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Synthesis, crystal structure, and NMR investigation of methyl α,α-dimethyl acetate-substituted π-allylpalladium complexes

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Dedicated to Professor Günther Wulff on the occasion of his 65th birthday

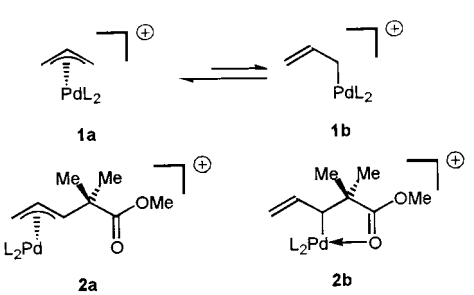
Abstract

The dimeric, trifluoroacetate-bridged π-allylpalladium complex **6** and the cationic allyl complex **8** were prepared and characterized by NMR spectroscopy as well as crystal structure analyses. The carbonyl group of the carboxylic ester moiety does not form a chelate with the metal atom. The activation enthalpy of a π–σ–π conversion could be determined to be 14.6 kcal mol^{-1} based on the dynamic NMR spectroscopy of the allylpalladium complex **8**. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Palladium; Allyl rotation; Crystal structure analysis; NMR spectroscopy

1. Introduction

The chemistry of π-allylpalladium complexes **1a** has been investigated intensively [1]. These complexes are known to be the key intermediates in the palladium-catalyzed allylic substitution, a reaction whose versatility is proven by numerous applications [2]. Furthermore, they are involved in isomerizations of alkynes to dienes [3], diene polymerizations [4], and elimination reactions of allylic compounds to dienes [5,6]. Based on various reactions and NMR spectroscopic investigations, η^1-complexes **1b** have been postulated to exist in an equilibrium with the η^3-species **1a**, the latter being the thermodynamically much more favored isomer [7]. Recently, intramolecular carboxylic ester [8] and keto [9] groups were found to function as ligands in complexes with a σ-palladium carbon bond, thus forming five-membered chelates. Thus, the hypothesis was developed that the carboxylic ester group might be able to serve as a ligand also in allyl complexes **2a**, thus favoring the formation of a σ-complex **2b**. The geminal dimethyl substitution pattern, incorporated in the methyl α,α-dimethyl acetate-substituted allylpalladium complexes, was chosen in order to avoid β-Pd–H elimination, which has been found to occur spontaneously when a β-hydrogen is available, thus giving dienoates [6] (Scheme 1).



Scheme 1.

2. Results and discussion

Allyl trifluoroacetates have proven themselves to be more suitable precursors of allylpalladium complexes [10] than the corresponding acetates [11] or carbonates

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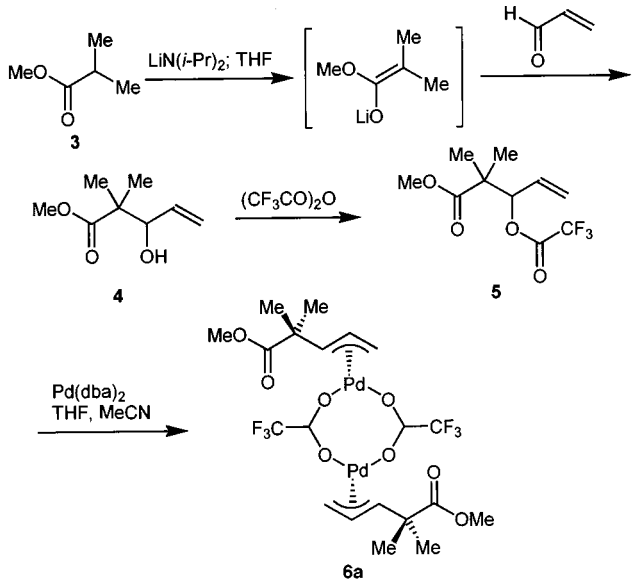


Scheme 2.

