Cationic Palladium η^3-Allyl Complexes with Hemilabile P,O-Ligands: Synthesis and Reactivity. Insertion of Ethylene into the Pd−Allyl Function

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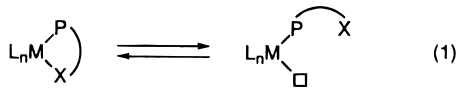
Cationic palladium allyl complexes $[(\eta^3\text{-}C_3H_5)Pd(\kappa^2P\text{^}O)]^+SbF_6^-$ (**2**[SbF_6], $P\text{^}O \equiv Ph_2P(CH_2)_2C(=O)OEt$; **3**[$SbF_6$], *o*-$Ph_2PC_6H_4C(=O)OEt$; **4**[$SbF_6$], $Ph_2P(CH_2)_2P(=O)Ph_2$) have been prepared. In all complexes the oxygen donor can be displaced by other ligands such as carbon monoxide and ethylene. Displacement of an ester donor occurs much more readily than displacement of the phosphine oxide function. Above 0 °C, the resulting ethylene complexes $[(\eta^3\text{-}C_3H_5)Pd(C_2H_4)(\kappa^1P\sim O)]^+$ react to give (1,2,5-η^3)-pent-1-en-5-yl complexes $[(H_2C{=}CH(CH_2)_3Pd(\kappa^2P\text{^}O)]^+$. A rate constant of *e.g.* $k(17\ °C) = (2.27 \pm 0.11) \times 10^{-4}\ s^{-1}$ was determined for $P,O \equiv Ph_2P(CH_2)_2C(O)OEt$ by ^1H NMR spectroscopy. Using **2**−**4** as catalyst precursors for ethylene dimerization, the allyl moiety is ultimately cleaved from the metal center as 1,4-pentadiene.

Introduction

Since their initial discovery in the 1950s,[1] transition-metal η^3-allyl complexes have been ubiquitous in organometallic chemistry. One of the key points of interest is their occurrence as intermediates in a variety of metal-mediated transformations of organic substrates. Closely related is the use of η^3-allyl complexes as precursors to homogeneous catalysts, namely for C−C linkage reactions. The basis for such reactions is the formation and breakage of metal−carbon bonds, and thus a catalyst precursor which already contains M−C bonds can provide a convenient entry into the catalytic cycle. Prominent examples are the nickel catalysts developed by Wilke *et al.* for the dimerization of propene[2] (Scheme 1).

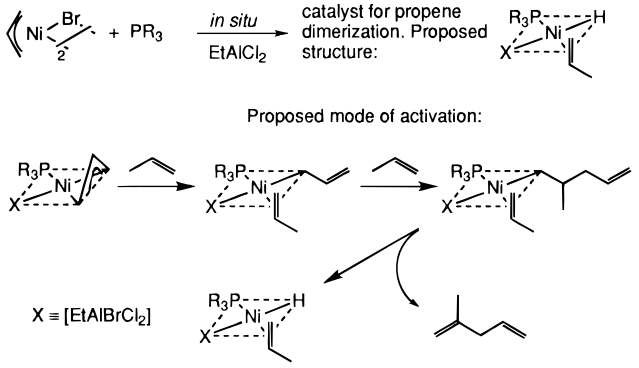
Late-transition-metal catalysts frequently employ alkyl- or arylphosphines as stabilizing and selectivity controlling ligands. These soft donor ligands form stable bonds to the late-metal center. In multidentate functionalized phosphine ligands, which in addition to the soft donor also contain hard donor sites, the latter coordinate only weakly to the metal center and can easily be displaced by other ligands. This property has been termed hemilabile.[3] In catalysis and stoichiometric reactions, such ligands have the potential of providing a coordination site for an incoming ligand and of stabilizing reactive intermediates by reversible coordination of the hard donor (eq 1).



