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Carbon monoxide as a building block in organic synthesis. Part V. * Involvement of palladium-hydride species in carbonylation reactions of monoterpenes. X-ray crystal structure of $[Ph_3PCH_2CH{=}CHPh]_4[PdCl_6][SnCl_6]$

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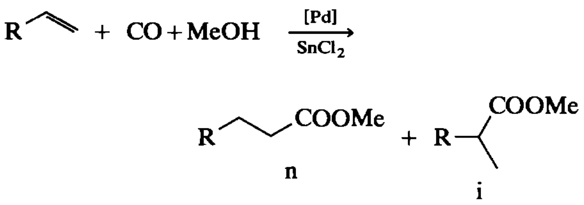
Abstract

A palladium precursor and $SnCl_2$ as cocatalyst were used under 4 MPa of carbon monoxide for the catalytic alkoxycarbonylation of several monoterpenes into C_{11} esters. The active catalyst involves a palladium-hydride species whose formation was investigated. In the case of the model substrate 3-phenylpropene, the source of the hydrido ligand was determined to be the alkene itself. Allylic hydrogen abstraction seems to be a general way to produce the active hydridopalladium species since monoterpenes having labile allylic hydrogens were converted under exceptional mild conditions. An X-ray crystal structure analysis was carried out on $[(Ph_3PCH_2CH{=}CHPh)_4(PdCl_6)(SnCl_6)]$.

Key words: Palladium; X-ray structure; Terpenes; Carbonylation; Hydroesterification

1. Introduction

The alkoxycarbonylation of alkenes which affords the corresponding esters with one more carbon atom is an elegant synthesis, provided that efficient and selective catalysis can be achieved. Previous studies show that nickel, cobalt, palladium, and platinum precursors [1–3] can conveniently be used to catalyze this reaction. However the best performances are achieved with palladium complexes. In particular, Knifton [4] has discovered that addition of tin chloride induces high selectivity for the formation of the linear ester according to eqn. (1).



(1)

This reaction, carried out on terminal alkenes, requires CO pressures up to 24 MPa. In an independent experiment a species was isolated to which the structure $[PdH(SnCl_3)(PPh_3)_2]$ was assigned from elemental analysis and a ν(Pd–H) band at 2040 cm^{-1} [4]. A catalytic pathway based on a palladium-hydride active

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* For Part IV, see ref. 1.

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species was proposed. Toniolo et al. [5] studied in detail this reaction with propene. Although significant quantities of black palladium were formed, they isolated two complexes, $[PdCl(COOMe)(PPh_3)_2]$ and $[PdCl(COPr)(PPh_3)_2]$. A careful analysis led these authors to conclude that a palladium-hydride species is involved and that a Pd–COOMe species does not occur in the catalytic cycle [6]. However, the origin of the Pd–H complex remains an open question, even though the alcohol could be the source of the hydride.

Recent results [7] on the preparation of lactones by cyclocarbonylation of unsaturated alcohols catalyzed by palladium(0) compounds support this hypothesis. The authors consider an oxidative addition of the alcohol function to palladium(0) in the proposed catalytic cycle to afford the active Pd-hydride species.

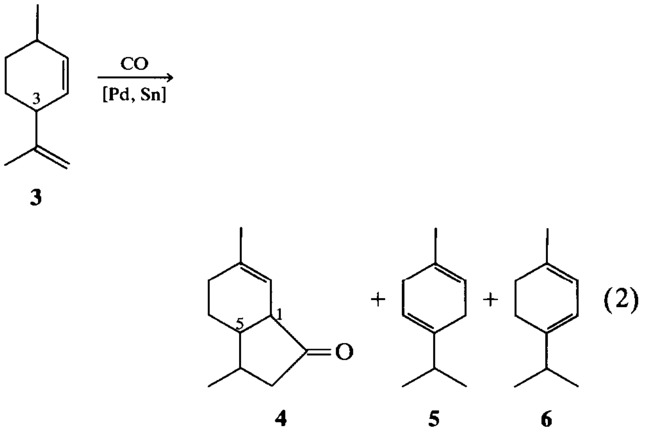
We have adapted Knifton's catalytic system to transform various natural alkenes, especially monoterpenes, at significantly lower pressures (4 MPa) [8]. We focussed particularly on the mechanism of carbonylation. Several monoterpenes have been used in the absence of alcohol in order to investigate the role of the substrate in the formation of the first palladium species. In addition, using 3-phenylpropene, we obtained an abundance of a crystalline material. An X-ray crystal structure determination revealed the presence of unexpected palladium(IV) and tin(IV) anions associated with phosphonium cations. Analysis of the origin of this complex showed that the active palladium-hydride species stems from allylic hydrogen abstraction from 3-phenylpropene and not from alcohol. Generalization of such hydride formation was investigated.

2. Results and discussion

Previous results on limonene, isopulegol and isopulegylacetate showed that $[PdCl_2(PPh_3)_2]$ in the presence of 2.5 equiv of $SnCl_2$ and 2 equiv of triphenylphosphine led to high yields of carbonylated products [9]. In particular isopulegol (**1**) gave the corresponding δ-valerolactone **2** regardless of whether or not methanol was present.

El Ali and Alper [7] obtained 4,4-dimethyl-γ-butyrolactone in the presence of palladium(0) phosphine precursors by carbonylation of 2-methyl-3-buten-2-ol at 4 MPa. For instance, $[Pd(PPh_3)_4]$ gave 25% yield. In our case, carbonylation of isopulegol, carried out at 4 MPa with $[Pd(PPh_3)_4]$ was not successful and abundant black palladium resulted. The same absence of reactivity was noted for a run with limonene (**7**) and methanol. Thus, we concluded that the mechanism proposed by El Ali and Alper [7] cannot be transposed to this case and that oxidative addition of the alcohol group (isopulegol or methanol), if it occurs, does not provide a stable hydride species.

Our present work therefore shows that catalytic activity results only from the simultaneous use of a palladium(II) complex, $[PdCl_2(PPh_3)_2]$, and tin(II) as anhydrous $SnCl_2$. In order to rule out the effects due to an alcohol, *trans*-isolimonene (**3**) was carbonylated in toluene at a constant CO pressure of 4 MPa at 100°C. After 16 h around 75% of the substrate was transformed and 56% of the cyclopentanone (**4**) was obtained, together with 19% of the isomerized starting material (eqn. 2.)

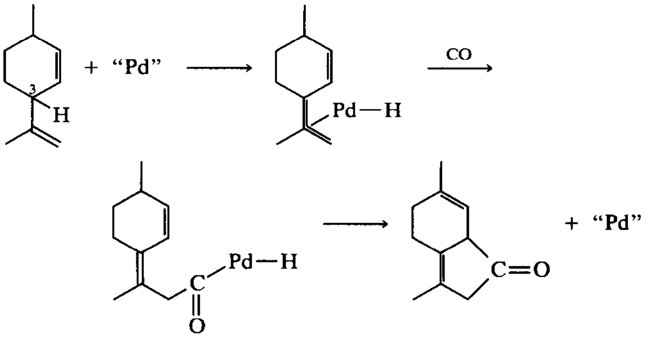


3

4 **5** **6**

(2)

The isomerization of **3** into α- and γ-terpinene, **5** or **6** or other isomers indicates a series of allylic cleavages giving rise to allylpalladium-hydride species. In **3** the first allylic activation should occur on C3 carbon (the terpene nomenclature has been adopted here) to produce an allylpalladium complex which has not been detected. Carbonylation of this allyl fragment followed by a reductive elimination step should produce a cyclopentenone compound and not the cyclopentanone (**4**) as was unambiguously confirmed by GC/MS and NMR spectroscopy.



We conclude that this allylic ligand needs to be eliminated in order to generate a palladium hydride complex, which is presumably $[PdH(SnCl_3)(CO)(PPh_3)_2]$. However, this complex is of low stability. Indeed, a solution collected after catalysis shows no ν(Pd–H) band in the IR. When saturated with carbon monoxide, this solution shows a ν(CO) band at 2054

cm^{-1}. This frequency was assigned by Kingston and Scollary [10] to $[Pd(CO)(SnCl_3)_2Cl]^-$. These observations lead us to propose that the species collected after catalysis could be $[PdCl(SnCl_3)(CO)(PPh_3)_2]$. All attempts to detect a hydride signal in the ^1H NMR spectrum failed.