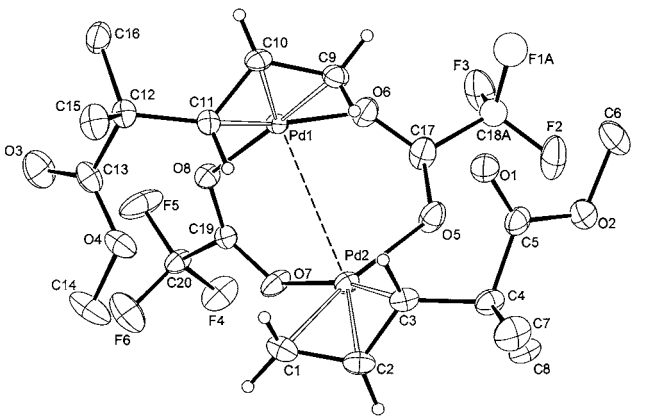


Fig. 1. ORTEP plot of **6a**. All non-allyl-hydrogen atoms have been omitted for clarity. Anisotropic displacement ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°) for **6a**: C1–C2 1.399(5), C1–Pd2 2.109(3), C2–C3 1.416(4), C2–Pd2 2.110(3), C3–C4 1.516(4), C3–Pd2 2.111(3), C9–C10 1.405(4), C9–Pd1 2.092(3), C10–C11 1.416(4), C10–Pd1 2.115(3), C11–C12 1.508(4), C11–Pd1 2.148(3), C17–O5 1.235(4), C17–O6 1.253(4), C19–O8 1.236(3), C19–O7 1.242(3), O5–Pd2 2.137(2), O6–Pd1 2.133(2), O7–Pd2 2.147(2), O8–Pd1 2.152(2), Pd1–Pd2 3.0621(5); C1–C2–C3 116.2(3), C2–C3–C4 123.5(3), C9–C10–C11 116.8(2), C10–C11–C12 122.9(3), O5–C17–O6 130.5(3), O8–C19–O7 131.4(3), C17–O5–Pd2 124.8(2), C17–O6–Pd1 121.4(2), C19–O7–Pd2 127.3(2), C19–O8–Pd1 120.9(2), C9–Pd1–O6 96.67(10), C10–Pd1–O6 128.49(10), C11–Pd1–O6 165.70(10), C9–Pd1–O8 173.50(10), C10–Pd1–O8 135.83(9), O6–Pd1–O8 89.76(8), C11–Pd1–O8 104.54(9), C1–Pd2–O5 165.41(11), C2–Pd2–O5 128.10(10), C3–Pd2–O5 96.46(10), C1–Pd2–O7 100.84(11), C2–Pd2–O7 130.28(10), C3–Pd2–O7 169.26(10), O5–Pd2–O7 93.66(9).

[12]. Thus, the enolate generated from methyl isobutyrate (**3**) with lithium diisopropylamide was added to acrolein to give the alcohol **4**, which was subsequently esterified by treatment with trifluoroacetic anhydride. The trifluoroacetate **5** thus obtained was allowed to react with palladium dibenzylidene acetone [$Pd(dba)_2$] following the protocol described by Vitagliano et al. [10]. Thereby, the dimeric palladium complex **6a** resulted, in which the two metal atoms are bridged by two trifluoroacetate groups. This complex was stable in air at room temperature for weeks; it is well soluble in a series of solvents from aqueous acetonitrile to *n*-hexane (Scheme 2).

The dimeric, trifluoroacetate-bridged structure **6a** which is not completely unprecedented in π-allylpalladium chemistry [13] was first assigned by means of mass spectrometry. The structure of complex **6a** was finally proven by the crystal structure analysis, the result of which is shown in Fig. 1. It shows that, indeed, the trifluoroacetate moiety bridges the palladium atoms. Although the two allyl groups are oriented in an *anti*-position, the molecule deviates from C_2 symmetry. The metal–metal distance of 3.0621(5) Å is within the range observed in the CSD for other binuclear acetate bridged Pd complexes.

The NMR spectroscopic investigation of the complex **6a** reveals a distinct dependence on the solvent, as illustrated by Fig. 2 which shows a 2.8–6 ppm range of the ^{1}H-NMR spectra recorded in acetonitrile-d_3, chloroform-d_1 and DMSO-d_6. Obviously, in acetonitrile-d_3, there are no structure dynamics and the signals can be easily assigned to a rigid allyl moiety. The relatively large difference in the chemical shifts of the two geminal H-5 signals (H-5 *syn* and H-5 *anti*) is known to be typical for allylpalladium complexes with a terminal CH_2 group [14]. However, the signals of this group disappear in DMSO-d_6, whereas the signals of H-3 and H-4 are observed at different chemical shifts, but the multiplicities are maintained.

A distinctly different ^{1}H-NMR spectrum was observed in chloroform-d_1: the signals were broadened, and the spectrum clearly showed the existence of two different species in a ratio of 60:40. This result was not only confirmed by H, H and H, C correlation measurements but is also evident by the appearance of two H-5 *anti* signals. In the ^{13}C-NMR spectra, one of the two species displayed sharp, the other broadened signals.

The different NMR spectra of the complex **6a** in the three solvents is tentatively interpreted as follows: In the rather unpolar chloroform-d_1, the dimeric structure of the complex is still maintained. However, in addition to the structure **6a**, present in the crystalline state, there are three more diastereomers **6b**–**d** which could exist in an equilibrium with **6a** due to π–σ–π conversions [7]. According to the NMR spectrum, two out of these four are present in the solution of the complex **6a** in chloroform-d_1. The structures of the diastereomers **6c** and **6d** seem to be less probable according to the ^{13}C-NMR spectrum: both the carbonyl and the trifluoromethyl carbon atoms are expected to have a different chemical

