystal structure analyses: Structure solution by direct methods and full-matrix least-squares refinement (SHELX97[14]). **1a**: triclinic, space group $P\bar{1}$, $a = 6.6750(10)$, $b = 6.886(2)$, $c = 8.514(2)$ Å, $\alpha = 92.77(2)$, $\beta = 101.55(2)$, $\gamma = 100.05(2)°$, $V = 376.12(15)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.934$ Mg m^{-3}, $T = 293$ K, 2593 measured, 2193 crystallographically unique, and 1955 reflections with $I > 2\sigma(I)$, $Mo_{K\alpha}$, $\lambda = 0.71069$ Å, $2\theta_{max} = 30°$, empirical absorption correction (PSI scan)[15] ($\mu = 2.276$ mm^{-1}), $R(F_o) = 0.0228$, $wR(F^2) = 0.0629$ (all data), 117 parameters, anisotropic thermal parameters, H atoms isotropic. **1b**: tetragonal, space group $P4_32_12$, $a = 6.3056(9)$, $c = 36.614(8)$ Å, $V = 1455.8(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.998$ Mg m^{-3}, $T = 20$ K, 7333 measured, 3579 crystallographically unique, and 2890 reflections with $I > 2\sigma(I)$, $Ag_{K\alpha}$, $\lambda = 0.56087$ Å, $2\theta_{max} = 56.2°$, no absorption correction ($\mu = 1.223$ mm^{-1}), $R(F_o) = 0.0756$, $wR(F^2) = 0.1708$ (all data), 109 parameters, anisotropic thermal parameters, no hydrogen positions. **2**: monoclinic, space group $P2_1/a$, $a = 12.648(4)$, $b = 10.679(3)$, $c = 12.697(3)$ Å, $\beta = 102.84(2)°$, $V = 1672.1(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.851$ Mg m^{-3}, $T = 293$ K, 4179 measured, 3644 crystallographically unique, and 2609 reflections with $I > 2\sigma(I)$, $Mo_{K\alpha}$, $\lambda = 0.71069$ Å, $2\theta_{max.} = 27°$, no absorption correction ($\mu = 2.059$ mm^{-1}), $R(F_o) = 0.0422$, $wR(F^2) = 0.1155$ (all data), 251 parameters, anisotropic thermal parameters, H atoms isotropic. **3**: orthorhombic, space group *Pcan* (no. 60), $a = 11.3290(13)$, $b = 12.7359(10)$, $c = 34.826(3)$ Å, $\alpha = 92.77(2)$, $\beta = 101.55(2)$, $\gamma = 100.05(2)°$, $V = 5024.8(8)$ Å^3, $Z = 12$, $\rho_{calcd} = 2.022$ Mg m^{-3}, $T = 293$ K, 11502 measured, 7328 crystallographically unique, and 3227 reflections with $I > 2\sigma(I)$, $Mo_{K\alpha}$, $\lambda = 0.71069$ Å, $2\theta_{max} = 30°$, empirical absorption correction (PSI scan)[15] ($\mu = 2.093$ mm^{-1}), $R(F_o) = 0.0411$, $wR(F^2) = 0.0992$ (all data), 379 parameters, anisotropic thermal parameters. **4**: triclinic, space group $P\bar{1}$, $a = 8.0018(12)$, $b = 11.6060(18)$, $c = 13.7106(18)$ Å, $\alpha = 75.120(11)$, $\beta = 86.160(11)$, $\gamma = 76.020(12)°$, $V = 1194.1(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.108$ Mg m^{-3}, $T = 293$ K, 4797 measured, 4214 crystallographically unique, and 3397 reflections with $I > 2\sigma(I)$, $Mo_{K\alpha}$, $\lambda = 0.71069$ Å, $\theta_{max} = 25°$, empirical absorption correction (PSI scan)[15] ($\mu = 2.838$ mm^{-1}), $R(F_o) = 0.0243$, $wR(F^2) = 0.0657$ (all data), 361 parameters, anisotropic thermal parameters. **5**: triclinic, $P\bar{1}$, $a = 6.1860(6)$,