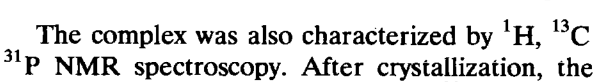
2.1. X-ray crystal structure of $[Ph_3PCH_2CH{=}CHPh]_4$-$[PdCl_6][SnCl_6]$

All the solutions obtained after catalysis contained a suspension of black material, mainly palladium, corresponding to *ca.* 5–10% of the palladium introduced. After sedimentation, the solutions were filtered out. Except for a few crystals identified by ^{31}P NMR spectroscopy and X-ray analysis as $[PdCl_2(PPh_3)_2]$, we obtained only a red crystalline material after carbonylation of 3-phenylpropene, which was the model compound to determine the best catalytic conditions to transform allyl- or propenyl-benzenes [8] and monoterpenes.

The title compound crystallizes in the *P*-1 triclinic space group. The centrosymmetric unit cell contains four $[Ph_3PCH_2CH{=}CHPh]^+$ phosphonium cations, one $[SnCl_6]^{2-}$ anion and one $[PdCl_6]^{2-}$ anion. The ORTEP view (Fig. 1) shows the two phosphonium groups and the two half anions (if we except the Cl* labelled atoms) which constitute the asymmetric unit. The Cl* labelled atoms have been added to show better the tin and palladium environments. The Sn^{IV} and Pd^{IV} atoms are both located on inversion centres (special positions 0, 0, 0 and 0, 1/2, 1/2, respectively, with octahedral environments of chlorine atoms). In both anions the chlorine atoms (those labelled Cl*) are related by inversion through the central metal atom. In the phosphonium cations, the phosphorus atoms are in regular tetrahedral environments of carbon atoms. The C–P–C angles values are between 106.9(3) and 111.8(3)°, and compare quite well with those determined in $[PPh_4]^+$ (107.2(3), 110.6(1) and 110.6(1) [11] and in $[PPh_3Et]^+$ (between 108.3(6) and 110.5(6)) [12].

The four P–C distances appear to be quite normal and are 1.784(5), 1.787(5) and 1.792(5) for the phenyl groups and 1.809(5) Å for the phenylpropenyl group. They compare to the P–C distance of 1.805(4) published for $[PPh_4]^+$ [11] and 1.789(13), 1.795(12), 1.805(13) and 1.819(14) Å found in $[Ph_3PEt]^+$ [12], the last distance being due to the phosphorus–ethyl bond. The tin–chlorine and palladium–chlorine bonds have the same length and range between 2.404(1) and 2.433(2) Å. They compare with those found in $[NH_2(CH_3)_2][SnCl_6]$ (2.437(1) and 2.450(1) Å) [13] and in $[NH_4]_2[PdCl_6]$ (2.300 Å) [14].

The molecular structure (Fig. 1) shows that the starting palladium(II) and tin(II) atoms have been oxidized to the IV oxidation state, although the reaction medium, which contains carbon monoxide, methanol and 3-phenylpropene, is reducing. More surprisingly, the structure reveals that a carbon–carbon double bond has been maintained on the phenylpropenyl group of the phosphonium salt, so that the alkene has been also oxidized. As previously indicated, some black palladium was always found in catalytic runs, where all the reagents were free of air and the solutions were transferred to a Schlenk tube under a 0.5 MPa residual CO pressure. Thus a redox reaction has taken place in the reaction medium to produce palladium(0) and palladium(IV) and tin(IV) from Pd^{II} and Sn^{II}. Moreover, the formation of the phosphonium salt can be considered as resulting from the coupling of triphenylphosphine and a cinnamyl cation. Thus a hydride was lost by the substrate and transferred to the palladium(II) complex, generating the active palladium-hydride species. It has already been reported [15] that an aryl or a vinyl ligand can be coupled with triphenylphosphine on palladium or rhodium to afford a phosphonium salt. In the presence of $SnCl_2$ (hydrated or not), the starting material will form the complex $[PdCl(SnCl_3)(PPh_3)_2]$ by analogy with the known isolated platinum complex [16]. Equation (3) summarizes the formation of phosphonium chloride. Such allylic phosphonium cations have been reported previously [17].



(3)

The complex was also characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy. After crystallization, the supernatant solution was shown by ^{31}P NMR spectroscopy to contain small amounts of the phosphonium salt, $[PdCl_2(PPh_3)_2]$, and $[Pd(CO)(PPh_3)_3]$, and traces of other unidentified species. The palladium-hydride complex was not detected under our conditions. This absence is not surprising since $[PdHCl(PPh_3)_2]$ has been prepared previously by addition of HCl to $[Pd(CO)(PPh_3)_3]$ at −50°C and was described as being only moderately stable at room temperature [18]. All these observations are consistent with the general equation (4):

$$
\begin{aligned}
&7[PdCl(SnCl_3)(PPh_3)_2] + 4\,PhCH_2CH{=}CH_2 \\
&\qquad + 4\,PPh_3CO \\
&[(PhCH{=}CHCH_2PPh_3)_4][PdCl_6][SnCl_6] \\
&\qquad + 4[PdH(SnCl_3)(PPh_3)_2] + 2[Pd(CO)(PPh_3)_3] \\
&\qquad + 2\,SnCl_2 \qquad (4)
\end{aligned}
$$

We have checked that under the same experimental conditions [Pd(PPh$_3$)$_4$] did not induce any carbonylation of 3-phenylpropene. We have also introduced the palladium(IV) precursor Na$_2$[PdCl$_6$] in the presence of tetraphenylphosphonium chloride and SnCl$_4$. Two salient features distinguish this system from the previous one: a modest yield of ester was obtained (25% instead of 75%) and large amounts of isomerized alkene were detected. Although palladium(IV) is very easily reduced to palladium(II), this system contributed to the catalysis only at a low level since usually only 4–5% isomerizations are observed.

From this X-ray molecular structure, we conclude that a small part of the substrate 3-phenylpropene is sacrificed as the source of a palladium-hydride species. This occurs through an allylic hydrogen abstraction.

To explore the generality of this catalytic reaction and the validity of our hypothesis, several monoterpenes with easily cleaved C–H allylic bonds were selected.

2.2. *Methoxycarbonylation of limonene, carvone, dihydrocarvone and pulegone*

As shown in Table 1, limonene **7**, carvone, **11**, dihydrocarvone, **14**, and pulegone, **18** were transformed into the corresponding esters **8**, **12**, **15**, **19** in high yield and good selectivity. By-products result from the formal addition of methanol to the C–C double bond, but they represent a maximum yield of 15% (compounds **9**, **13**, **16**).

In two cases some isomerization of the substrate occurred (not greater than 10%) by migration of the