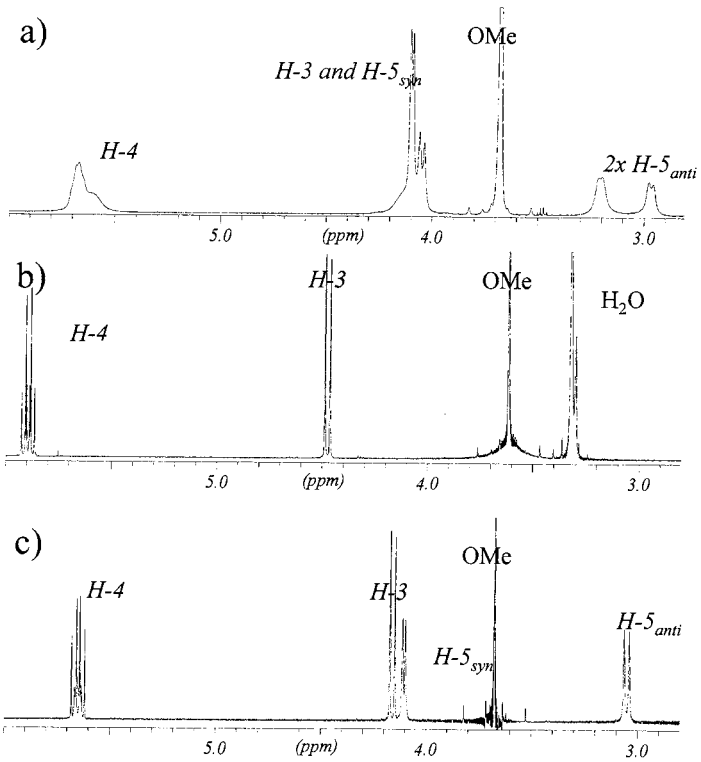


Fig. 2. Details of the ^{1}H-NMR spectra of **6** in (a) chloroform-d_1, (b) DMSO-d_6, and (c) acetonitrile-d_3.

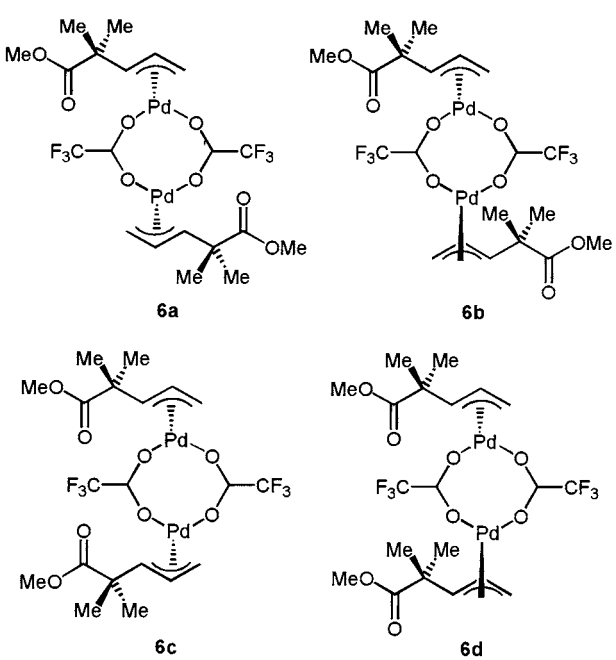
and magnetic environment in these isomers. Since the ^{13}C-NMR spectrum in chloroform-d_1 (see Section 3) does not display different chemical shifts of those carbon atoms, the structures of **6c** and **6d** should not apply. As a consequence, an equilibrium between the two dimeric diastereomers **6a** and **6b** is assumed to exist in chloroform-d_1 (Scheme 3).

On the other hand, it seems to be plausible that the more polar and strongly coordinating solvent acetonitrile-d_3 will be able to cleave the dimeric complex **6a**. Thus, the structure of the monomer **7a** is assigned to the complex in acetonitrile. This is in accordance with the NMR data shown below (the numbering of the protons refers to formula **7a**). The complex is also assumed to be monomeric in the strongly coordinating solvent DMSO-d_6, so that the structure **7b** is assigned [15]. However, a rapid exchange of the protons of the geminal CH_2 group indicates a $\pi-\sigma-\pi$ conversion in DMSO-d_6 (Scheme 4).

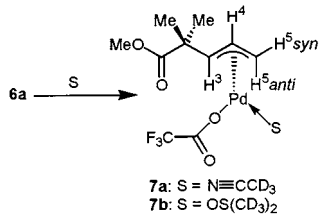
The dimeric complex **6** serves as a precursor for the preparation of the cationic allylpalladium compound **8**. For this purpose, **6a** was treated with bis(diphenylphosphino)ethene (dppe) and $HBF_4{\cdot}OEt_2$ in diethyl ether, again following the protocol of Vitagliano et al. [10]. The complex **8** thus prepared was found to be a colorless solid which was air-stable (Scheme 5).

A crystalline sample of **8**, obtained from chloroform–cyclohexane, turned out to be suitable for an X-ray structure analysis, the result of which is shown in Fig. 3. Similar to the structure of palladium allyl complexes with chiral phosphine ligands [16], both phosphorus atoms are coordinated to the metal which occupies a nearly square planar configuration.

