# Palladium(0)- and Nickel(0)-Catalyzed [3 + 2] Co-Cyclization Reactions of Bicyclopropylidene with Alkenes☆

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Bicyclopropylidene (**1**) readily undergoes a palladium(0)-catalyzed [3 + 2] co-cyclization with electron deficient alkenes (methyl acrylate, methyl *trans*-crotonate, methyl cinnamate and diethyl fumarate) as well as with some strained alkenes (norbornene, norbornadiene) by distal ring cleavage of one of the three-membered rings of **1**. All these co-cyclizations are regioselective with respect to **1** as well as regio- and stereoselective with respect to the alkenes to give the corresponding 4-methylenespiro[2.4]heptane-*trans*-6-carboxylates **2a**−**5** with the electron deficient alkenes and the cycloadducts **6** and **7** with the strained alkenes in acceptable to good yields (56 to 83%). In contrast to palladium(0) catalysts nickel(0) complexes catalyze both distal ring opening of **1** and oxidative coupling of the two double bonds when **1** is reacted with e.g. diethyl fumarate. The result is a mixture of the methylenecyclopentane derivative **5** with the [2 + 2] cycloadduct **8** and the cotrimer **9**.

## Introduction

Cycloaddition reactions are the archetypes for synthetic efficiency, as they are highly atom economical and frequently regio- as well as diastereoselective. The prototype is the widely used [4 + 2] cycloaddition (Diels-Alder reaction) to yield six-membered carbo- or heterocycles in one step. For the construction of five-membered carbocycles our group[1a][1b][1c][1d][1e] and Trost et al.[1d][1e][1f] have developed a metal-catalyzed [3 + 2] cycloaddition methology in recent years. Crucial for the general applicability of this methodology is the selection of a suitable and conveniently accessible $C_3$-building block which can be modified with a wide range of substituents. We have demonstrated that methylenecyclopropane and its derivatives with substituents on the three-membered ring or on the double bond fulfill these conditions and undergo [3 + 2] co-cyclizations in the presence of a catalytically active nickel(0) or palladium(0) complex[2][3] with a wide range of alkenes bearing both electron withdrawing or electron donating substituents[1a][1b][1c]. For a few examples, [3 + 2] cycloadditions of methylenecyclopropanes have been achieved in the absence of a transition metal catalyst[4][5][6].

A complementary variant of this [3 + 2] cycloaddition methodology was simultaneously developed by Trost et al., and uses 2-(trimethylsilylmethyl)allyl acetate or substituted derivatives thereof as building blocks for a (trimethylenemethane)palladium [PdTMM] intermediate which acts as the cycloaddend[7][8]. A closer look at both methods reveals that the [PdTMM] intermediates responsible for the [3 + 2] co-cyclizations cannot be the same, since the species derived from methylenecyclopropanes undergo [3 + 2] cycloadditions with both electron-rich and electron-poor alkenes, whereas the reactive species in the Trost reagents only react with electron-poor alkenes. In addition, the palladium(0)-catalyzed "cyclodimerization" of substituted methylenecyclopropanes occurs with poor regioselectivity[1a], while the Trost reagents derived from mono- or disubstituted derivatives cycloadd with good regioselectivity[8]. Indeed, computational studies have revealed that different reaction mechanisms with different [PdTMM] intermediates are responsible for the observed differences in reactivities and product distributions of the palladium-catalyzed [3 + 2] cycloadditions between substituted methylenecyclopropanes and substituted 2-(trimethylsilylmethyl)allyl acetates onto alkenes[9][10].

In this report we describe the palladium(0)- and nickel(0)-catalyzed [3 + 2] co-cyclizations of the now readily available bicyclopropylidene **1**[11] onto some electron-deficient alkenes as well as norbornene and norbornadiene. The most striking result is the observation that these cyclo-

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codimerizations occur with high regioselectivities which differ considerably from those observed with (dimethylmethylene)cyclopropane[1a] and to some extent also from that with 2-(1-trimethylsilyl-1-cyclopropyl)allyl pivalate[12][13].

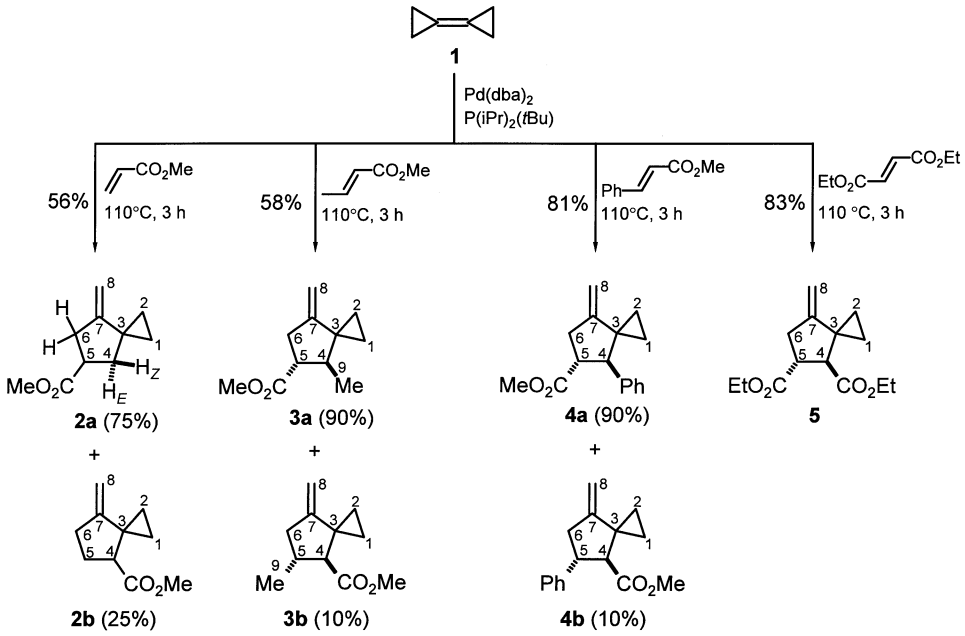
## Results and Discussion

In the presence of a catalytic amount of a palladium(0) complex [2.5−4.2 mol%; preferably $Pd(dba)_2/(iPr)_2P(tBu)$, molar ratio 1:1][14] bicyclopropylidene (**1**) reacts readily with alkyl acrylates, such as methyl acrylate, methyl *trans*-crotonate, methyl cinnamate and diethyl fumarate under [3 + 2] cycloaddition to produce the corresponding 4-methylenespiro[2.4]heptane derivatives **2**−**5** in 56−83% yield (Scheme 1).

The assignments of structure and isomer distribution of the methylenespiro[2.4]heptane derivatives **2**−**5** rest on mass spectrometric data and detailed analyses of their $^1H$- and $^{13}C$-NMR spectra (see Experimental Section).

Whereas methylenecyclopropane[15] as well as isopropylidene and (diphenylmethylene)cyclopropane[3c][16] all cycloadd to norbornene and norbornadiene in the presence of the above mentioned palladium(0) catalyst to give the corresponding methylenecyclopentane-annelated products, bicyclopropylidene **1** reacts in the same regioselective mode as with acrylates to give the methylenespiro[2.4]heptane-annelated compounds **6** and **7** in good yields. In addition to **6**, norbornene and **1** form a mixture of four isomeric 2:1 cotrimers in 4.9% yield.