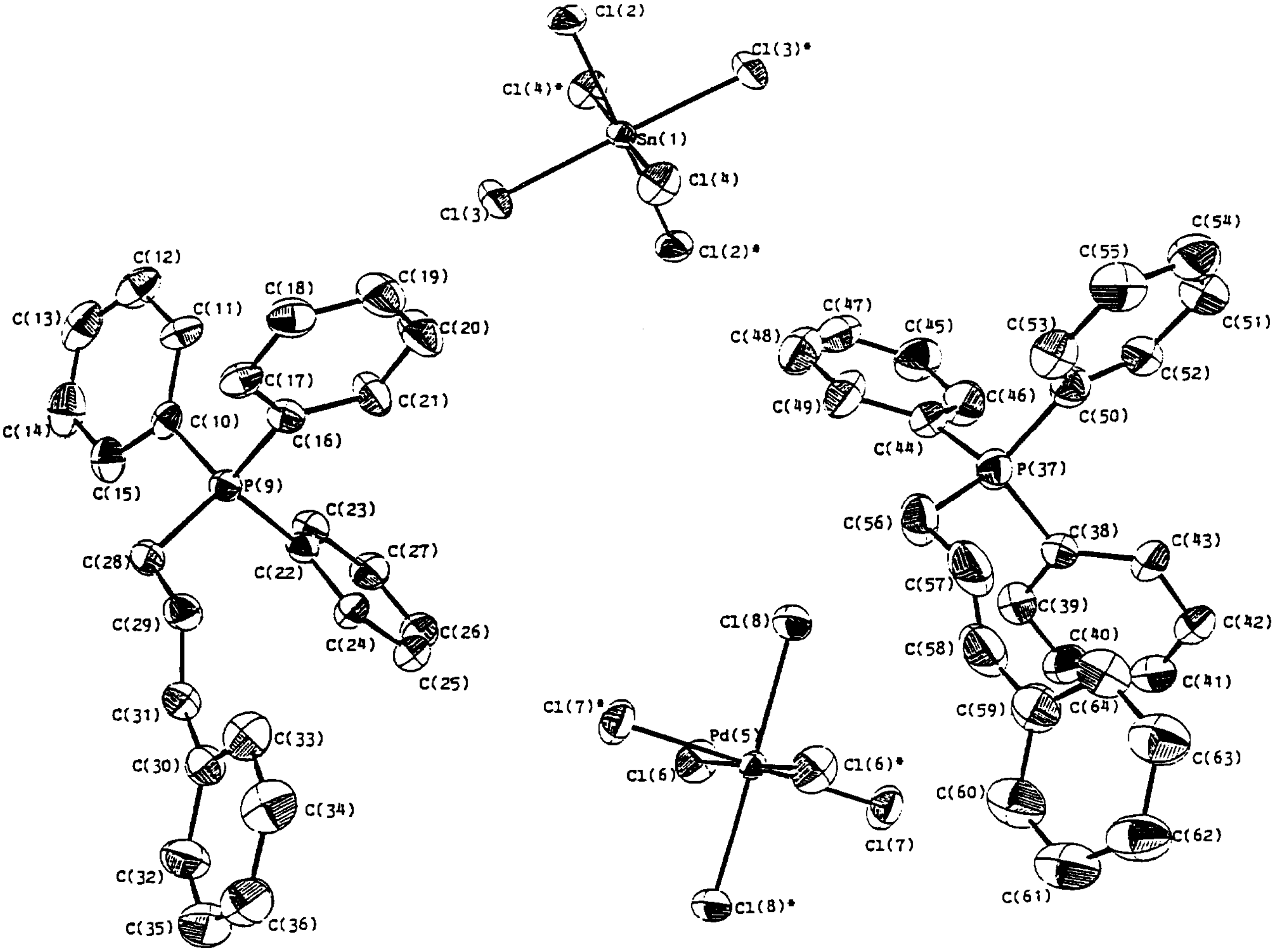
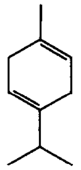


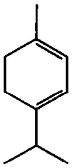
Fig. 1. Perspective ORTEP drawing of [Ph$_3$PCH$_2$CH=CHPh)$_4$(PdCl$_6$)(SnCl$_6$)] showing 50% thermal ellipsoids for non-hydrogen atoms. For more clarity, only two phosphonium groups have been represented as well as the complete coordination spheres for palladium and tin (chlorine atoms with stars). Bond lengths (Å) of interest are: Sn (1)–Cl (2), 2.432(1); Sn (1)–Cl (3), 2.412(1) and Sn (1)–Cl (4), 2.404(1); Pd (5)–Cl (6), 2.433(2); Pd (5)–Cl (7), 2.404(2) and Pd (5)–Cl (8), 2.421(2); P (9)–C (10), 1.784(5); P (9)–C (28), 1.809(5); C (29)–C (31), 1.292(7). The Sn^{IV} and Pd^{IV} atoms are in octahedral environments and the P atom is tetrahedral.

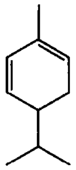
carbon–carbon double bond. Characterization of these isomerized compounds, **10** and **17** is based on their mass spectrometry fragmentations and confirmed by ^{13}C NMR spectroscopy. All the substrates have a 2-substituted propenyl structure and a cyclohexyl or cyclohexenyl framework where an allylic hydrogen atom is bonded to the carbon atom attached to the propenyl group. Thus the alkene provides the hydrogen atom necessary to generate the palladium hydride. In addition, the external C–C double bond is accessible for coordination to the palladium, so high conversion rates have been achieved.

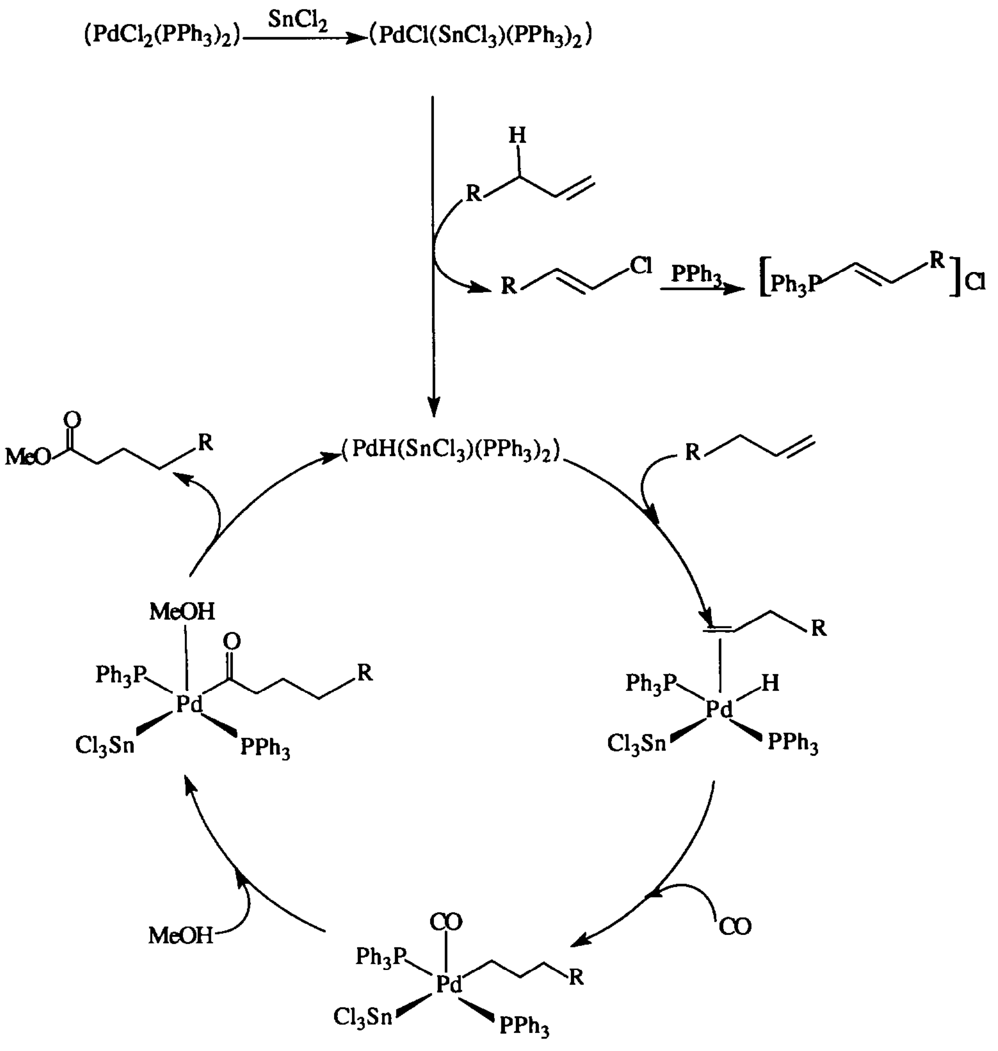
2.3. Attempted carbonylation of α- or γ-terpinene and α-phellandrene

These three terpenes, **20–22**, were tested in the alkoxycarbonylation reaction, because there is no external carbon–carbon double bond. Two internal C–C bonds give reduced access to coordination to palladium since steric hindrance is reinforced by the methyl and isopropyl substituents in the 1 and 4 positions (**20** and **21**) or in the 2 and 5 positions (**22**). Thus C–H allylic abstraction should be difficult. Under the experimental conditions used for the monoterpenes, the three substrates do not react at all and were recovered unchanged after 16 h.


α-terpinene (**20**)


γ-terpinene (**21**)


α-phellandrene (**22**)

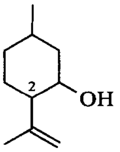
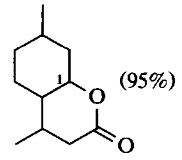
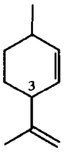
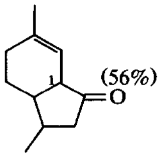
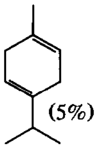
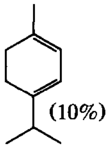
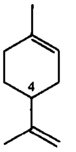
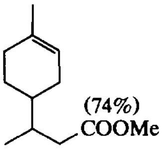
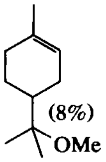
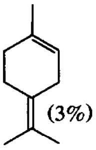
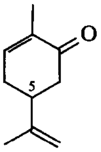
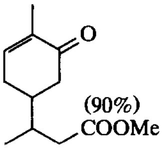
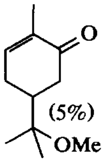
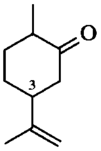
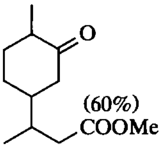
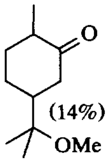
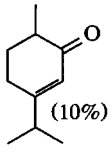
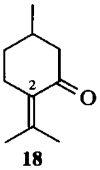
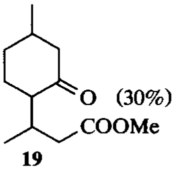


Scheme 1.