(1)

We report here the preparation of cationic palladium η^3-allyl complexes with bidentate P,O-ligands[4] and their reactivity toward ethylene. We have previously described the application of these complexes as well-defined catalyst precursors for the cooligomerization of carbon monoxide with ethylene[5] and the codimerization of styrene with ethylene.[5a,6]

Scheme 1



Results and Discussion

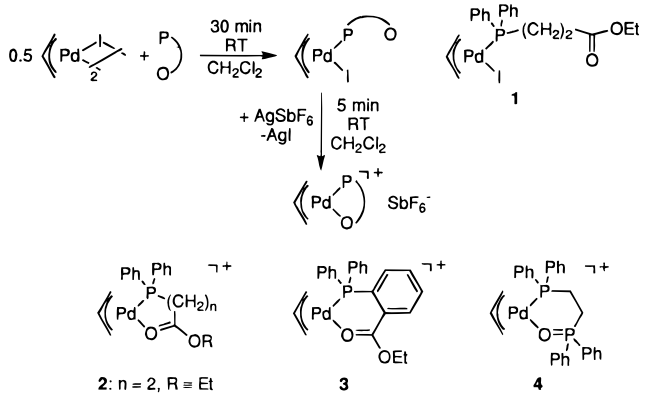
Preparation and Characterization of η^3-Allyl Complexes. Cationic palladium allyl complexes were prepared by the general procedure outlined in Scheme 2. Compound **1** was isolated for comparison of its spectroscopic properties, but generally the reaction solution of the compounds $[(\eta^3\text{-}C_3H_5)Pd(I)(\kappa^1P\sim O)]$ was allowed to directly react with $AgSbF_6$. When $[(\eta^3\text{-}C_3H_5)PdI]_2$ was employed, better results were obtained in the halide abstraction reaction than with the corresponding chloro dimer. The analogs of **2** with $n = 1$ (R ≡ Me)

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

(1) Smidt, J.; Hafner, W. *Angew. Chem.* **1959**, *71*, 284.
(2) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185−206.
(3) Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658−2666.
(4) (a) Empsall, H. D.; Hyde, E. M.; Pawson, D.; Shaw, B. *J. Chem. Soc., Dalton Trans.* **1977**, 1292−1298. (b) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466−467. (c) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115−5125. (d) Higgins, S. J.; Taylor, R.; Shaw, B. L. *J. Organomet. Chem.* **1987**, *325*, 285−292. (e) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27−110 and references cited therein.
(5) (a) Britovsek, G. J. P.; Keim, W.; Mecking, S.; Sainz, D.; Wagner, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1632−1634. (b) Keim, W.; Maas, H.; Mecking, S. *Z. Naturforsch.* **1995**, *50B*, 430−438.
(6) The application of analogous nickel complexes as catalyst precursors for the oligomerization of ethylene has been described recently: Bonnet, M. C.; Dahan, F.; Ecke, A.; Keim, W.; Schulz, R. P.; Tkatchenko, I. *J. Chem. Soc., Chem. Commun.* **1994**, 615−616.

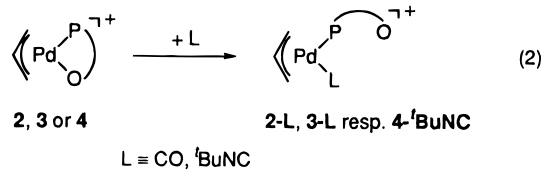
S0276-7333(96)00061-1 CCC: $12.00

Scheme 2



and $n = 3$ (R ≡ Et) can also be prepared by this procedure in good yields. Compounds **2**−**4** were isolated as light brown or white solids. **2** can be handled at room temperature under an inert-gas atmosphere for brief periods of time. **3** and **4** are less thermosensitive, and they can also be exposed to air without any apparent decomposition. In the ^{1}H NMR spectra, the protons H^1, H^2, and H^5 of the allyl ligand give rise to sharp signals, whereas the resonances of the protons *trans* to the oxygen donor, H^3 and H^4, are broad at room temperature due to *syn*−*anti* exchange—a behavior well-known for square-planar allyl complexes with a hard and a soft donor ligand[7] (numbering H^1(syn)H^2(anti)$C^1C^2H^5C^3H^4$-(syn)H^3(anti); C^1 is *trans* to P). Coordination of the ester or phosphine oxide function causes characteristic changes in the IR and NMR spectra; representative data are given in Table 1. The wavenumber of the carbonyl band in **2** and **3** is lowered by *ca.* 80 cm^{-1} compared to the free ligand or **1**. The NMR signals of the OCH_2 protons and the carbonyl carbon atom are shifted downfield. Correspondingly, in complex **4** ν(P═O) is lowered in comparison to the free ligand, and the ^{31}P NMR signal of the phosphine oxide function is shifted toward lower field.