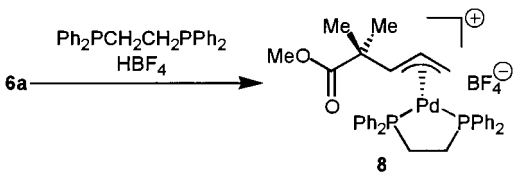
As expected, the methyl α,α-dimethyl-acetate group occupies the *syn*-position. A coordination between pal-



Scheme 3.



Scheme 4.



Scheme 5.

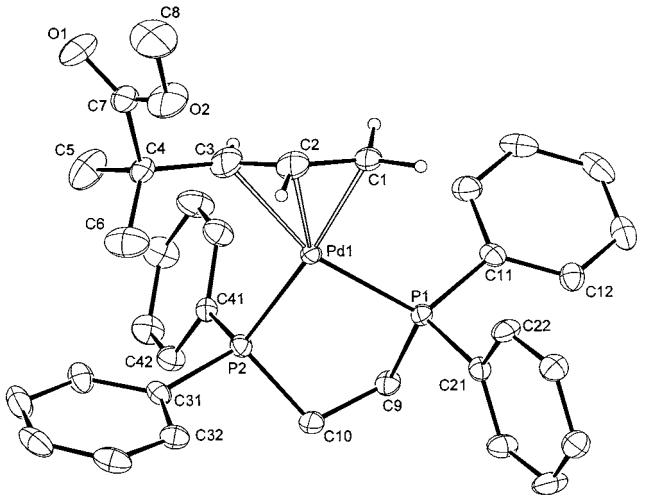
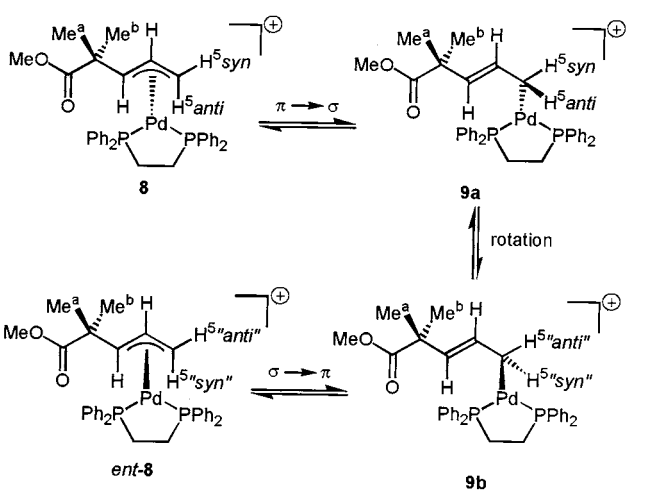


Fig. 3. ORTEP plot of the cationic part of **8**. The BF_4^- anion, one molecule of $CHCl_3$ solvent and all non-allyl hydrogen atoms have been omitted for clarity. Anisotropic displacement ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°) for **8**: Pd1–C1 2.155(3), Pd1–C2 2.191(3), Pd1–C3 2.282(3), Pd1–P1 2.2936(7), Pd1–P2 2.3121(7), C1–C2 1.397(5), C2–C3 1.360(5), C3–C4 1.528(5); C1–Pd1–P1 97.79(8), C2–Pd1–P1 132.53(9), C3–Pd1–P1 162.45(9), C1–Pd1–P2 173.38(8), C2–Pd1–P2 139.99(9), C3–Pd1–P2 108.99(9), P1–Pd1–P2 86.30(2), C3–C2–C1 123.3(3), C2–C3–C4 126.3(3).

ladium and the carbonyl group of the carboxylic ester moiety was not found in the complex **8**, either. Remarkably, the ester moiety is even oriented away from the metal. This conformation is the preferred one in the crystalline state, but from elimination studies [6] on substrates in which the dimethyl moiety was replaced by a single methyl substituent one can conclude that this is probably not the favored conformation in solution.

The temperature-dependent ^{1}H-NMR spectra [17] of **8** in $CDCl_3$, shown in Fig. 4, reveal the dynamic structure of this complex. At -20°C, the spectrum displays the signals which are typical of a rigid allyl structure: sharp signals of the terminal CH_2 group, which differ by almost 2 ppm, and two singlets of the diastereotopic methyl groups. The dynamic behavior of the complex becomes evident in the spectra measured at 15 and 50°C. Broadening of the H-5 *syn* and H-5 *anti* signals and of the methyl singlets is apparent at 15°C. Finally at 50°C, the former diastereotopic methyl groups collapse to one singlet. A plausible interpretation of this dynamic behavior is given by the π–σ–π mechanism which easily explains the degenerated rotation of the allyl moiety shown in Scheme 6. In detail, this process involves (i) a switch of palladium by conversion of the π to a σ bond, (ii) rotation about the C-4, C-5 single bond, thus transforming the conformer **9a** to **9b** and bringing the palladium from the rear to the front side, and (iii) reconversion of the σ into a π bond. The overall process is thus a degenerated process leading from **8** to enantiomer *ent*-**8**. It is evident that H-5 *syn* becomes H-5 '*syn*', and H-5 *anti* becomes H-5 '*anti*' and the methyl groups Me^a and Me^b become equivalent.