2.4. Catalytic cycle

Recently, several platinum complexes containing the $SnCl_3$ ligand have been isolated and characterized, including $[PtH(SnCl_3)(PPh_3)_2]$, $[Pt(SnCl_3)(alkyl)(PPh_3)_2]$, $[PtH(SnCl_3)(CO)(PPh_3)_2]$, and $[Pt(SnCl_3)(acyl)(PPh_3)_2]$ [19]. As previously proposed by Knifton and Toniolo [4,6], we consider that the active species is the 16-electron complex $[PdH(SnCl_3)(PPh_3)_2]$ as shown in Scheme 1, resulting from the C–H allylic abstraction from for instance, the C4 atom of limonene, followed by the elimination of the corresponding chloroalkene, presumably assisted by triphenylphosphine. As soon as this hydrido-palladium species is formed, coordination of the alkene can occur. By the classical succession of

TABLE 1. Carbonylation of monoterpenes [a]

Alkene	Name (method)	Product (yield) [b]	By-product (yield) [b]
 **1**	isopulegol (A) or (B)	 (95%) **2** (4 diastereoisomers)	
 **3**	*trans*-isolimonene (B)	 (56%) **4** (2 diastereoisomers)	 (5%) **5**  (10%) **6**
 **7**	limonene (A)	 (74%) **8**	 (8%) **9**  (3%) **10**
 **11**	carvone (A)	 (90%) **12**	 (5%) **13**
 **14**	dihydrocarvone (A)	 (60%) **15**	 (14%) **16**  (10%) **17**
 **18**	pulegone (A)	 (30%) **19**	

[a] Run conditions. Method A: alkene, 100 mmol; $[PdCl_2(PPh_3)_2]$, 1 mmol; $SnCl_2$, 2.5 mmol; PPh_3, 2 mmol; MeOH, 100 mmol; toluene, 25 ml; CO, 4 MPa; 16 h. Method B: identical to method A but with no methanol. [b] Determined by GPC after catalytic runs.

hydride transfer, CO insertion, an acyl intermediate is produced. In Scheme 1 a concerted mechanism is proposed wherein methanol is coordinated before releasing the ester and regenerating the palladium-active species.

Work is in progress to isolate intermediate complexes, particularly in the case of *trans*-isolimonene.

3. Conclusion

Palladium can abstract an allylic hydrogen atom from the substrate to produce the active hydrido-palladium species which is involved in the catalytic alkoxycarbonylation reaction of monoterpenes. To the best of our knowledge, this has not yet been proposed in the literature. This new route allowed us to prepare new products such as **2**, **4**, **8**, **12**, **15** and **19** quite easily.

4. Experimental section

4.1. Chemicals

Olefins were purchased from Aldrich (**1** and **7**), Fluka (**3**, **11** and **18**), Janssen (**14**) and Prolabo (**13**). Reagents and solvents were of commercial grade and used as received. The palladium complexes [$PdCl_2(PPh_3)_2$] and [$Pd(PPh_3)_4$] were prepared according to the literature [20]. Anhydrous tin(II) chloride was used without further purification.

4.2. General procedure for alkoxycarbonylation of alkenes

Method A: 0.7019 g (1 mmol) of dichlorobis(triphenylphosphine)palladium(II) 0.474 g (2.5 mmol) of tin(II) chloride and 0.524 g (2 mmol) of triphenylphosphine were added to a dinitrogen-saturated mixture of olefin (100 mmol), 3.2 g (100 mmol) methanol and 25 ml toluene. Method B: 0.7019 g (1 mmol) of dichlorobis (triphenylphosphine)palladium(II) 0.474 g (2.5 mmol) of tin(II) chloride and 0.524 g (2 mmol) of triphenylphosphine were added to a dinitrogen-saturated mixture of olefin (100 mmol) in 25 ml toluene.

In each case, the mixture was stirred for 5 min in order partially to dissolve the solid catalyst and was then introduced into a stainless steel autoclave previously purged with dinitrogen and then evacuated. The autoclave was heated to 97°C under 4 MPa of carbon monoxide at constant pressure. After 16 h, the autoclave was cooled and then slowly depressurized. Some metallic black palladium was deposited on the autoclave inner surface. The greenish-yellow reaction mixture was submitted to quantitative GPC analysis. Gas phase chromatographic analyses were performed on a Carlo Erba MFC 500 apparatus equipped with a 30 m × 0.5 mm macrobore column fitted with Carbowax 20M stationary phase and flame ionization detector.

Identification of the reaction products was checked by GC/MS on a Hewlett Packard apparatus MSD 5890/5970.

Palladium complexes were separated from the crude solution by addition of 200 ml of pentane and decantation of the deeply coloured oily layer. After concentration by rotary evaporation, esters were purified by distillation under vacuum with a spinning band column BR24T (column: 8 mm bore × 24″ height; band: PTFE, 5500 rpm).

Terpenoid products exist as several diastereoisomers which could sometimes be separated: crystalline lactone **2** obtained by carbonylation of isopulegol was recrystallized from heptane and isolated with more than 99% purity. Other products were regioisomerically pure. All pure compounds were analyzed by NMR spectroscopy (Bruker AC 200 for ^1H and WM 250 for ^{13}C), IR (IRFT Perkin-Elmer 1710) and elemental analysis to confirm their structure.

4.3. X-ray analysis

0.3526 g (0.5 mmol) of dichlorobis(triphenylphosphine)palladium(II), 0.2382 g (1 mmol) of tin(II) chloride dihydrate and 0.2636 g (1 mmol) of triphenylphosphine were added to a nitrogen-saturated mixture of 5.97 g (50 mmol) 3-phenylpropene, 4 ml methanol and 40 ml toluene. The mixture was stirred for 5 min and introduced into a stainless-steel autoclave to perform the carbonylation as previously described (method A). After reaction, a small quantity of claret coloured viscous oil was found in addition to the usual yellow-green solution. GPC analysis of the light phase gave the following composition: 47% methyl 4-phenylbutanoate, 22% methyl 2-methyl-3-phenyl-propanoate, 5% 2-phenyl-butanoate, 17% 1-phenyl-propene and some free triphenylphosphine in methanol-toluene solvent. The heavy oil was collected by diluting it with acetone and was allowed to stand for several months under a nitrogen atmosphere. Claret-coloured crystals slowly grew along with a few yellow crystals, identified as [$PdCl_2(PPh_3)_2$]. The yield of isolated product was 40%.

4.4. Crystal data

Intensity data were collected at room temperature on a Nonius CAD4 diffractometer using Mo $K\alpha$ radiation. The accurate cell dimensions and orientation matrix were obtained from least squares refinements of the setting angles of 25 well-defined reflections. No decay of the intensities of two standard reflections was observed during the course of data collection. The usual corrections for Lorentz and polarization effects were applied. An empirical absorption correction (DIFABS) [21] was applied. Computations were performed with the program CRYSTAL [22] adapted to a Microvax II computer. Scattering factors and corrections for anomalous dispersion were from reference [23]. The structure was resolved by direct method (SHELXS) [24] and refined by least squares with anisotropic thermal parameters for all non hydrogen atoms. Hydrogen atoms were located on a Fourier difference map and their coordinates were refined with an overall u[iso] thermal parameter. Of 7033 observed reflections, 4746 with $I > 3\sigma(I)$ were used to refine the structure to $R = 0.033$ and $R_w = 0.035$. More details of crystal data and data collection parameters are in Table 2. Selected bond lengths and angles and other data are listed in Tables 3–5. Full data have been deposited with the Cambridge Crystallographic Data Centre.