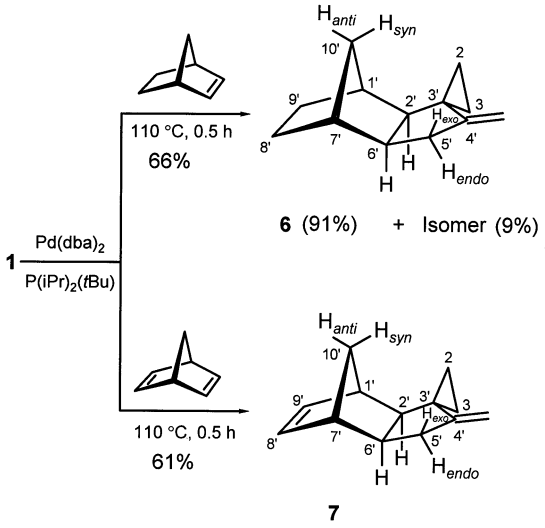
Scheme 1. Pd(0)-catalyzed cyclocodimerization of **1** with alkyl acrylates




Apparently, these cycloadditions proceed highly regioselectively with respect to **1** because the only detectable and isolated products possess the 4-methylenespiro[2.4]heptane skeleton. Regioselectivity is also observed with respect to the alkyl acrylates since in most cases ca. 90% of the products have the carboxylate group in the β-position relative to the spirocarbon atom. In addition, the configuration of the β-substituted alkyl acrylates is retained in the cycloadducts.

This regiochemical outcome is remarkable since isopropylidene- and cyclopentylidenecyclopropane under the same conditions react with these alkyl acrylates with retention of the alkylidene groups[1a][1c]. The Pd(0)-catalyzed [3 + 2] cycloadditions of 2-(1-trimethylsilyl-1-cyclopropyl)alkyl pivalate with electron deficient alkenes on the other hand are solvent dependent, giving both cyclopropylidenecyclopentane and 4-methylenespiro[2.4]heptane derivatives[12]; e.g. with methyl cinnamate in dioxane both the 2-phenyl-4-cyclopropylidenecyclopentanecarboxylate and its isomer **4a** were formed in the ratio 1:2.3, whereas in toluene, the same solvent as used in this study, **4a** was the sole product[12].

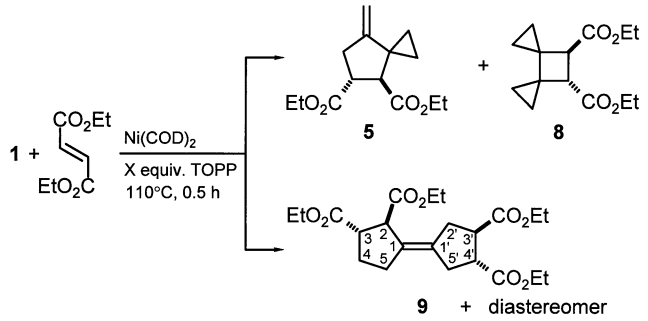
Scheme 2. Pd(0)-catalyzed cyclocodimerization of **1** with norbornene and norbornadiene



The structural assignments of **6** and **7** are primarily based on their $^1$H-NMR spectra. Characteristic for the *exo* orientation of the *cis*-annelated five-membered ring is the splitting of the hydrogen atom signals of the bridging methylene group[15] (see Experimental Section).

When a nickel(0) instead of a palladium(0) catalyst is used, the reaction of **1** with diethyl fumarate proceeds in a much more complex fashion. Besides the codimer **5**, the only product of the Pd(0)-catalyzed reaction, a second codimer **8** and a cotrimer **9** are formed, the former resulting from a simple [2 + 2] cycloaddition of the two double bonds, the latter by [3 + 2] co-cyclization of two fumarate molecules to each of the two three-membered rings of **1**.

Scheme 3. Ni(0)-catalyzed cyclocooligomerization of **1** with diethyl fumarate



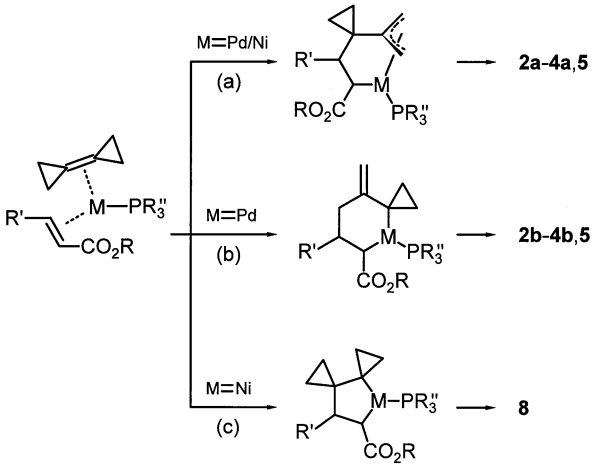

| | Yield (%) | | |
|---|---|---|---|
| X | **5** | **8** | **9** |
| 1 | 10 | 31 | 16[a] |
| 2 | 12 | 46 | 18[a] |
| 3 | 25 | 23 | 9[a] |

(a) 2 Diastereomers in the ratio ~ 1:1.

The catalyst precursors used were bis(1,5-cyclooctadiene)nickel(0) and tris(*o*-phenylphenyl) phosphite in the ratios 1:1 to 1:3, a combination which had been found most effective in other codimerizations of substituted methylenecyclopropanes with alkenes[1a][1c]. As shown in Scheme 3, yields and ratios of the products **5**, **8** and **9** depended on the Ni to ligand ratio to a certain extent. The best yield of the [2 + 2] cycloadduct **8** was obtained with a Ni to ligand ratio of 1:2, wheras the [3 + 2] cycloadduct **5** was preferred with a Ni to ligand ratio of 1:3. It is interesting to note that the same catalyst precursor causes isopropylidene- and cyclopentylidenecyclopropane to [3 + 2] cycloadd to electron deficient alkenes to give both alkylidenecyclopentane and α,α′-dialkylmethylenecyclopentane derivatives in nearly equal amounts. Moreover, a substituted acrylate such as methyl cinnamate cycloadds in such a way to the three-carbon unit that the carboxylate group ends up in the α-positon to the dialkylated carbon atom[1a][1c].