$b = 6.9912(7)$, $c = 12.3635(12)$ Å, $\alpha = 84.686(2)$, $\beta = 78.684(2)$, $\gamma = 68.044(2)^\circ$, $V = 486.16(8)$ Å^3, $Z = 1$, $\rho_{\mathrm{calcd}} = 1.852$ Mg m^{-3}, $T = 133$ K, 5719 measured, 2771 crystallographically unique, and 2771 reflections with $I > 2\sigma(I)$, $\mathrm{Mo_{K\alpha}}$, $\lambda = 0.71069$ Å, $2\theta_{\max} = 30^\circ$, empirical absorption correction (SADABS)[16] ($\mu = 1.390$ mm^{-1}), $R(F_o) = 0.0320$, $wR(F^2) = 0.0785$ (all data), 153 parameters, anisotropic thermal parameters, H-atoms isotropic. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-156869 – CCDC-156874. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Classification of Terpenoids according to the Methylerythritolphosphate or the Mevalonate Pathway with Natural ^{12}C/^{13}C Isotope Ratios: Dynamic Allocation of Resources in Induced Plants[**]

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Dedicated to Professor Ernst-G. Jäger
on the occasion of his 65th birthday

Plant volatiles, whose biosynthesis is induced by feeding insects, may serve as markers to allow the parasites of the herbivores to find their hosts.[1, 2] Thus, they benefit the plant indirectly, and have been called the "plant's cry for help".[3] Major constituents of such induced volatile blends include terpenoids, aromatic compounds, and degradation and transformation products derived from fatty acids. Mono- and diterpenoids are produced in the plastids from isopentenyl diphosphate (IDP) formed through the methylerythritol phosphate pathway (MEP pathway), while the IDP for sesquiterpenoids is assembled by the well-known mevalonic acid pathway (MVA pathway) in the cytosol (Scheme 1).[4–6] However, this classical allocation of terpenoids to pathways is not completely strict. While administration of deuterium-labeled 5-deoxy-D-xylulose, an early precursor of IDP in the MEP pathway, in principle confirmed the normal allocation of pathways in herbivore-induced biosynthesis, the ^{1}H/^{2}H isotope signature of 4,8-dimethylnona-1,3,7-triene (DMNT, **4**; Figure 1) demonstrated a significant contribution from both pathways.[7] In another example, the incorporation of ^{13}C-labeled glucose into sesquiterpenes from chamomile resulted in an isotope signature that required contributions from both pathways.[8] Moreover, careful analysis of sitosterol (isolated from cell cultures of *Catharanthus roseus*), which is assembled from two units of farnesyl diphosphate, clearly demonstrated a contribution (approximately 6%) from the mevalonate-independent MEP pathway.[9] This classification of pathways, based on externally added precursors, is open to criticism, as administration may affect the natural balance of the cellular intermediates and result in shifted mass fluxes though the complex interacting pathways. Even the use of physiologically neutral precursors, such as glucose, has an impact on the metabolic network. Phototrophic organisms need to be kept under heterotrophic conditions to avoid dissipation of this valuable precursor into unwanted anabolic activities.[5] An alternative to precursor-based approaches is provided by analysis of the isotope ratio of relevant compounds, at natural abundance level, using isotope-ratio mass spectrometry (IRMS).[10] By linking an isotope-ratio mass spectrometer to a gas chromatograph, with online combustion of the eluting compounds to CO_2 und H_2O (GC-C-IRMS), analysis of the isotopic signature of individual compounds of complex mixtures is possible.[11]

Owing to thermodynamic and kinetic isotope effects, the natural abundance of carbon isotopes exhibits minor local and temporal shifts from a global average value. In the biosphere these shifts are related to the isotope effects of the reactions catalyzed by enzymes involved in the physiological processes. Prominent examples exhibiting very high discrimination of carbon isotopes were reported for the different modes of CO_2 fixation by C_3 and C_4 plants, which utilize ribulose diphosphate carboxylase or phosphoenolpyruvate carboxylase.[12] Further metabolism may additionally affect the isotope ratio, but in general these effects are less pronounced. Here we report that the different groups of terpenoid volatiles also exhibit significant differences in their ^{12}C/^{13}C ratio, which depend upon whether the universal building block IDP is produced predominantly from the MVA or MEP pathway (Scheme 1).

The isotope ratios of monoterpenes as $\delta(^{13}\mathrm{C})$ values (see Experimental Section for definition) have already been determined by others, mainly to evaluate the origin and authenticity of compounds, and were observed within the range -26 to -30‰.[13, 14] The value for ocimene (**2**; Figure 1), which is released from leaves of the lima bean (*Phaseolus lunatus*, used here as a model plant), was measured by us to be -29.0‰, a value that fits perfectly into the expected range (Figure 2). In contrast, the value of -37.4‰ for DMNT (an oxidative degradation product of the sesquiterpenoid ner-

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[**] We thank Dr. H. Bischoff (Bayer AG, Wuppertal) for cerivastatin and Steffen Rühlow for his committed technical assistance.