4.5. *Experiments with [Pd(PPh$_3$)$_4$] and with Na$_2$[PdCl$_6$], SnCl$_4$, Ph$_4$PCl*

1.1556 g (1 mmol) of tetrakis(triphenylphosphine) palladium was added to a dinitrogen-saturated mixture of 13.62 g (100 mmol) limonene, 3.2 g (100 mmol) methanol and 25 ml toluene. The usual procedure (*vide supra*) was followed and a colourless solution was collected at the end of the run with an extensive black deposit of palladium on the autoclave inner surface. The reaction mixture contained only starting limonene and triphenylphosphine in the methanol–toluene solution, as determined by GPC.

TABLE 3. Selected bond lengths (A) and bond angles (deg): [$(Ph_3PCH_2CH{=}CHPh)_2$, 1/2 ($PdCl_6$) 1/2 ($SnCl_6$)].

Sn(1)–Cl(2)	2.432(1)	Pd(5)–Cl(6)	2.433(2)
Sn(1)–Cl(3)	2.412(1)	Pd(5)–Cl(7)	2.404(2)
Sn(1)–Cl(4)	2.404(1)	Pd(5)–Cl(8)	2.421(2)
P(9)–C(10)	1.784(5)	P(9)–C(16)	1.787(5)
P(9)–C(22)	1.792(5)	P(9)–C(28)	1.809(5)
C(28)–C(29)	1.494(8)	C(29)–C(31)	1.292(7)
C(30)–C(31)	1.469(6)	P(37)–C(38)	1.791(6)
P(37)–C(44)	1.786(6)	P(37)–C(50)	1.800(6)
P(37)–C(56)	1.816(7)	C(56)–C(57)	1.542(9)
C(57)–C(58)	1.222(9)	C(58)–C(59)	1.53(1)
Cl(3)–Sn(1)–Cl(2)	89.94(5)	Cl(7)–Pd(5)–Cl(6)	89.86(6)
Cl(4)–Sn(1)–Cl(2)	89.94(6)	Cl(8)–Pd(5)–Cl(6)	89.89(7)
Cl(4)–Sn(1)–Cl(3)	89.91(6)	Cl(8)–Pd(5)–Cl(7)	89.16(6)
C(16)–P(9)–C(10)	109.3(3)	C(22)–P(9)–C(10)	110.1(2)
C(22)–P(9)–C(16)	107.2(2)	C(28)–P(9)–C(10)	106.9(3)
C(28)–P(9)–C(16)	111.8(3)	C(28)–P(9)–C(22)	111.5(2)
C(29)–C(28)–P(9)	116.3(4)	C(31)–C(29)–C(28)	123.7(6)
C(44)–P(37)–C(38)	109.6(3)	C(50)–P(37)–C(38)	108.9(3)
C(50)–P(37)–C(44)	109.5(3)	C(56)–P(37)–C(38)	109.8(3)
C(56)–P(37)–C(44)	108.1(3)	C(56)–P(37)–C(50)	111.0(3)
C(39)–C(38)–P(37)	119.0(5)	C(57)–C(56)–P(37)	113.0(5)
C(58)–C(57)–C(56)	119.1(8)	C(59)–C(58)–C(57)	122.1(8)

TABLE 2. Crystallographic data

Chemical formula	$C_{54}H_{48}P_2Pd_{1/2}Sn_{1/2}Cl_6$
fw	1084.2
Crystal system	triclinic
Space group	$P1$
Z	2
a, Å	10.792(2)
b, Å	14.739(2)
c, Å	17.084(2)
α, deg	91.33(1)
β, deg	99.75(1)
γ, deg	108.33(1)
V, Å^3	2535(11)
F(000)	1104
(calcd), g.cm^{-3}	1.42
(Mo Kα) cm^{-1}	8.47
Cryst. size, mm	0.18×0.20×0.34
Diffractometer	CAD4
Monochromator	graphite
Radiation	Mo Kα (0.71070)
Temperature°C	20
Scan type	$\omega/2\theta$
Scan range θ, deg	$1.0 + 0.345 \tan\theta$
2θ range, deg	2–46
Reflctn collected	7033
Reflctn used (criteria)	4746 ($I > 3\sigma(I)$)
Computing program	CRYSTALS
R	0.0331
R_w *	0.0352
Absorption correction	min. 0.877 max. 1.116
Weighting scheme	unit weights
rms (shift/e.s.d) (last ref.)	0.26
1.s parameters	724
Residual electron density, e Å^{-3}	0.75

* $R_w = [\Sigma_i W_i(F_o - F_c)^2 \Sigma_i W_i F_o^2]^{1/2}$

0.3651 g (1 mmol) of disodium hexachloropalladate, 0.2605 g (1 mmol) of tin tetrachloride and 1.50 g (4 mmol) of tetraphenylphosphonium chloride were added to a dinitrogen-saturated mixture of 13.62 g (100 mmol) of limonene, 3.2 g (100 mmol) methanol and 25 ml toluene. The usual procedure (*vide supra*) was followed and a dark solution was collected at the end of the run. The reaction mixture was washed with aqueous $NaHCO_3$. After the usual work-up, GPC analysis gave the following composition: terpinolene (**10**) 40%, ester (**8**) 25%, α-terpinyl-methyl-ether (**9**) 12%, limonene (**7**) 8% and several other unidentified products.

4.6. *Spectroscopic data*

4.6.1. *(1R, 5S, 6S, 9R)-5,9-[dimethyl-2-oxabicyclo-[4.4.0]decan-3-one] (2a)*

Bp: 130°C (1 kPa); mp: 39.3°C; mass spectrum m/e 182 (M+), 81 (main peak); IR (neat) 1731 cm^{-1} (C=O); ^{13}C NMR (62.5 MHz, $CDCl_3$, δ) 171.4 (s, C_3), 77.9 (d, C_1), 41.9 (d, C_6), 40.9 (t, C_{10}), 38.9 (t, C_4), 34.0 (t, C_8), 30.9 (d, C_9), 28.9 (d, C_5), 27.3 (t, C_7), 21.8 (q, C_{11}), 14.8 (q, C_{12}); elemental anal. Calcd. for $C_{11}H_{18}O_2$

TABLE 4. Fractional parameters for: [(Ph_3PCH_2CH=CHPh)]-[$SnCl_6$][$PdCl_6$]