From the temperature dependence of the NMR spectra, the coalescence temperature could be determined to amount to 22 ± 2°C, which allowed us to calculate the activation enthalpy of the rotation which converts **8** into *ent*-**8** [18], based on the difference in the chemical shifts of the diastereotopic methyl groups in the non-dynamic system (40 Hz). The rate constant at the coalescence temperature was determined to be $K_{295\,K} = 89\ s^{-1}$. The activation enthalpy of the allyl rotation combined with π–σ–π processes could be calculated: $\Delta G^{\neq} = 14.6$ kcal mol^{-1} [19]. Thus, an insight into the dynamic behavior of allylpalladium complexes is opened, which could be helpful in understanding π–σ–π conversions frequently occurring in palladium-catalyzed elimination and substitution reactions.



Scheme 6.

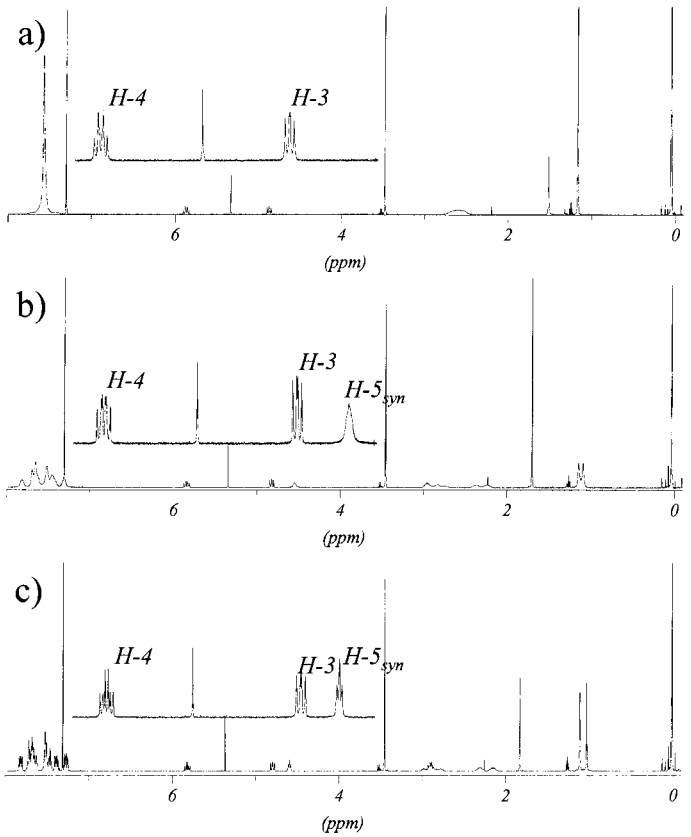


Fig. 4. VT ^{1}H-NMR spectra of **8** in chloroform-d_1 at (a) 50, (b) 15, and (c) −20°C.

3. Experimental

The following spectrometers were used: NMR spectra: Varian VXR 300 and Bruker DRX 500; TMS as internal standard. Mass spectra: Hewlett–Packard 5890/5870 (GC–MS) and Finnigan MAT Incos 50 (CI). IR spectra: Bruker Vector 22. Elemental analyses were carried out by Institut für Pharmazeutische Chemie, Universität Düsseldorf. All reactions were carried out under an atmosphere of dry nitrogen. THF and diethyl ether were predried with KOH and distilled under N_2 from sodium/benzophenone. Acetonitrile of HPLC grade was dried over 3 Å molecular sieves. Reactions at temperatures below −20°C were monitored by a thermocouple connected to a resistance thermometer (Ebro). General remarks concerning the handling of lithium enolates and other organolithium compounds are given in Ref. [20].

3.1. Methyl 3-hydroxy-2,2-dimethylpent-4-enoate (4)

A 100 ml two-necked flask, connected to a combined nitrogen/vacuum line, was equipped with a magnetic stirrer and a septum. A thermocouple was introduced through the septum. During the following manipulations, N_2 atmosphere was maintained in all flasks. Anhydrous THF (10 ml) and diisopropylamine (3.1 ml, 22 mmol) were injected through the septum by syringes. The mixture was stirred at −78°C, and a 1.6 M solution of BuLi in hexane (13.0 ml, 21.5 mmol) was added in such a way that the temperature did not exceed −70°C. After stirring for 30 min at 0°C, the mixture was again cooled to −78°C. In a 50 ml two-necked flask, connected to the combined nitrogen/vacuum line, a solution of methyl isobutyrate (**3**) (2.3 ml, 20 mmol) in anhydrous THF (20 ml) was stirred at −78°C. This mixture was added by means of a cannula to the slightly evacuated 100 ml flask containing the solution of lithium diisopropylamide. After stirring for 30 min at −78°C, acroleine (1.5 ml, 22 mmol) was added slowly by syringe so that the temp did not exceed −70°C. The mixture was allowed to reach room temperature overnight and a saturated aqueous solution NH_4Cl (20 ml) was added. The mixture was transferred into a separatory funnel and the organic layer was separated off. The aqueous phase was extracted with diethyl ether. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated in a rotary evaporator. The crude product thus obtained was purified by distillation. Yield: 2.9 g (92%); b.p. 49°C (0.5 torr); ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 1.17$, 1.18 (2 × s, 6H, CH_3C), 2.94 (br s, 1H, OH), 3.70 (s, 3H,