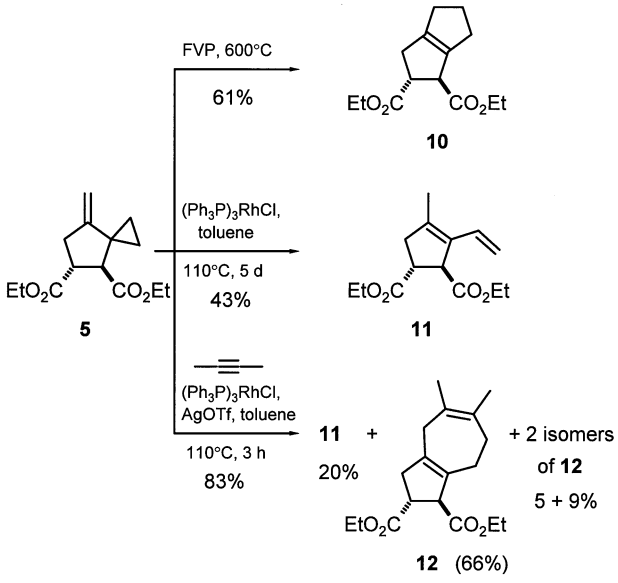
The mechanism of the above mentioned palladium(0)-catalyzed [3 + 2] co-cyclizations of **1** with the observed regioselectivities is not yet completely understood. According to the concepts of Fujimoto et al.[10] and their calculations carried out for unsubstituted methylenecyclopropane and ethylene, one would expect the regioisomers **2b−4b** to be the sole products [Scheme 4, path (b)]. In reality, these isomers are found as the minor products, **2a−4a** being the preferred ones (75−90%). Regioisomers of this type are observed with dialkylmethylenecyclopropanes[1a][1c]. Since **1** possesses two cyclopropylidene groups, ring opening can also occur according to path (a) in Scheme 4 which would explain the observed regioselectivity. A mechanism via a "TMM-Pd" intermediate with charge separation as proposed by Trost, Fenske et al. for Trost′s synthesis of methylenecyclopentanes[9], would also explain the observed regiochemistry.

Scheme 4. Proposed routes for the metal-catalyzed cycloadditions of **1** to alkenes




In conclusion, the Pd(0)-catalyzed [3 + 2] co-cyclization of bicyclopropylidene (**1**) to alkenes offers a new route to 4-methylenespiro[2.4]heptane derivatives. The vinylcyclopropane moieties in these products appear to be particularly useful for further elaborations. Some exploratory experiments show that **5** undergoes smooth thermal rearrangement to **10** as shown in Scheme 5 (cf. ref.[12]). Rho-

Scheme 5. Examples of synthetically useful further transformations of 4-methylenespiro[2.4]heptanes **2−5**



dium(I) catalysts are able to either induce isomerization of **5** to the ethenylcyclopentene derivative **11** or in the presence of an alkyne as e.g. 2-butyne to catalyze a [5 + 2] cycloaddition to give the bicyclo[5.3.0]decadiene derivative **12**. The latter type of reaction has previously been realized only in an intramolecular fashion[18].

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## Experimental Section

All experiments were carried out under argon in anhydrous solvents. − FT-IR: Bruker IFS 66, measured as oils between NaCl plates. − $^1$H and $^{13}$C NMR: Bruker AM 200, AM 250, AMX 300 and AMX 400 instrument in $CDCl_3$ soln, [$^{13}$C, additional DEPT (Distortionless Enhancement by Polarization Transfer)]; chemical shifts relative to solvent signals, recalculated relative to TMS. − MS (EI) and MS (HR-EI): Finnigan MAT 95 and Varian CH 5 spectrometers at 70 eV. MS (HR-EI): preselected ion peak matching at R >> 10000 to be within ± 2 ppm of the exact masses. − TLC: Macherey-Nagel precoated sheets, 0.25 mm Sil G/UV$_{254}$. − Column chromatography: Merck silica gel, grade 60, 230−400 mesh.

*Starting Materials*: Bis(dibenzylideneacetone)palladium [Pd(dba)$_2$][19], bis(1,5-cyclooctadiene)nickel [Ni(COD)$_2$][20], P(*i*Pr)$_2$(*t*Bu)[21], bicyclopropylidene (**1**)[11] and tris(*o*-phenylphenyl) phosphite (TOPP)[22] were prepared according to published procedures.

*General Procedure for the Palladium(0)-Catalyzed Cycloaddition of Acrylates to Bicyclopropylidene* (**1**): A solution of the catalyst, Pd(dba)$_2$ (2.2−4.2 mol%) and P(*i*Pr)$_2$(*t*Bu) (2.2−4.2 mol%), and the acrylate (2.0−2.3 equiv.) in toluene (10 ml), was heated under reflux (110°C) and a solution of **1** (1.0 equiv.) in toluene (10 ml) was added dropwise within 0.5 h, then the reaction mixture was heated under reflux for another 3 h until the reaction was complete (GC control). Fractional distillation of the reaction mixture first yielded the solvent together with the excess acrylate, and as a second fraction the product which was checked for purity by gas chromatography (GC).

*Methyl 7-Methylenespiro[2.4]heptane-5-carboxylate* (**2a**) *and Methyl 7-Methylenespiro[2.4]heptane-4-carboxylate* (**2b**): According to the general procedure, methyl acrylate (3.85 g, 44.7 mmol) and **1** (1.58 g, 19.7 mmol) in the presence of Pd(dba)$_2$ (0.33 g, 0.57 mmol) and P(*i*Pr)$_2$(*t*Bu) (0.10 g, 0.57 mmol) gave 2.76 g of a colorless liquid (b.p. 60−63°C/3 mbar) which contained (determined by GC) 16.7% of **2b** [calcd. 0.46 g (yield 14%)], 7.6% of dimeric methyl acrylate, 49.3% of **2a** [calcd. 1.36 g (yield 42%)], and seven unknown components.

**2a** was obtained 99.9% pure by preparative GC. − IR (film): $\tilde{\nu}$ = 3075 cm$^{-1}$, 2997, 2952, 1740, 1652, 1436, 1367, 1260, 1170, 1019, 949, 865. − $^1$H NMR (200 MHz): δ = 4.58 (brs, 8-H$_E$) 4.28 (brs, 8-H$_Z$), 3.68 (s, $CO_2CH_3$), 2.98 (pseudoquint., $^3J_{5,4}$ = 9.6, $^3J_{5,4'}$ = 7.2, $^3J_{5,6}$ = 8.2 Hz, 5-H), 2.76 (brd, $^3J_{6,5}$ = 8.2 Hz, 6-H), 2.15 (dd, $^2J_{4,4'}$ = 12.4, $^3J_{4,5}$ = 9.6 Hz, 4-H), 1.81 (dd, $^2J_{4',4}$ = 12.4, $^3J_{4',5}$ = 7.2 Hz, 4′-H), [0.83 (m), 0.78 (m), 0.65 (m), 1-H and 2-H]. − $^{13}$C NMR (50 MHz): δ = 175 (s, CO), 154.9 (s, C-7), 97.9 (t, $^1J$ = 156 Hz, C-8), 51.3 (q, $^1J$ = 147 Hz, $CO_2CH_3$), 42.1 (d, $^1J$ = 134 Hz, C-5), 39.4 (t, $^1J$ = 132 Hz, C-4), 37.4 (t, $^1J$ = 133 Hz, C-6), 24.5 (s, C-3), [19.1 (t, $^1J$ = 161 Hz), 15.2 (t, $^1J$ = 161 Hz), C-1 and C-2]. − MS (EI); *m/z* (%): 166 (8) [M$^+$], 135 (9) [M$^+$ − $OCH_3$], 107 (100) [M$^+$ − $CO_2CH_3$], 91 (91), 79 (56), 77 (23). − MS (HR-EI): 166.0993 ($C_{10}H_{14}O_2$: calcd. 166.0994). − $C_{10}H_{14}O_2$ (166.2): calcd. C 72.26, H 8.49; found C 71.96, H 8.47.