	x	y	z	U_{eq}
Sn(1)	0.00000	0.00000	0.00000	0.0387
Cl(2)	0.1584(2)	0.0055(1)	−0.0869(1)	0.0628
Cl(3)	−0.0505(2)	0.1328(1)	−0.0618(1)	0.0643
Cl(4)	0.1732(2)	0.1105(1)	0.0964(1)	0.0695
Pd(5)	0.00000	0.50000	0.50000	0.0358
Cl(6)	−0.2306(2)	0.4423(1)	0.4318(1)	0.0784
Cl(7)	−0.0637(2)	0.4204(1)	0.61521(9)	0.0749
Cl(8)	0.0338(2)	0.3581(1)	0.4462(1)	0.0768
P(9)	0.3330(1)	0.7475(1)	0.01666(8)	0.0413
C(10)	0.2551(5)	0.7035(4)	−0.0837(3)	0.0455
C(11)	0.2864(6)	0.6320(4)	−0.1214(3)	0.0581
C(12)	0.2235(7)	0.5973(5)	−0.1982(4)	0.0715
C(13)	0.1337(8)	0.6359(6)	−0.2374(4)	0.0801
C(14)	0.1029(7)	0.7068(6)	−0.2015(4)	0.0831
C(15)	0.1639(6)	0.7426(5)	−0.1235(4)	0.0688
C(16)	0.4697(5)	0.7042(4)	0.0454(3)	0.0442
C(17)	0.5914(5)	0.7519(4)	0.0238(3)	0.0502
C(18)	0.6935(6)	0.7141(5)	0.0431(4)	0.0645
C(19)	0.6761(7)	0.6335(5)	0.0823(5)	0.0754
C(20)	0.5564(7)	0.5867(5)	0.1024(5)	0.0781
C(21)	0.4534(6)	0.6225(4)	0.0850(4)	0.0630
C(22)	0.2187(5)	0.7030(4)	0.0825(3)	0.0434
C(23)	0.0972(5)	0.6338(4)	0.0535(3)	0.0513
C(24)	0.2543(6)	0.7350(4)	0.1619(3)	0.0563
C(25)	0.0468(6)	0.6284(5)	0.1846(4)	0.0626
C(26)	0.1676(7)	0.6985(5)	0.2131(4)	0.0656
C(27)	0.0123(6)	0.5971(4)	0.1061(4)	0.0636
C(28)	0.3859(6)	0.8770(4)	0.0198(3)	0.0538
C(29)	0.4742(6)	0.9299(4)	0.0948(4)	0.0546
C(30)	0.5295(6)	1.0519(4)	0.2087(4)	0.0605
C(31)	0.4438(6)	0.9884(4)	0.1396(4)	0.0604
C(32)	0.4855(7)	1.1204(5)	0.2418(4)	0.0795
C(33)	0.6534(7)	1.0477(5)	0.2429(4)	0.0724
C(34)	0.7311(7)	1.1109(6)	0.3065(4)	0.0815
C(35)	0.5630(8)	1.1827(5)	0.3042(5)	0.0864
C(36)	0.6863(8)	1.1788(5)	0.3375(4)	0.0836
P(37)	0.3561(2)	0.2353(1)	0.5350(1)	0.0623
C(38)	0.2722(6)	0.2224(4)	0.6180(3)	0.0597
C(39)	0.1508(7)	0.2382(5)	0.6093(4)	0.0780
C(40)	0.0845(8)	0.2294(6)	0.6729(4)	0.0838
C(41)	0.1366(8)	0.2044(6)	0.7438(4)	0.0844
C(42)	0.2577(9)	0.1930(6)	0.7525(4)	0.0837
C(43)	0.3275(8)	0.2013(6)	0.6909(4)	0.0779
C(44)	0.2407(6)	0.1767(5)	0.4469(3)	0.0629
C(45)	0.0625(8)	0.0399(6)	0.3796(5)	0.0912
C(46)	0.1442(8)	0.0896(5)	0.4495(4)	0.0833
C(47)	0.0770(8)	0.0784(7)	0.3086(4)	0.0835
C(48)	0.1676(8)	0.1661(7)	0.3057(4)	0.0922
C(49)	0.2505(8)	0.2153(6)	0.3745(4)	0.0853
C(50)	0.4852(6)	0.1813(4)	0.5543(3)	0.0620
C(51)	0.5548(8)	0.0501(5)	0.5979(5)	0.0879
C(52)	0.4571(7)	0.0921(5)	0.5822(4)	0.0752
C(53)	0.6115(7)	0.2284(5)	0.5393(4)	0.0752
C(54)	0.6798(8)	0.0967(6)	0.5850(5)	0.0894
C(55)	0.7080(7)	0.1849(6)	0.5547(5)	0.0864
C(56)	0.4244(8)	0.3615(5)	0.5196(4)	0.0802
C(57)	0.5296(9)	0.4194(6)	0.5910(5)	0.1041
C(58)	0.4966(9)	0.4649(6)	0.6397(5)	0.1063
C(59)	0.5960(9)	0.5254(5)	0.7114(4)	0.0829
C(60)	0.5500(8)	0.5919(5)	0.7455(5)	0.0882
C(61)	0.6264(9)	0.6458(5)	0.8134(6)	0.0918
C(62)	0.7448(8)	0.6351(5)	0.8477(5)	0.0927
C(63)	0.7899(8)	0.5708(6)	0.8145(5)	0.0930
C(64)	0.7169(9)	0.5171(6)	0.7461(5)	0.0943

(mw = 182.26): C, 72.49; H, 9.95; O, 17.56. Found: C, 72.94; H, 10.00; O, 16.65%.

4.6.2. 5,9-[dimethyl-2-oxabicyclo[4.4.0]decan-3-one] (2b)

Bp: 120–125°C (1 kPa); mass spectrum *m/e* 182 (M^+), 81 (main peak); ^{13}C NMR (62.5 MHz, $CDCl_3$, δ) 171.3 (s, C_3), 82.4 (d, C_1), 45.0 (d, C_6), 40.4 (t, C_{10}), 38.1 (t, C_4), 33.7 (t, C_8), 31.8 (d, C_5), 30.9 (d, C_9), 27.8 (t, C_7), 21.7 (q, C_{11}), 19.0 (q, C_{12}).

4.6.3. 5,9-[dimethyl-2-oxabicyclo[4.4.0]decan-3-one] (2c)

Bp: 115–120°C (1 kPa); mass spectrum *m/e* 182 (M^+), 81 (main peak); ^{13}C NMR (62.5 MHz, $CDCl_3$, δ) 171.5 (s, C_3), 80.4 (d, C_1), 39.2 (t, C_{10}), 37.8 (d, C_6), 33.9 (t, C_4), 33.2 (t, C_8), 30.4 (d, C_9), 25.8 (d, C_5), 21.7 (q, C_{11}), 18.4 (t, C_7), 17.9 (q, C_{12}).

4.6.4. 5,9-[dimethyl-2-oxabicyclo[4.4.0]decan-3-one] (2d)

Bp: 110°C (1 kPa); mass spectrum *m/e* 182 (M^+), 81 (main peak); ^{13}C NMR (62.5 MHz, $CDCl_3$, δ) 173.3 (s, C_3), 74.7 (d, C_1), 40.7 (d, C_6), 38.1 (t, C_{10}), 35.4 (t, C_4), 33.7 (t, C_8), 31.4 (d, C_9), 27.9 (t, C_7), 25.8 (d, C_5), 21.7 (q, C_{11}) 21.6 (q, C_{12}).

4.6.5. Cis-4,8-[dimethyl-bicyclo [4.3.0] non-8 en-2-one] (4a)

Bp: 98°C (1 kPa); mass spectrum *m/e* 164 (M^+), 79 (main peak) IR (neat) 1740 cm^{-1} ν(C=O); ^{13}C NMR (62.5 MHz, $CDCl_3$, δ) 218.8 (s, C_2), 136.4 (t, C_8), 116.1 (d, C_9), 49.7 (d, C_1), 45.5 (s, C_3), 41.5 (s, C_3), 31.4 (d, C_4), 26.4 (t, C_7), 23.9 (q, C_{10}), 22.3 (t, C_6), 19.2 (q, C_{11}).

4.6.7. Trans-4,8-[dimethyl-bicyclo [4.3.0] non-8 en-2-one] (4b)

Bp: 105°C (1 kPa); mass spectrum *m/e* 164 (M^+), 79 (main peak) IR (neat) 1740 cm^{-1} (C=O); ^{13}C NMR (62.5 MHz, $CDCl_3$, δ) 219.1 (s, C_2), 136.6 (t, C_8), 116.3 (d, C_9), 52.5 (d, C_1), 42.3 (s, C_3), 38.5 (s, C_3), 31.8 (d, C_4), 29.3 (t, C_7), 23.5 (q, C_{10}), 20.1 (t, C_6), 15.4 (q, C_{11}).