OCH_3), 4.18 (d, $J = 6.6$ Hz, 1H, CHCH=CH_2), 5.22 (ddd, $J = 10.4$, $J = 1.7$, $J = 1.0$ Hz, 1H, CH=CH_2), 5.30 (ddd, $J = 17.1$, $J = 1.7$, $J = 1.2$ Hz, 1H, CH=CH_2), 5.85 (ddd, $J = 6.6$, $J = 10.4$, $J = 17.1$ Hz, 1H, CH=CH_2); ^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta = 19.88$, 22.46 (CH_3), 46.78 ($C(CH_3)_2$), 52.01 (OCH_3), 77.90 (CHCH=), 117.61 (CH=CH_2), 136.21 (CH=CH_2), 177.81 (CO); IR (neat): ν (cm^{-1}) = 3497, 2982, 2952, 1728; GC–MS: m/z (%) = 141 (0.5) [$M^+ - OH$], 127 (1) [$M^+ - OCH_3$], 109 (2) [$M^+ - OMe - H_2O$], 102 (100) [$(CH_3)_2C$=C-$(OCH_3)OH^+$]. The physical and spectroscopic data are in accordance with those described in the literature [21].

3.2. Methyl 2,2-dimethyl-3-trifluoroacetoxy-pent-4-enoate (5)

A 25 ml flask, connected to a combined nitrogen/vacuum line, was equipped with a magnetic stirrer and a septum. Trifluoroacetic anhydride (7.5 ml, 54 mmol) were injected and methyl 3-hydroxy-2,2-dimethylpent-4-enoate (**4**) (2.9 g, 18.3 mmol) was added dropwise. The mixture was stirred overnight and the product obtained by distillation. Yield: 3.78 g (81%); b.p. 36°C (2 torr); ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 1.21$, 1.27 (2 × s, 6H, CH_3C), 3.70 (s, H, OCH_3), 5.41 (d, $J = 17.4$ Hz, 1H, CH=CH_2), 5.42 (d, $J = 10.1$ Hz, 1H, CH=CH_2), 5.67 (d, $J = 7.3$ Hz, 1H, CHCH=CH_2), 5.81 (ddd, $J = 7.3$, $J = 10.1$, $J = 17.4$ Hz, 1H, CH=CH_2); ^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta = 19.99$, 21.58 (CH_3), 46.21 ($C(CH_3)_2$), 52.35 (OCH_3), 82.67 (CHCH=), 114.64 (q, $J = 283$ Hz, CF_3), 121.94 (CH=CH_2), 130.01 (CH=CH_2), 156.37 (q, $J = 42$ Hz, $COCF_3$), 175.22 ($COOCH_3$). IR (neat): ν (cm^{-1}) = 2990, 2957, 1792, 1742, 1473, 1437, 1375, 1323, 1265, 1224, 1172, 991, 947, 854, 774, 730, 706; GC–MS: m/z (%) = 254 (1) [M^+], 239 (5) [$M^+ - CH_3$], 223 (1) [$M^+ - OCH_3$], 195 (14) [$M^+ - COOMe$], 194 (14) [$M^+ - CO - MeOH$)], 153 (46) [CH_2=CHCHOCOCF_3^+], 141 (32), 125 (18), 73 (100); Anal. Calc. for $C_{10}H_{13}F_3O_4$: C, 47.25; H, 5.15. Found: C, 47.17; H, 5.26%.