**2b**: $^1$H NMR (250 MHz): δ = 4.60 (t, $^4J_{E8,6}$ = 1.8 Hz, 8-H$_E$), 4.29 (t, $^4J_{Z8,6}$ = 2.2 Hz, 8-H$_Z$), 3.68 (m, 4-H), 3.64 (s, $CO_2CH_3$), 2.73 (pseudoquint., $^2J_{6',6}$ = 12.4, $^3J_{6',5}$ = 7.4 Hz, 6′-H), 2.50 (pseudoquint. of dd, $^2J_{6,6'}$ = 12.4, $^3J_{6,5'}$ = 8.2, $^4J_{E8,6}$ = 1.8, $^4J_{Z8,6}$ = 2.2 Hz, 6-H), 1.95−2.15 (m, 5-H), [0.91−1.08 (m), 0.64−0.80 (m), 1-H and 2-H]. − $^{13}$C NMR (62.5 MHz): δ = 174.9 (CO), 156.2 (C, C-7), 97.9 ($CH_2$, C-8), 51.4 (CH, C-4), 51.0 ($CO_2CH_3$), 32.6 ($CH_2$, C-6), 28.0 (C, C-3), 27.8 ($CH_2$, C-5), [19.1 ($CH_2$), 14.6 ($CH_2$), C-1 and C-2]. − MS (EI); *m/z* (%): 166 (88) [M$^+$], 151 (18) [M$^+$ − $CH_3$], 135 (9) [M$^+$ − $OCH_3$], 107 (86) [M$^+$ − $CO_2CH_3$], 106 (70) [M$^+$ − H − $CO_2CH_3$], 91 (100) [$C_7H_7^+$], 79 (84), 77 (35). − MS (HR-EI): 166.0993 ($C_{10}H_{14}O_2$: calcd. 166.0994).

*Methyl 7-Methylene-4-methylspiro[2.4]heptane-trans-5-carboxylate* (**3a**) *and Methyl 7-Methylene-5-methylspiro[2.4]heptane-trans-4-carboxylate* (**3b**): According to the general procedure, methyl *trans*-crotonate (4.45 g, 44.4 mmol) and **1** (1.72 g, 21.5 mmol) in the presence of Pd(dba)$_2$ (0.33 g, 0.57 mmol) and P(*i*Pr)$_2$(*t*Bu) (0.10 g, 0.57 mmol) gave 2.36 g of a colorless liquid (b.p. 70°C/3 mbar) which contained 85.5% of **3a** and 9.4% of **3b** besides traces of toluene and methyl crotonate (determined by GC, 58% yield). **3a**: IR (film): $\tilde{\nu}$ = 3078 cm$^{-1}$, 2995, 2957, 1737, 1652, 1436, 1368 1260, 1167, 1020, 949, 864. − $^1$H NMR (300 MHz): δ = 4.54 (t, $^4J_{E8,6}$ = 2.1 Hz, 8-H$_E$), 4.28 (t, $^4J_{Z8,6}$ = 2.3 Hz, 8-H$_Z$), 3.66 (s, $CO_2CH_3$), 2.70 (ddd, $^3J_{6,5}$ = 9.8, $^4J_{E8,6}$ = 2.1, $^4J_{Z8,6}$ = 2.3 Hz, 6-H), 2.45 (td, $^3J_{5,6}$ = $^3J_{5,4}$ = 9.8, $^3J_{5,6'}$ = 8.0 Hz, 5-H), 2.29 (dq, $^3J_{4,5}$ = 9.6, $^3J_{4,9}$ = 6.8 Hz, 4-H), 0.84 (ddd, $^3J_{Z2,Z1}$ = 10.0, $^3J_{Z2,E1}$ = 6.3, $^2J_{Z2,E2}$ = 4.2 Hz, 2-H$_Z$), 0.74 (d, $^3J_{9,4}$ = 6.8 Hz, 9-H), 0.73 (ddd, $^2J_{E1,Z1}$ = 4.3, 1-H$_E$), 0.60 (ddd, 1-H$_Z$), 0.35 (ddd, 2-H$_E$). − $^{13}$C NMR (75.5 MHz): δ = 174.7 (s, CO), 154.9 (s, C-7), 98.0 (t, $^1J$ = 154 Hz, C-8), 51.0 (q, $^1J$ = 147 Hz, $CO_2CH_3$), 49.9 (d, $^1J$ = 134 Hz, C-5), 41.7 (d, $^1J$ = 130 Hz, C-4), 36.0 (t, $^1J$ = 133 Hz, C-6), 28.5 (s, C-3), 14.3 (q, $^1J$ = 126 Hz, C-9) 13.4 (t, $^1J$ = 162 Hz, C-2), 12.9 (t, $^1J$ = 161 Hz, C-1). − MS (EI); *m/z* (%): 180 (100) [M$^+$], 165 (36) [M$^+$ − $CH_3$], 152 (35) [M$^+$ − $C_2H_4$], 149 (48) [M$^+$ − $OCH_3$], 137 (30), 121 (28) [M$^+$ − $CO_2CH_3$]. − MS (HR-EI): 180.1150 ($C_{11}H_{16}O_2$: calcd. 180.1150). − $C_{11}H_{16}O_2$ (180.2): calcd. C 73.30, H 8.95; found C 73.46, H 8.85.

**3b**: IR (film): $\tilde{\nu}$ = 3079 cm$^{-1}$, 2995, 2955, 1739, 1653, 1436, 1369, 1260, 1156, 1020, 950, 863, 743. − $^1$H NMR (250 MHz): δ = 4.56 (t, $^4J_{E8,6}$ = 1.8 Hz, 8-H$_E$), 4.25 (t, $^4J_{Z8,6}$ = 2.1 Hz, 8-H$_Z$), 3.66 (d, $^3J_{4,5}$ = 9.8 Hz, 4-H), 3.63 (s, $CO_2CH_3$), 2.76 (dddd, $^2J_{6,6'}$ = 15.6, $^3J_{6,5}$ = 6.6, $^4J_{E8,6}$ = 1.8, $^4J_{Z8,6}$ = 2.1 Hz, 6-H), 2.42−2.53 (m, 5-H), 2.15 (dddd, $^2J_{6',6}$ = 15.6, $^3J_{6',5}$ = 8.8, $^4J_{E8,6'}$ = 1.8, $^4J_{Z8,6'}$ = 2.1 Hz, 6′-H), 1.07 (d, $^3J_{9,5}$ = 6.2 Hz, 9-H), [0.96−1.08 (m), 0.60−0.94 (m), 1-H and 2-H]. − $^{13}$C NMR (75.5 MHz): δ = 173.1 (s, CO), 155.5 (s, C-7), 97.7 (t, $^1J$ = 154 Hz, C-8), 57.5 (d, $^1J$ = 130 Hz, C-4), 50.7 (q, $^1J$ = 146 Hz, $CO_2CH_3$), 40.8 (t, $^1J$ = 133 Hz, C-6), 35.8 (d, $^1J$ = 132 Hz, C-5), 26.9 (s, C-3), 18.9 (q, $^1J$ = 125 Hz, C-9), 16.8 (t, $^1J$ = 162 Hz, C-2), 15.5 (t, $^1J$ = 161 Hz, C-1). − MS (EI); *m/z* (%): 180 (28) [M$^+$], 165 (8) [M$^+$ − $CH_3$], 152 (8) [M$^+$ − $C_2H_4$], 137 (6), 121 (100) [M$^+$ − $CO_2CH_3$], 120 (25), 105 (60), 93 (36), 91 (43), 79 (38), 77 (36). − MS (HR-EI): 180.1150 ($C_{11}H_{16}O_2$: calcd. 180.1150).