TABLE 5. Anisotropic thermal parameters

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	0.0345(3)	0.0380(3)	0.0468(3)	0.0027(2)	0.0096(2)	0.0133(2)
Cl(2)	0.064(1)	0.072(1)	0.077(1)	0.0110(8)	0.0366(8)	0.0271(8)
Cl(3)	0.059(1)	0.063(1)	0.105(1)	0.0345(9)	0.0250(9)	0.0321(8)
Cl(4)	0.064(1)	0.070(1)	0.066(1)	−0.0093(8)	−0.0014(8)	0.0008(8)
Pd(5)	0.0417(3)	0.0371(3)	0.0281(3)	0.0019(2)	0.0028(3)	0.0113(3)
Cl(6)	0.058(1)	0.104(1)	0.073(1)	−0.002(1)	−0.0026(9)	0.019(1)
Cl(7)	0.104(1)	0.078(1)	0.0530(9)	0.0168(8)	0.0206(9)	0.017(1)
Cl(8)	0.124(2)	0.077(1)	0.062(1)	−0.0060(9)	−0.001(1)	0.056(1)
P(9)	0.0395(8)	0.0408(8)	0.0454(8)	0.0044(6)	0.0129(6)	0.0115(6)
C(10)	0.045(3)	0.047(3)	0.045(3)	0.008(3)	0.015(3)	0.003(3)
C(11)	0.058(4)	0.063(4)	0.058(4)	−0.010(3)	0.020(3)	0.011(3)
C(12)	0.075(5)	0.083(5)	0.062(4)	−0.016(4)	0.024(4)	0.004(4)
C(13)	0.096(6)	0.101(6)	0.047(4)	−0.005(4)	0.008(4)	−0.013(5)
C(14)	0.092(6)	0.093(6)	0.064(5)	0.009(4)	−0.016(4)	0.015(5)
C(15)	0.072(4)	0.068(4)	0.065(4)	0.009(3)	0.004(3)	0.022(4)
C(16)	0.035(3)	0.044(3)	0.059(3)	0.003(3)	0.015(3)	0.010(2)
C(17)	0.043(3)	0.055(4)	0.055(3)	0.000(3)	0.018(3)	0.010(3)
C(18)	0.046(4)	0.077(5)	0.079(4)	−0.002(4)	0.017(3)	0.018(3)
C(19)	0.066(5)	0.091(5)	0.112(6)	0.018(5)	0.022(4)	0.050(4)
C(20)	0.081(5)	0.089(5)	0.136(7)	0.056(5)	0.048(5)	0.054(4)
C(21)	0.056(4)	0.061(4)	0.107(5)	0.033(4)	0.033(4)	0.028(3)
C(22)	0.044(3)	0.042(3)	0.054(3)	0.008(3)	0.018(3)	0.017(3)
C(23)	0.043(3)	0.052(3)	0.064(4)	0.005(3)	0.019(3)	0.009(3)
C(24)	0.060(4)	0.066(4)	0.046(3)	0.006(3)	0.013(3)	0.021(3)
C(25)	0.065(4)	0.072(4)	0.071(4)	0.018(3)	0.035(4)	0.023(4)
C(26)	0.092(5)	0.078(5)	0.051(4)	0.010(3)	0.029(4)	0.036(4)
C(27)	0.052(4)	0.067(4)	0.085(5)	0.009(4)	0.030(4)	0.014(3)
C(28)	0.063(4)	0.045(3)	0.055(4)	0.005(3)	0.013(3)	0.016(3)
C(29)	0.056(4)	0.042(3)	0.071(4)	0.001(3)	0.019(3)	0.012(3)
C(30)	0.068(4)	0.049(4)	0.065(4)	0.006(3)	0.015(3)	0.014(3)
C(31)	0.061(4)	0.055(4)	0.069(4)	0.005(3)	0.015(3)	0.021(3)
C(32)	0.085(5)	0.073(5)	0.087(5)	−0.011(4)	−0.002(4)	0.033(4)
C(33)	0.066(4)	0.073(5)	0.079(5)	−0.003(4)	0.019(4)	0.018(4)
C(34)	0.055(4)	0.097(6)	0.092(5)	−0.003(4)	0.011(4)	0.010(4)
C(35)	0.104(6)	0.074(5)	0.089(5)	−0.016(4)	0.015(5)	0.029(5)
C(36)	0.088(6)	0.076(5)	0.080(5)	−0.012(4)	0.014(4)	−0.002(4)
P(37)	0.081(1)	0.054(1)	0.055(1)	0.0099(8)	0.0093(9)	0.0203(9)
C(38)	0.083(5)	0.056(4)	0.053(4)	0.003(3)	0.008(3)	0.033(3)
C(39)	0.097(6)	0.091(5)	0.065(4)	0.015(4)	0.006(4)	0.047(5)
C(40)	0.092(6)	0.133(7)	0.070(5)	0.003(5)	0.016(4)	0.068(5)
C(41)	0.111(6)	0.109(6)	0.067(5)	−0.004(4)	0.020(4)	0.059(5)
C(42)	0.147(8)	0.150(8)	0.044(4)	0.016(4)	0.023(4)	0.097(7)
C(43)	0.108(6)	0.136(7)	0.048(4)	0.006(4)	0.008(4)	0.077(5)
C(44)	0.074(4)	0.069(4)	0.054(4)	0.010(3)	0.017(3)	0.029(4)
C(45)	0.092(6)	0.096(6)	0.078(5)	−0.012(4)	−0.001(4)	0.014(5)
C(46)	0.103(6)	0.077(5)	0.068(5)	0.011(4)	0.015(4)	0.016(4)
C(47)	0.084(5)	0.147(8)	0.056(4)	−0.017(5)	0.000(4)	0.054(5)
C(48)	0.089(6)	0.0146(8)	0.059(5)	0.016(5)	0.011(4)	0.032(5)
C(49)	0.091(6)	0.111(6)	0.063(5)	0.015(4)	0.024(4)	0.022(5)
C(50)	0.068(4)	0.058(4)	0.058(4)	0.004(3)	0.010(3)	0.017(3)
C(51)	0.108(6)	0.083(5)	0.097(6)	0.022(4)	0.027(5)	0.049(5)
C(52)	0.090(5)	0.069(5)	0.082(5)	0.018(4)	0.031(4)	0.031(4)
C(53)	0.068(5)	0.065(4)	0.084(5)	0.005(4)	0.006(4)	0.004(4)
C(54)	0.090(6)	0.098(6)	0.093(6)	−0.009(5)	0.002(5)	0.046(5)
C(55)	0.055(4)	0.101(6)	0.107(6)	−0.012(5)	−0.001(4)	0.016(4)
C(56)	0.110(6)	0.060(4)	0.075(5)	0.011(4)	−0.004(4)	0.021(4)
C(57)	0.152(9)	0.090(6)	0.127(8)	0.053(6)	0.049(7)	0.058(6)
C(58)	0.157(9)	0.115(7)	0.138(8)	0.058(6)	0.069(7)	0.089(7)
C(59)	0.127(7)	0.048(4)	0.085(5)	0.002(4)	0.008(5)	0.016(5)
C(60)	0.087(6)	0.062(5)	0.131(7)	0.014(5)	0.035(5)	0.015(4)
C(61)	0.113(7)	0.071(5)	0.136(8)	0.000(5)	0.068(6)	0.026(5)
C(62)	0.099(6)	0.072(5)	0.111(7)	−0.014(5)	0.031(5)	0.010(5)
C(63)	0.088(6)	0.083(6)	0.118(7)	0.001(5)	0.026(5)	0.030(5)
C(64)	0.133(8)	0.086(6)	0.103(6)	−0.003(5)	0.023(6)	0.062(6)

4.6.8. Methyl 3-(4'-methyl-3'-cyclohexenyl)butanoate (8)

Bp: 107°C (1 kPa); mass spectrum m/e 196 (M^+), 122 [25*], 68 [26*], IR (neat) 1741 cm^{-1} (C=O); ^1H NMR (250 MHz, $CDCl_3$, δ ppm) 5.35 (s, 1H, $H_{2'}$), 3.65 (s, 3H, MeO), 2.40 (dd, $J = 14.6$, 5.0 Hz, 1H, H_{2a}), 2.11 (dd, $J = 14.6$, 2.4 Hz, 1/2H, H_{2b} first diastereoisomer), 2.08 (dd, $J = 14.6$, 2.4 Hz, 1/2 H, H_{2b} second diastereoisomer), 2.0–1.0 (m, 8H, H_3, $2H_{3'}$, $H_{4'}$, $3H_{5'}$, $2H_{6'}$), 1.62 (s, 3H, $Me_{7'}$), 0.91 (d, $J = 6.5$ Hz, 3/2 H, Me_4 first diastereoisomer), 0.90 (d, $J = 6.5$ Hz, 3/2 H, Me_4 second diastereoisomer); ^{13}C NMR (62.5 MHz, $CDCl_3$, δ ppm) 173.5 (s, C_1), 134.0 (s, $C_{1'}$), 121.5 (d, $C_{2'}$), 51.3 (q, MeO), 39.3 + 39.6 (t, C_2), 38.8 + 39.0 (d, $C_{4'}$), 35.1 + 35.2 (d, C_3), 31.4 + 31.3 (t, $C_{6'}$), 29.8 + 28.5 (t, $C_{3'}$), 26.3 + 27.4 (t, $C_{5'}$), 24.0 (q, $C_{7'}$), 17.2 + 16.8 (q, C_4); elemental anal. Calcd. for $C_{12}H_{20}O_2$ (mw = 196.29): C, 73.43; H, 10.27; O, 16.30. Found: C, 73.31; H, 10.36; O, 16.05%.