3.3. Bis[(3,4,5-η)-methyl-2,2-dimethylpent-3-enyloate]-bis(μ-trifluoroacetato)-dipalladium(II) (6)

A 10 ml two-necked flask equipped with a magnetic stirrer and connected to a combined nitrogen/vacuum line was charged with $Pd(dba)_2$ (1.1 g, 2 mmol) and anhydrous THF (16 ml) was added. A solution of methyl 2,2-dimethyl-3-trifluoroacetoxy-pent-4-enoate (**5**) (0.56 g, 2.2 mmol) in acetonitrile (4 ml) was added. The mixture was stirred until the color turned from purple to grayish green (ca. 30 min). The solvent was distilled off, the residue was extracted with a 10% solution of acetonitrile in water (4 × 25 ml), and the filtered extract was evaporated. The crude product was used in the next reaction without further purification. An analytical sample was crystallized from diethyl ether–pentane. Yield: 0.69 g (95%); m.p. (diethyl ether–pentane) 151°C; ^{1}H-NMR (500 MHz, CD_3CN): $\delta = 1.36$, 1.38 (2 × s, 6H, CH_3), 3.05 (d, $J = 12.0$ Hz, 1H, CH=CH_2-*anti*), 3.68 (s, 3H, OCH_3), 4.10 (d, $J = 6.9$ Hz, 1H, CH=CH_2-*syn*), 4.16 (d, $J = 11.6$ Hz, 1H, $(CH_3)_2$CCH), 5.65 (ddd, $J = 6.9$, $J = 11.6$, $J = 12.0$ Hz, 1H, CH=CH_2); ^{1}H-NMR (500 MHz, DMSO): $\delta = 1.32$ (s, 6H, CH_3), 3.62 (s, 3H, OCH_3), 4.47 (d, $J = 12.1$ Hz, 1H, CHCH=CH_2), 5.89 (dt, $J = 12.1$, $J = 9.5$ Hz, 1H, CH=CH_2); ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 1.41$ (s, 6H, CH_3), 2.97 (br d, $J = 10.8$ Hz, 0.4H, CH=CH_2-*anti* species A), 3.21 (br s, 0.6H, CH=CH_2-*anti* species B), 3.68 (s, 3H, OCH_3), 4.02–4.17 (br m, 2H, CHCH=CH_2 species A + B), 5.60 (br s, 0.4H, CH=CH_2 species A), 5.68 (br s, 0.4H, CH=CH_2 species B); ^{13}C-NMR (125 MHz, DMSO): $\delta = 24.50$ (br, CH_3), 43.82 ($C(CH_3)_2$), 52.02 (OCH_3), 58.43 (CH=CH_2), 98.80 (($CH_3)_2CCH$), 114.38 (CH=CH_2), 116.30 (q, $J = 293$ Hz, CF_3), 159.50 (q, $J = 34$ Hz, $COCF_3$), 173.85 ($COOCH_3$); ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 23.22$, 26.39 (CH_3), 44.39 ($C(CH_3)_2$), 52.45 (OCH_3), 55.90 (br, CH=CH_2, species A), 57.64 (CH=CH_2, species B), 85.23 (($CH_3)_2CCH$, species B), 88.05 (br, $(CH_3)_2CCH$, species A), 107.97 (br, CH=CH_2, species A), 109.04 (CH=CH_2, species B), 116.14 (q, $J = 290$ Hz, CF_3), 164.91 (q, $J = 39$ Hz, $COCF_3$), 174.34 ($COOCH_3$); CI-MS (NH_3): m/z (%) = 740 (0.1) [$M^+ + NH_4$], 643 (6) [$M^+ + H - CF_3CO$], 626 (6) [$M^+ + NH_4 - CF_3CO$]; distribution of intensities for [$M^+ + H - CF_3CO$]: m/z [calc., found (%)] = 619 (2.5, 8), 620 (9.5, 4), 621 (26.8, 33), 622 (63.5, 64), 623 (73.7, 74), 624 (82.5, 79), 625 (75.2, 76), 626 (100, 100), 627 (45.6, 55), 628 (75.6, 62), 629 (14.7, 31), 630 (33.5, 20), 631 (6.5, 6), 632 (7.9, 8); Anal. Calc. for $C_{20}H_{26}F_6O_8Pd_2$: C, 33.31; H, 3.63. Found: C, 33.29; H, 3.55%.

3.3.1. Crystal data for 6a

$C_{20}H_{26}F_6O_8Pd_2$, $M = 721.21$ g mol^{-1}, yellow, crystal dimensions $0.49 \times 0.39 \times 0.35$ mm, monoclinic $P12/n$ (no. 14), at 100 K $a = 12.665(3)$, $b = 13.206(2)$, $c = 15.943(4)$ Å, $\beta = 103.61(2)$, $V = 2591.8(9)$ Å^3, $Z = 4$, $\rho = 1.848$ g cm^{-3}, $\mu = 1.472$ mm^{-1}, $\lambda = 0.71069$ Å. X-ray diffraction data were collected using an Enraf–Nonius CAD4 diffractometer employing ω–2θ scans yielding a total of 5903 reflections. The structure was solved by direct methods using SHELXS-86 [22], and atomic positions and displacement parameters were refined using full-matrix least-squares based on F^2 using SHELXL-93 (Sheldrick, 1993). The trifluoromethyl group attached to C17 shows an 80:20 disorder, with fluorine atoms F2 and F3 shared. Disordered atoms and hydrogen atoms were refined with isotropic displacement parameters. Refinement of 427 parameters using all reflections converged at $R = 0.0282$, $wR = 0.1022$, highest residual electron density peak 0.741 e

Å^{-3}. For information about available supplementary material for **6a** see Section 4.