*Methyl 7-Methylene-4-phenylspiro[2.4]heptane-trans-5-carboxylate* (**4a**) *and Methyl 7-Methylene-5-phenylspiro[2.4]heptane-trans-4-carboxylate* (**4b**): According to the general procedure, methyl cinnamate (7.84 g, 48.4 mmol) and **1** (1.70 g, 21.25 mmol) in the presence of Pd(dba)$_2$ (0.31 g, 0.54 mmol) and P(*i*Pr)$_2$(*t*Bu)

(0.094 g, 0.54 mmol) gave 4.2 g (81%) of a colorless liquid (b.p. 55−60°C/$10^{-4}$ mbar) which contained 90.4% of **4a** and 9.6% of **4b** (determ. by GC).

**4a**[12]: $^1$H NMR (400 MHz): δ = 7.27 (t, $^3J$ = 8.2 Hz, *m*-$H_{Ph}$), 7.19 (t, $^3J$ = 7.6 Hz, *p*-$H_{Ph}$), 7.14 (d, $^3J$ = 8.0 Hz, *o*-$H_{Ph}$), 4.67 (t, $^4J_{E8,6} = {}^4J_{E8,6'}$ = 2.0 Hz, 8-$H_E$), 4.39 (t, $^4J_{Z8,6} = {}^4J_{Z8,6'}$ = 2.2 Hz, 8-$H_Z$), 3.58 (s, $CO_2CH_3$), 3.51 (d, $^3J_{4,5}$ = 9.3 Hz, 4-H), 3.16 (td, $^3J_{5,4} = {}^3J_{5,6}$ = 9.2, $^3J_{5,6'}$ = 8.2 Hz, 5-H), 2.87 [m, $^3J_{6,5}$ = 9.2, $^3J_{6',5}$ = 8.2, $^4J_{6,Z8} = {}^4J_{6',Z8}$ = 2.2, $^4J_{6,E8} = {}^4J_{6',E8}$ = 2.0 Hz, 6(6′)-H], 0.79 (ddd, $^3J_{Z2,E1}$ = 9.6, $^3J_{Z2,Z1}$ = 6.5, $^2J_{Z2,E2}$ = 4.0 Hz, 2-$H_Z$), 0.63 (ddd, 2-$H_E$), 0.55 (ddd, 1-$H_Z$), 0.39 (ddd, 1-$H_E$). − $^{13}$C NMR (121 MHz): δ = 174.9 (s, CO), 155.1 (s, C-7), 139.9 (s, *ipso*-$C_{Ph}$), 128.7 (d, $^1J$ = 156 Hz, *o*-$C_{Ph}$), 128.1 (d, $^1J$ = 160 Hz, *m*-$C_{Ph}$), 126.5 (d, $^1J$ = 160 Hz, *p*-$C_{Ph}$), 98.3 (t, $^1J$ = 155 Hz, C-8), 54.3 (d, $^1J$ = 129 Hz, C-4), 51.7 (q, $^1J$ = 147 Hz, $CO_2CH_3$), 49.5 (d, $^1J$ = 133 Hz, C-5), 36.8 (t, $^1J$ = 132 Hz, C-6), 29.5 (s, C-3), [15.5 and 15.4 (t, $^1J$ = 162 Hz), C-1 and C-2]. − MS (EI); *m/z* (%): 242 (4) [$M^+$], 227 (14) [$M^+ - CH_3$], 183 (64) [$M^+ - CO_2CH_3$], 182 (100), 167 (64), 165 (22), 155 (40), 153 (24), 141 (33), 91 (48).

**4b**: $^{13}$C NMR (121 MHz, 9.6% as a mixture with 90.4% of **4a**): δ = 155.4 (s, C-7), 98.4 (t, C-8), 57.6 (d, C-4), 46.7 (d, C-5), 41.2 (t, C-6), 27.5 (s, C-3). − MS (from GC/MS coupling, 70 eV); *m/z* (%): 242 (12) [$M^+$], 183 (100) [$M^+ - CO_2CH_3$], 167 (30), 165 (12), 155 (20), 153 (15), 151 (17), 141 (27), 91 (38).

*Diethyl 7-Methylenespiro[2.4]heptane-trans-4,5-dicarboxylate* (**5**): According to the general procedure, diethyl fumarate (8.50 g, 49.4 mmol) in toluene (10 ml) and **1** (1.97 g, 24.6 mmol) in toluene (10 ml) in the presence of $Pd(dba)_2$ (600 mg, 1.04 mmol) and P(*i*Pr)$_2$(*t*Bu) (180 mg, 1.04 mmol) gave 5.44 g of **5** [94% pure (GC), 83% yield] as a colorless liquid (b.p. 90−95°C/1.5 bar). − IR (film): $\tilde{\nu}$ = 3079 $cm^{-1}$, 2983, 2955, 1734, 1653, 1447, 1371, 1345, 1185, 1096, 1031, 962, 865, 796. − $^1$H NMR (200 MHz): δ = 4.62 (t, *J* = 2 Hz, 8-$H_E$), 4.33 (t, *J* = 2 Hz, 8-$H_Z$), 4.15 (m, $CO_2CH_2CH_3$), 3.36 (q, *J* = 8.6 Hz, 5-H), 3.21 (d, *J* = 8.6 Hz, 4-H), 2.93 (ddt, $J_{6,6'}$ = 16, $J_{6,5}$ = 8.6, $J_{6,8}$ = 2 Hz, 6-H), 2.71 (ddt, $J_{6',6}$ = 16, $J_{6',5}$ = 8.6, $J_{6',8}$ = 2 Hz, 6-H), 1.25 (t, *J* = 7.2 Hz, $CO_2CH_2CH_3$), 0.59−1.06 [m, 1(2)-H]. − $^{13}$C NMR (50.3 MHz): δ = 173.3 and 171.8 (s, CO), 153.4 (s, C-7), 98.9 (t, $^1J$ = 157 Hz, C-8), 60.4 and 60.3 (t, $^1J$ = 148 Hz, $CO_2CH_2CH_3$), 52.2 (d, $^1J$ = 134 Hz, C-4), 45.0 (d, $^1J$ = 134 Hz, C-5), 35.5 (t, $^1J$ = 131 Hz, C-6), 26.8 (s, C-3), 16.2 and 15.5 [t, $^1J$ = 162 Hz, C-1(2)], 14.0 and 13.9 (q, $^1J$ = 131 Hz, $CO_2CH_2CH_3$). − MS (EI); *m/z* (%): 252 (13) [$M^+$], 223 (9), 206 (9), 179 (25), 178 (45), 105 (100). − MS (HR-EI): 252.1361 ($C_{14}H_{20}O_4$: calcd. 252.1362). − $C_{14}H_{20}O_4$ (252.3): calcd. C 66.64, H 7.99; found C 66.88, H 8.21.