4.6.9. Methyl 3-(4'-methyl-3'-oxo-4'-cyclohexenyl)butanoate (12)

Bp: 130°C (1 kPa); mass spectrum m/e 210 (M^+), 109 (main peak); IR (neat) 1735 cm^{-1} (ester), 1676 cm^{-1} (ketone); ^1H NMR (200 MHz, $CDCl_3$, δ) 6.72 (m, 1H, $H_{3'}$), 3.66 (s, 3H, MeO), 2.51–1.92 (m, 8H, $2H_2$, H_3, $2H_{4'}$, $H_{5'}$, $2H_{6'}$), 1.75 (m, 3H, $3H_{7'}$), 0.94 (d, $J = 6.3$ Hz, 3/2H, H_4 first diastereoisomer), 0.93 (d, $J = 6.3$ Hz, 3/2H, H_4 second diastereoisomer); ^{13}C NMR (62.5 MHz, $CDCl_3$, δ) 199.1 + 199.2 (s, $C_{1'}$), 172.9 (s, C_1), 144.3 + 144.2 (d, $C_{3'}$), 135.2 (s, $C_{2'}$), 51.1 (q, OMe), 40.6 + 41.9 (t, $C_{6'}$), 39.8 + 39.7 (d, $C_{5'}$), 38.4 + 38.3 (t, C_2), 33.8 + 33.8 (d, C_3), 29.9 + 28.5 (t, $C_{4'}$), 16.1 + 16.1 (q, C_4), 15.2 (q, $C_{7'}$); elemental anal. Calcd. for $C_{12}H_{18}O_3$ (mw = 210.27): C, 68.55; H, 8.63; O, 22.83. Found: C, 68.43; H, 8.67; O, 22.96%.

4.6.10. Methyl 3-(4'-methyl-3'-oxo-cyclohexyl)butanoate (15)

Bp: 110°C (1 kPa); mass spectrum m/e 212 (M^+), 138 [25*], 111 (main peak); IR (neat) 1737 cm^{-1} (νC=O ester) 1713 cm^{-1} (νC=O ketone); ^1H NMR (200 MHz, $CDCl_3$, δ ppm) 3.65 (s, 3H, MeO), 2.5–1.1 (m, 11H, $2H_2$, H_3, H_2, $2H_{3'}$, $2H_{4'}$, $H_{5'}$, $2H_{6'}$), 0.99 (d, $J = 3.2$ Hz, 3H, $Me_{7'}$), 0.90 (d, $J = 4.0$ Hz, 3/2 H, Me_4 first diastereoisomer), 0.88 (d, $J = 4.0$ Hz, 3/2 H, second diastereoisomer); ^{13}C NMR (62.5 MHz, $CDCl_3$, δ ppm) 211.6 + 211.8 (s, $C_{1'}$), 172.8 (s, C_1), 51.0 (q, MeO), 44.3 (d, $C_{2'}$ or $C_{5'}$), 44.2 (d, $C_{5'}$ or $C_{2'}$), 45.2 + 43.8 (t, $C_{6'}$), 38.3 (t, C_2), 34.4 (t, $C_{3'}$), 34.4 (d, C_3), 29.8 + 27.4 (t, $C_{4'}$), 15.9 + 15.7 (q, C_4), 13.9 (q, $C_{7'}$).

4.6.11. Methyl 3-(4'-methyl-2'-oxo-cyclohexyl)butanoate (19)

Bp: 110°C (1 kPa); mass spectrum m/e 212 (M^+), 112 [25*]; IR (neat) 1737 cm^{-1} (νC=O ester), 1708 cm^{-1} (νC=O ketone); ^1H NMR (200 MHz, $CDCl_3$, δ ppm) 3.67 ppm (s, 3H, MeO), 2.5–1.2 (m, 11H, $2H_2$, H_3, $H_{2'}$, $2H_{3'}$, $2H_{4'}$, $H_{5'}$, $2H_{6'}$), 1.1–0.8 (m, 6H, Me_4 + $Me_{7'}$, four diastereoisomers); ^{13}C NMR (62.5 MHz, $CDCl_3$, δ ppm) 210.9 + 210.8 [27*] and 212.7 + 212.4 [28*] (s, $C_{1'}$), 173.0 + 173.3 [27*] and 173.0 + 172.9 [28*] (s, C_1), 52.9 + 53.6 [27*] and 54.6 + 54.3 [28*] (d, $C_{2'}$), 51.1 (q, MeO), 50.5 + 50.6 [27*] and 48.0 + 48.0 [28*] (t, $C_{6'}$), 38.9 + 37.7 [27*] and 38.2 + 39.1 [28*] (t, C_2), 35.1 + 35.0 [27*] and 33.2 + 33.0 [28*] (d, $C_{5'}$), 33.6 + 33.7 [27*] and 29.5 + 29.4 [28*] (t, $C_{4'}$), 28.3 + 28.9 [27*] and 28.7 + 29.0 [28*] (d, C_3), 27.6 + 28.4 [27*] and 26.0 + 25.2 [28*] (t, $C_{3'}$), 22.0 [27*] and 20.3 + 20.1 [28*] (q, $C_{7'}$), 16.2 + 17.3 [27*] and 16.6 + 17.6 [28*] (q, C_4); elemental anal. Calcd. for $C_{12}H_{20}O_3$ (mw = 212.29): C, 67.89; H, 9.50; O, 22.61. Found: C, 68.02; H, 9.62; O, 22.55%.

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References and notes

1 Part IV of the series, T. Baig, J. Molinier and Ph. Kalck, *J. Organomet. Chem., 455* (1993) 219; Preliminary communication, T. Chenal, R. Naigre, I. Ciprès, J.C. Daran, Ph. Kalck and J. Vaissermann, *J. Chem. Soc., Chem. Commun., 9* (1993) 747.
2 A. Muller, in J. Falbe (ed.), *New synthesis with carbon monoxide*, Springer, New York, 1980, p. 243.
3 J. Tsuji, *Organic synthesis with palladium compounds*, Springer, Berlin, 1980, p. 81.
4 J.F. Knifton, *J. Org. Chem., 41* (1976) 2885.
5 R. Bardi, A. Del Pra, A.M. Prazzeni and L. Toniolo, *Inorg. Chim. Acta, 35* (1979) L345.
6 G. Cavinato and L. Toniolo, *J. Organomet. Chem., 398* (1990) 187.
7 B. El Ali and H. Alper, *J. Org. Chem., 56* (1991) 5357.
8 I. Ciprès, J. Jenck and Ph. Kalck, *J. Mol. Cat., 58* (1990) 387.
9 T. Chenal, I. Ciprès, J. Jenck, Ph. Kalck and Y. Pérès, *J. Mol. Cat., 78* (1993) 351.
10 J.K. Kingston and G.R. Scollary, *J. Chem. Soc. A*, (1971) 3765.
11 J. Hilary, A. Bandery and A.H. Thomas, *Acta Crystallogr., C44* (1988) 1683.
12 S. Belanger and A.L. Beauchamp, *Acta Crystallogr., B37* (1981) 1415.
13 M.H. Ben Ghozlen and A. Daoud, *Acta Crystallogr., C49* (1993) 388.

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* Reference number with asterisk indicates a note in the list of references.

14 J.D. Bell, D. Hall and T.N. Waters, *Acta Crystallogr., 21* (1966) 440.

15 J.P. Colman, L.S. Hegedus, J.R. Norton and R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Sciences Books, Mill Valley, CA 1987.

16 P.S. Pregosin and S. Ning Sze, *Helv. Chim. Acta, 65* (1978) 177.

17 M.B. Hossain and D. Van Der Helm, *Acta Crystallogr., C43* (1987) 1764.

18 K. Kudo, M. Hidai, T. Murayama and Y. Uchida, *J. Chem. Soc., Chem. Commun.*, (1970) 1701.

19 M. Gomez, G. Muller, D. Sainz and J. Sales, *Organometallics, 10* (1991) 4036.

20 (a) J.M. Jenckins and J.C. Verkade, *Inorg. Synth., 11* (1968) 108; (b) D.R. Coulson, L.C. Satek and S.O. Grim, *Inorg. Synth., 13* (1972) 121.

21 N. Walker and D. Stuart, *Acta Crystallogr., A39* (1983) 59.

22 D. Watkin, J.R. Carruthers and P.W. Betteridge, CRYSTALS *User Guide*, Chemical Crystallography Laboratory, University of Oxford, 1986.

23 *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch, Birmingham, 1974.

24 G.M. Sheldrick, SHELXS 86, *Program for Crystal Structure Solution*, University of Göttingen, Germany, 1986.

25 Characteristic fragment via Mac Lafferty rearrangment.

26 Retro Diels-Alder fragment.

27 Two major diastereoisomers, presumably with a *trans*-substituted cyclohexane ring.

28 Two minor diastereoisomers, presumably with a *cis*-substituted cyclohexane ring.