3.4. [1,2-Bis(diphenylphosphino)ethane]-[(3,4,5-η)methyl-2,2-dimethylpent-3-enyloate]-palladium-tetrafluoroborate (**8**)

A 10 ml two-necked flask equipped with a magnetic stirrer was charged with bis[(3,4,5-η)-methyl-2,2-dimethylpent-3-enyloate]-bis(μ-trifluoracetato)-dipalladium(II) (**6**) (180 mg, 0.25 mmol) and anhydrous diethyl ether (4 ml) was added. A solution of tetrafluoroboric acid etherate (81 mg, 0.5 mmol) in diethyl ether (1 ml) was added, followed by a solution of 1,2-bis(diphenylphosphino)ethane (199 mg, 0.5 mmol) in diethyl ether (10 ml). A viscous, colorless substance immediately precipitated and the mixture was stirred until a fluffy suspension formed. The precipitate was filtered off, dissolved in chloroform and the solution filtered. Addition of diethyl ether gave the crude complex. An analytical sample was crystallized from chloroform–cyclohexane. Yield: 0.29 g (80%); ^{1}H-NMR (500 MHz, $CDCl_3$, 253 K/−20°C): $\delta =$ 1.01, 1.09 (2 × s, 6H, CH_3), 2.07–2.19 (m, 1H, PCH_2), 2.23–2.35 (m, 1H, PCH_2), 2.72–3.00 (m, 2H, PCH_2), 2.90 (dd, $J = 12.9$, $J = 9.5$ Hz 1H, CH=CH_2-*anti*), 3.44 (s, 3H, OCH_3), 4.58 (dd, $J = 7.4$, $J = 5.7$ Hz, 1H, CH=CH_2-*syn*), 4.78 (dd, $J = 12.9$, $J = 9.8$ Hz, 1H, $(CH_3)_2$CCH), 5.80 (ddd, $J = 7.4$, $J = 12.9$, $J = 12.9$ Hz, 1H, CH=CH_2), 7.23–7.84 (m, 20H, H_{arom}); ^{1}H-NMR (500 MHz, $CDCl_3$, 323 K/50°C): $\delta = 1.11$ (s, 6H, CH_3), 2.55 (br s, 4H, PCH_2), 3.42 (s, 3H, OCH_3), 4.82 (dd, $J = 13.2$, $J = 10.2$ Hz, 1H, $(CH_3)_2$CCH), 5.80 (dt, $J = 13.2$, $J = 10.3$ Hz, 1H, CH=CH_2), 7.52 (br s, 20H, H_{arom}); ^{13}C-NMR (125 MHz, $CHCl_3$, 293 K/20°C): $\delta = 26.8$ (dd, $J = 13$, $J = 31$ Hz, PCH_2), 26.9 (br, CH_3), 28.0 (br, CH_3), 30.5 (dd, $J = 14$, $J = 32$ Hz, PCH_2), 44.6 (dd, $J = 1$, $J = 2$ Hz, $C(CH_3)_2$), 52.3 (OCH_3), 65.7 (dd, $J = 5$, $J = 26$ Hz, CH=CH_2), 105.6 (dd, $J = 6$, $J = 32$ Hz, $(CH_3)_2$CCH), 118.9 (dd, $J = 7$, $J = 7$ Hz, CH=CH_2), 129–135 (m, C_{arom}), 175.5 (dd, $J = 2$, $J = 5$ Hz, $COOCH_3$); EIMS (70 eV): m/z (%) = 358 (1), 261 (16), 217 (12), 180 (32), 154 (75), 121 (30), 117 (72), 83 (81), 78 (100).

3.4.1. Crystal data for **8**

$C_{35}H_{38}BCl_3F_4O_2P_2Pd$, $M = 852.15$ g mol^{-1}, colorless, crystal dimensions 0.36 × 0.26 × 0.16 mm, monoclinic $C12/c1$ (no. 15), at 100 K $a = 34.5672(16)$, $b = 10.2172(5)$, $c = 21.0234(10)$ Å, $\beta = 97.022(2)°$, $V =$ 7369.4(6) Å^3, $Z = 8$, $\rho = 1.536$ g cm^{-3}, $\mu = 0.860$ mm^{-1}, $\lambda = 0.71073$ Å. X-ray diffraction data were collected using a Siemens SMART diffractometer employing ω-scans to cover reciprocal space up to 33.13° with 83.2% completeness, integration of raw data yielded a total of 28 833 reflections, merged into 11 682 unique reflections with $R_{int} = 0.0431$ after applying Lorentz, polarization and absorption correction. The structure was solved by direct methods using SHELXS-97 (Sheldrick, 1990), and atomic positions and displacement parameters were refined using full-matrix least-squares based on F^2 using SHELXL-97 (Sheldrick, 1997). Hydrogen atoms bound to allylic carbon atoms C1, C2 and C3 were located from difference Fourier maps and fixed during further refinement, all other hydrogen atoms were riding on the corresponding atom using idealized geometry. Refinement of 436 parameters using all reflections converged at $R =$ 0.0477, $wR = 0.1018$, highest residual electron density peak 1.535 e Å^{-3}.

4. Supplementary material

Complete lists of atom coordinates and anisotropic displacement parameters as well as tables of bond lengths and bond angles are available upon request from the authors. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and can be obtained free of charge by applying to: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) quoting the reference nos. CCDC-139801 and CCDC-139802 for compounds **8** and **6a**, respectively.

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