*4′-Methylenespiro[cyclopropane-1,3′-exo-tricyclo[5.2.1.0$^{2,6}$]decane]* (**6**): To the dark red solution of $Pd(dba)_2$ (0.45 mg, 0.78 mmol) and diisopropyl-*tert*-butylphosphane (0.14 mg, 0.78 mmol) in toluene (20 ml) which was heated under reflux, a solution of norbornene (4.25 g, 45.1 mmol) and **1** (3.14 g, 80% purity, 31.4 mmol) in toluene (10 ml) was added dropwise within 0.5 h (color change from red to green!). Fractional distillation gave, after the excess norbornene and the solvent, 3.58 g (66%) of a colorless liquid (b.p. 35−40°C/$10^{-3}$ bar) which contained 91% of **6** and 9% of an unidentified isomer of **6**. The black residue was taken up in pentane (20 ml), the slurry filtered over Florisil, and the solution concentrated to give a colorless powder (0.41 g, 4.9%) which contained four cotrimers of two molecules of norbornene and one molecule of **1** (molecular mass found: 268 by GC/MS coupling).

**6**: $^1$H NMR (400.1 MHz): δ = [4.39 (t, $^4J \approx$ 2 Hz) and 4.20 (t, $^4J \approx$ 2 Hz), =$CH_2$], 2.74 (tdd, $^2J_{5',5'}$ = 17.7, $^3J_{endo\text{-}5',6'}$ = 10.8, $^4J_{endo\text{-}5',=CH_2} \approx$ 2 Hz, 5′-$H_{endo}$], 2.12 (ddt, $^2J_{5',5'}$ = 17.7, $^3J_{exo\text{-}5',6'}$ = 4.4, $^4J_{exo\text{-}5',=CH_2} \approx$ 2 Hz, 5′-$H_{exo}$), 2.12 (m, 6′-H), [1.97 (br. s) and 1.87 (br. s), 7′-H and 1′-H], 1.74 (d, $^3J_{2',6'}$ = 7.6 Hz, 2′-H), 1.49 (md, $^2J_{10',10'}$ = 10.0 Hz, 10′-$H_{syn}$), [1.41 (m, 2 H), 1.13 (md, *J* = 8.4 Hz, 1 H) and 1.00 (md, *J* = 8.4 Hz, 1 H), 8′-H and 9′-H], 0.94 (md, $^2J_{10',10'}$ = 10.0 Hz, 10′-$H_{anti}$), [0.80 (m, 1 H) and 0.74−0.61 (m, 3 H), 2-H and 3-H]. − $^{13}$C NMR (100.6 MHz): δ = 159.3 (s, C-4′), 96.5 (t, $^1J$ = 155 Hz, =$CH_2$), 55.4 (d, $^1J$ = 135 Hz, C-2′), 45.2 (d, $^1J$ = 135 Hz, C-6′), 43.2 (d, $^1J$ = 141 Hz, C-1′), 40.7 (d, $^1J$ = 141 Hz, C-7′), 39.8 (t, $^1J$ = 127 Hz, C-5′), 33.0 (t, $^1J$ = 132 Hz, C-10′), 29.0 (s, C-3′), [29.1 and 28.3 (t, $^1J$ = 132 Hz), C-8′ and C-9′], [20.1 (t, $^1J$ = 162 Hz) and 12.5 (t, $^1J$ = 161 Hz), C-2 and C-3]. − MS (EI); *m/z* (%): 174 (53) [$M^+$], 159 (15), 145 (22), 131 (45), 117 (25), 107 (80), 106 (78), 91 (100). − $C_{13}H_{18}$ (174.3): calcd. C 89.59, H 10.41; found C 89.67, H 10.48. The assignments of the $^1$H and $^{13}$C NMR signals were established by COSY and $^1$H/$^{13}$C correlation experiments.

*4′-Methylenespiro[cyclopropane-1,3′-exo-tricyclo[5.2.1.0$^{2,6}$]dec-8-ene]* (**7**): According to the procedure for the cycloaddition of **1** to norbornene, the reaction of **1** (2.49 g, 31.1 mmol) with norbornadiene (6.60 g, 72 mmol) in the presence of $Pd(dba)_2$ (0.75 mg, 1.30 mmol) and diisopropyl-*tert*-butylphosphane (0.22 mg, 1.3 mmol), yielded by fractional distillation 3.50 g of a colorless liquid, b.p. 45°C/0.1 bar, purity 92.4% (GC) (calcd. yield 61%), containing five impurities of 1−2% each. − $^1$H NMR (200.1 MHz): δ = [6.11 (dd) and 6.00 (dd, $^3J_{8',9'}$ = 5.8, $^3J_{8',7'} = {}^3J_{1',9'}$ = 3.1 Hz), 8′-H and 9′-H], [4.41 (m) and 4.23 (m, $^4J_{exo\text{-}5',=CH_2} \approx$ 2 Hz, =$CH_2$], 2.78 (tdd, $^2J_{5',5'}$ = 17.4, $^3J_{endo\text{-}5',6'}$ = 10.6, $^4J_{endo\text{-}5',=CH_2} \approx$ 2 Hz), 5′-$H_{endo}$], [2.56 (br. s) and 2.49 (br. s), 7′-H and 1′-H], 2.22−2.07 [m, 5′(6′)-$H_{exo}$], 1.74 [d, $^3J_{2',6'}$ = 7.6 Hz, 2′(6′)-H], 1.64 (md, $^2J_{10',10'}$ = 8.9 Hz, 10′-$H_{syn}$), 1.22 (quint d, $^2J_{10',10'}$ = 8.9 Hz, *J* = 3.7 Hz, 10′-$H_{anti}$), 0.9−0.6 [m, 2(3)-H]. − $^{13}$C NMR (100.6 MHz): δ = 159.2 (s, C-4′), [136.5 (d, $^1J$ = 168 Hz) and 135.3 (d, $^1J$ = 168 Hz), C-8′ and C-9′], 94.6 (t, $^1J$ = 155 Hz, =$CH_2$), 52.8 (d, $^1J$ = 138 Hz, C-2′), [48.5 (d, $^1J$ = 144 Hz), 45.9 (d, $^1J$ = 144 Hz), C-7′ and C-1′], 42.5 (d, $^1J$ = 138 Hz, C-6′), 42.3 (t, $^1J$ = 133 Hz, C-10′), 38.1 (t, $^1J$ = 128 Hz, C-5′), 30.0 (s, C-3′), [21.5 (t, $^1J$ = 160 Hz) and 11.9 (t, $^1J$ = 161 Hz), C-2 and C-3]. − MS (EI); *m/z* (%): 172 (4) [$M^+$], 106 (68), 91 (100). − $C_{13}H_{16}$ (172.3): calcd. C 90.64, H 9.36; found C 90.48, H 0.41. The assignments of the $^1$H and $^{13}$C signals have been established by COSY and $^1$H/$^{13}$C correlation experiments.