The strength of the palladium−oxygen bond relative to other ligands is of interest in estimating the coordination behavior of the P,O-ligand in the active species in catalysts with these ligands[5] (monodentate P or bidentate P,O), and it is also decisive for the activation of complexes **2**−**4** as catalyst precursors (*vide infra*). Therefore, the cationic complexes were reacted with *tert*-butyl isocyanide and carbon monoxide (eq 2). CO was



(2)

of special interest, as it is one of the substrates used in reactions with these complexes as catalyst precursors.[5] The reactivity toward ethylene is discussed in the next section. Addition of 1 equiv of ^{t}BuNC resulted in complete displacement of the ester or phosphine oxide donor; only the IR bands of the uncoordinated oxygen donor and coordinated isonitrile are observed (complex **2-^{t}BuNC**, ν(CO) 1732 cm^{-1}, ν(CN) 2209 cm^{-1}; **4-^{t}BuNC**, ν(P═O) 1196 cm^{-1}, ν(CN) 2209 cm^{-1} (free ^{t}BuNC, ν 2139 cm^{-1})). The ester function is also readily displaced upon bubbling carbon monoxide through a CH_2Cl_2 solution of the complexes (**2-CO**, ν(CO ester) 1732 cm^{-1}, ν(CO) 2135 cm^{-1}; **3-CO**, ν(CO ester) 1697 cm^{-1}, ν(CO) 2132 cm^{-1}). The carbonyl complex **2-CO** was also characterized by ^{13}C NMR spectroscopy utilizing ^{13}C-enriched carbon monoxide (δ 180.5 (Pd—CO), 171.6 (d, C(O)O), 61.7 (OCH_2); for complete data *cf.* Experimental Section). The IR band of the coordinated carbonyl ligand is very similar to that of gaseous CO (2143 cm^{-1}), indicating weak binding to the cationic palladium center.[8] Accordingly, when a solution of **2-CO** is purged

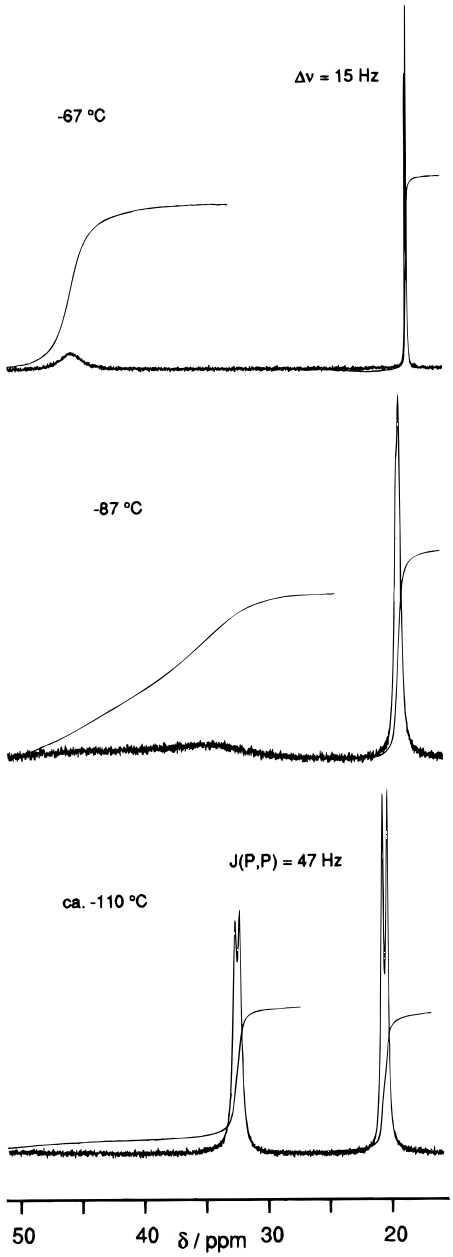


Figure 1. ^{31}P{^{1}H} NMR spectra of the equilibrium **4** + C_2H_4 ⇌ **4-E** (*cf.* eq 5; 121 MHz, CD_2Cl_2, total 5 equiv of ethylene).

(7) (a) Vrieze, K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; pp 441−487. (b) Meyer, H.; Zschunke, A. *J. Organomet. Chem.* **1984**, *269*, 209−216.