*Nickel(0)-Catalyzed Cocyclodimerization of* **1** *with Diethyl Fumarate:* A solution of $Ni(COD)_2$ (0.12 g, 0.44 mmol), tris(*o*-phenylphenyl) phosphite (TOPP) (0.47 g, 0.88 mmol) and diethyl fumarate (9.98 g, 58.0 mmol) in toluene (10 ml) was heated under reflux (110°C), and a solution of **1** (1.7 g, 21.2 mmol) in toluene (10 ml) was added with stirring during 20 min. After another 0.5 h stirring at 110°C the reaction was complete (GC control). The products were separated by fractional distillation. After removal of toluene and excess diethyl fumarate 3.3 g of a colorless liquid (b.p. 50−60°C/$10^{-3}$ mbar) was obtained which contained 73.9% of **8** [2.44 g (yield 46%)] and 20.3% of **5** [0.67 g (yield 12%)] (GC analysis). As a second fraction 1.8 g of a colorless liquid distilled at 120−140°C/$10^{-4}$ mbar which contained two isomers of compound **9** [46.7% and 44.4% (GC analysis) (yield 18%) besides five unidentified components (1−3% each)].

**8**: From the first fraction 0.33 g of pure compound **8** crystallized after standing at room temperature for two weeks, it was separated by filtration and dried in vacuo; m.p. 46°C. − $^1$H NMR (200 MHz): δ = 4.12 (q, $^3J$ = 7.1 Hz, $CO_2CH_2CH_3$), 3.72 (s, $CHCO_2Et$), 1.23 (t, $^3J$ = 7.1 Hz, $CO_2CH_2CH_3$), [0.52 (m), 0.21 (m), $CH_2$]. − $^{13}$C NMR (50 MHz): δ = 171.5 (s, CO), 60.1 (t, $^1J$ = 147 Hz, $CH_2CH_3$), 43.3 (d, $^1J$ = 140 Hz, CH), 14.0 (q, $^1J$ = 126 Hz,

$CO_2CH_2CH_3$), [7.3 (t, $^1J$ = 162 Hz), 6.3 (t, $^1J$ = 162 Hz), $CH_2$]. − MS (EI); *m/z* (%): 252 (0.2) [$M^+$], 206 (17), 178 (42), 149 (23), 133 (30), 105 (100), 91 (42), 79 (35), 77 (26). − $C_{14}H_{20}O_4$ (252.3): calcd. C 66.64, H 7.99; found C 66.70, H 8.12.

**9**: From the second fraction 0.9 g of the mixture of two diastereomers of tetraethyl 1,1′-bicyclopentylidene-2,3,3′,4′-tetracarboxylate (**9**) in the ratio 89.5:10.5 could be isolated by preparative gas chromatography. − $^1$H NMR (400.1 MHz): δ = 4.20 (m, 8 H, $CO_2CH_2CH_3$), 3.56 (m, 1 H, 2-H), 3.20 (dt, $J_{3,2} \approx J_{3,4trans} \approx 7.6$, $J_{3,4cis} \approx 6.4$ Hz, 1 H, 3-H), 3.12 (t, $J_{4',5'} = J_{3',4'} = 8.4$, $J_{4',5'cis} \approx 0$ Hz, 1 H, 4′-H), 3.08 (m, 1 H, 3′-H), 2.76−2.62 [m, 2 H, 2′(5′)-$H_{trans}$], 2.49−2.38 (m, 2 H, 5′-$H_{cis}$ and 2′-$H_{cis}$), 2.31 [m, 1 H, 5-$H_{trans}$], 2.27 (m, 1 H, 5-H), 2.13 (m, $J_{4,4}$ = 12.0, $J_{4trans,3} = J_{4trans,5trans}$ = 7.2, $J_{4cis,5cis}$ = 4.4 Hz, 1 H, 4-$H_{trans}$), 1.85 (dq, $^2J_{4,4}$ = 12.0, $^3J_{4,3} = {}^3J_{4,5} = {}^3J_{4,5'}$ = 7.6 Hz, 1 H, 4-$H_{cis}$), 1.22 (m, 12 H, $CO_2CH_2CH_3$) (numbering of the H atoms see Scheme 3; the assignments of the signals to the individual H atoms were based on a COSY experiment). − $^{13}$C NMR (50.3 MHz): δ = [173.3 (s) and 172.6 (s), $CO_2$Et], [132.5 (s) and 130.8 (s), C-1 and C-1′], [60.4 (t, $^1J$ = 148 Hz) and 60.2 (t, $^1J$ = 148 Hz), $CO_2CH_2CH_3$], [50.5 (d, $^1J$ = 134 Hz), 48.3 (d, $^1J$ = 132 Hz), 47.0 (d, $^1J$ = 133 Hz), 46.3 (d, $^1J$ = 133 Hz), C-2, C-3, C-3′, C-4′], [35.0 (t, $^1J$ = 131 Hz), 33.2 (t, $^1J$ = 131 Hz), 30.5 (t, $^1J$ = 131 Hz), 28.4 (t, $^1J$ = 132 Hz), C-4, C-5, C-2′, C-5′], 13.7 (q, $^1J$ = 127 Hz, $CO_2CH_2CH_3$). − MS (from GC/MS coupling, 70 eV); major isomer: *m/z* (%): 424 (<1) [$M^+$], 350 (28), 276 (100), 203 (54), 131 (36); minor isomer: *m/z* (%): 424 (<1%), 350 (28), 276 (100), 203 (51), 131 (36).

*Diethyl Bicyclo[3.3.0]oct-1(5)ene-2,3-dicarboxylate* (**10**): Diethyl 7-methylenespiro[2.4]heptane-*trans*-4,5-dicarboxylate (**5**) (1.65 g, 93.8% purity, 6.1 mmol) was slowly distilled from a round-bottom flask at 60−80°C and $10^{-3}$ mbar through a 30-cm quartz pyrolysis tube kept at 600°C. The pyrolysate which was collected in a cooled trap, was a yellow oil (crude yield 1.28 g) and according to GC consisted of one major **10** [74%, calculated yield 0.95 g (61%)] and five minor components (5.1, 2.4, 1.6, 5.3 and 5.4%, respectively). − $^1$H NMR (200 MHz): δ = 4.20 (m, $CO_2CH_2CH_3$), 3.90 (dt, $J_{3,4'}$ = 7.7, $J_{3,4}$ = 6.8, $J_{2,3}$ = 9.0 Hz, 3-H), 3.68 (m, 2-H), 2.61 (dd, $J_{4',4}$ = 15.4, $J_{4',3}$ = 7.7 Hz, 4′-H), 2.41 (dd, $J_{4',4}$ = 15.4, $J_{4,3}$ = 6.8 Hz, 4-H), 2.19 (quasi s, 6-H, 7-H, 8-H), 1.23 (t, $J$ = 6.8 Hz, $CO_2CH_2CH_3$). − $^{13}$C NMR (50.3 MHz): δ = [174.2 (s) and 172.6 (s), $CO_2$Et], [146.3 (s) and 141.5 (s), C-1 and C-5], [60.5 (t) and 60.3 (t), $CO_2CH_2CH_3$], [50.4 (d) and 49.7 (d), C-2 and C-3], [32.1 (t), 29.1 (t), 28.8 (t) and 27.3 (t), C-4, C-6, C-7, C-8], 13.8 (q, $CO_2CH_2CH_3$).

*Diethyl 2-Ethenyl-1-methylcyclopent-1-ene-trans-3,4-dicarboxylate* (**11**): Compound **5** [640 mg (93.4%), 2.37 mmol] and [RhCl(PPh$_3$)$_3$] (0.21 g, 0.23 mmol) were added to toluene (20 ml) in a 100 ml Schlenk flask. The resulting red suspension was heated at 110°C. After 5 d, when no starting material **5** was detectable any more by GC, the reaction mixture was filtered through a silica gel pad to remove the catalyst, the silica gel washed with toluene (2 × 20 ml), and the solvent removed in a rotatory evaporator. The residue weighed 300 mg (50% based on the starting material **5**) and according to GC consisted of one major product **11** [85%, calculated yield 255 mg (43%)], and three minor components (1.5, 1.0 and 2.6%, respectively). **11**: IR (film): $\tilde{\nu}$ = 2981 cm$^{-1}$, 2933, 1733, 1446, 1372, 1185, 1096, 1032, 862. − $^1$H NMR (200 MHz): δ = 6.49 (dd, $J_{E7,6}$ = 17.5, $J_{Z7,6}$ = 11.0 Hz, 6-H), 5.14 (d, $J_{E7,6}$ = 17.5 Hz, 7-$H_E$), 5.04 (d, $J_{Z7,6}$ = 11.0 Hz, 7-$H_Z$), 4.14 (q, $J$ = 7.1 Hz, $CO_2CH_2CH_3$), 4.13 (q, $J$ = 7.1 Hz, $CO_2CH_2CH_3$), 4.01 (m, 3-H), 3.26 (dt, $J_{4,5'}$ = 9.1, $J_{4,5}$ = 5.4 Hz, 4-H), 2.86 (ddq, $J_{5',5}$ = 17.5, $J_{5',4}$ = 9.1, $J_{5',8}$ = 1.5 Hz, 5′-H), 2.69 (ddq, $J_{5',5}$ = 17.5, $J_{5,4}$ = 5.4, $J_{5,8}$ = 0.5 Hz, 5-H), 1.79 (dd, $J$ = 1.5, $J$ = 0.5 Hz, $CH_3$), 1.24 (t, $J$ = 7.1 Hz, $CO_2CH_2CH_3$), 1.23 (t, $J$ = 7.1 Hz, $CO_2CH_2CH_3$). − $^{13}$C NMR (75.5 MHz): δ = [174.7 (s) and 174.4 (s), $CO_2$Et], [140.4 (s) and 131.7 (s), C-1 and C-2], 129.7 (d, C-6), 114.2 (t, C-7), [61.2 (t) and 61.0 (t), $CO_2CH_2CH_3$], [54.7 (d) and 45.5 (d), C-3 and C-4], 41.6 (t, C-5), [14.38 (q) and 14.25 (q), $CO_2CH_2CH_3$ and 1-$CH_3$]. − MS (EI); *m/z* (%): 252 (8) [$M^+$], 223 (20) [$M^+ - C_2H_5$], 206 (21) [$M^+ - C_2H_6O$], 195 (71) [$M^+ - C_4H_9$], 179 (45) [$M^+ - CO_2C_2H_5$], 178 (100) [$M^+ - C_3H_6O_2$], 121 (90), 105 (53), 91 (40). − MS (HR-EI): 252.1361 ($C_{14}H_{20}O_4$: calcd. 252.1362). − $C_{14}H_{20}O_4$ (252.3): calcd. C 66.64, H 7.99; found C 66.60, H 7.78.

*Diethyl 3,4-Dimethylbicyclo[5.3.0]deca-1(7),3-diene-trans-8,9-dicarboxylate* (**12**): To a red solution of [RhCl(PPh$_3$)$_3$] (0.25 g, 0.27 mmol) and silver triflate (70 mg, 0.27 mmol) in toluene (20 ml) in a 100 ml Schlenk flask were added compound **5** [1.22 g (93%), 4.50 mmol] and 2-butyne (0.27 g, 5 mmol) dissolved in toluene (10 ml). The reaction mixture which had turned yellow, was heated at 110°C for 3 h, when all the starting material had disappeared according to GC. The mixture was filtered through a silica gel pad, and the filtrate evaporated to dryness. The residue weighed 1.14 g (83%) and according to GC consisted of one major (66%) and three minor components (20, 5 and 9%, respectively). The crude product was chromatographed on silica gel eluting with ether/hexane (1:1). The major product was identified as the cycloadduct **12** and the main byproduct as the isomer **11** of the starting material **5**. **12**: IR (film): $\tilde{\nu}$ = 2980 cm$^{-1}$, 2931, 1734, 1447, 1373, 1181, 1096, 1031, 860. − $^1$H NMR (200 MHz): δ = 4.14 (q, $J$ = 6.3 Hz, $CO_2CH_2CH_3$), 4.12 (q, $J$ = 6.3 Hz, $CO_2CH_2CH_3$), 3.64 (dm, $J_{8,9}$ = 7.2 Hz, 8-H), 3.31 (q, $J$ = 7.5 Hz, 9-H), 2.66 (brs, 10-H), 2.59 (m, 2-H), 2.18 [m, 5(6)-H], 1.95 (m, 2′-H), 1.50−1.85 [m, 5(6)-H], 1.63 (brs, 3-$CH_3$, 4-$CH_3$), 1.19 (t, $J$ = 6.3 Hz, $CO_2CH_2CH_3$), 1.18 (t, $J$ = 6.3 Hz, $CO_2CH_2CH_3$). − $^{13}$C NMR (75.5 MHz): δ = [174.7 (s) and 174.1 (s), $CO_2$Et], [134.7 (s), 131.7 (s), 130.3 (s) and 129.5 (s), C-1, C-3, C-4 and C-7], [60.7 (t), 2 $CO_2CH_2CH_3$], [58.9 (d) and 43.7 (d), C-8 and C-9], [41.8 (t), 34.6 (t), 32.3 (t) and 25.8 (t), C-2, C-5, C-6 and C-10)], [21.4 (q) and 19.8 (q), 3-$CH_3$ and 4-$CH_3$], [14.4 (q) and 14.2 (q), $CO_2CH_2CH_3$]. − MS (EI), *m/z* (%): 306 (24) [$M^+$], 260 (40) [$M^+ - C_2H_6O$], 233 (30) [$M^+ - CO_2C_2H_5$], 232 (100) [$M^+ - C_3H_6O_2$], 178 (14), 159 (46). − MS (HR-EI): 306.1831 ($C_{18}H_{26}O_4$ calcd. 306.1831). − $C_{18}H_{26}O_4$ (306.4): calcd. C 70.56, H 8.55; found C 70.25, H 8.37.

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☆ Dedicated to Professor *Dieter Seebach* on the occasion of his 60th birthday.

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