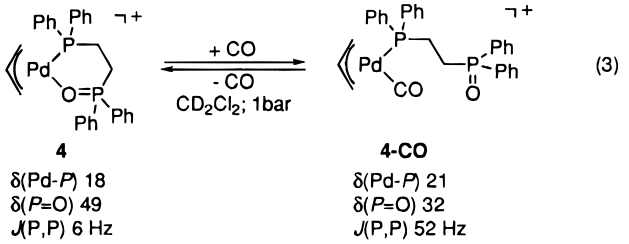
(8) In blank experiments, with CO bubbled through neat CH_2Cl_2, no free carbon monoxide could be detected by IR or ^{13}C NMR spectroscopy; obviously the solubility is too low.

Table 1. Spectroscopic Data for Complexes 1−4 and Free Ligands[a]

complex or ligand	^{1}H NMR δ(OCH_2R)	δ(C=O) or δ(P=O)	^{13}C and ^{31}P NMR δ(OCH_2R)	δ(Ph$_2$PCH_2)	IR (CH_2Cl_2) ν(C=O) or ν(P=O)/cm^{-1}
$Ph_2P(CH_2)_2C(O)OEt$	4.06	173.0	60.5	−15.0	1730
o-$Ph_2PC_6H_4C(O)OEt$	4.20	166.9	61.2	−3.9	1709
1	4.03	172.3	61.1	+19.1	1731
2	4.36	180.9	65.8	+22.6	1655
3	4.45	171.3	65.8	+22.3	1641
$Ph_2P(CH_2)_2P(O)Ph_2$		33.1		−11.4	1190
4		48.6		+19.8	1127

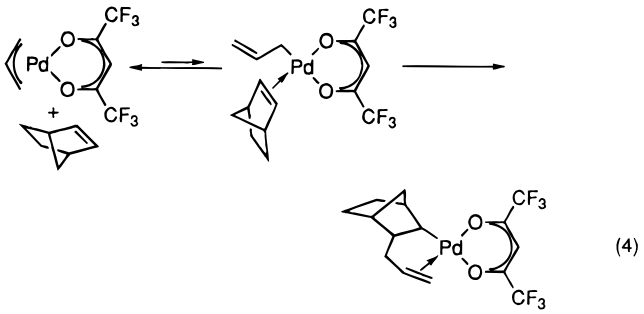
[a] Room temperature; NMR solvent: CD_2Cl_2, CH_2Cl_2−CD_2Cl_2, or $CDCl_3$ (for a given compound, no significant deviations of the chemical shifts measured in different solvents were observed).

with argon, the carbonyl complex is completely converted back to **2** again. The phosphine−phosphine oxide complex **4** shows a markedly different behavior toward CO: At room temperature, no reaction with carbon monoxide was detected by IR spectroscopy. Variable-temperature ^{31}P NMR spectroscopy[9] established, however, that **4** is in a temperature-dependent dynamic equilibrium with the carbonyl complex **4-CO** (eq 3).



The spectroscopic observations resemble those obtained with ethylene, depicted in Figure 1 and described in more detail in the following section. Above −30 °C, interconversion between **4** and **4-CO** is fast on the NMR time scale, resulting in one averaged signal each for the phosphine and the phosphine oxide functions. At room temperature, the chemical shifts and the coupling constants of these signals are nearly identical with the spectrum of **4**, in accordance with the IR spectroscopic results. Below −30 °C, two sets of signals emerge (**4**, δ 49.5 and 18.1, ^3J(P,P) = 6 Hz; **4-CO**, δ 32 and 21.0, ^3J(P,P) = 52 Hz (CD_2Cl_2, −87 °C)). Complex **4-CO** is the major species at temperatures below *ca.* −50 °C (1 atm of CO). In conclusion, the P,O-ligands in all the cationic allyl complexes display hemilabile behavior; however, the phosphine oxide donor binds significantly more strongly to the palladium center than an ester donor.

Reactions with Ethylene. The reaction of (η^3-allyl)-metal intermediates with olefins, resulting in net insertion of the olefin into the allyl−metal moiety, is assumed to be a key step in various economically important processes, *e.g.* the oligomerization[2,10a,b] or polymerization[10b−d] of dienes and the codimerization of dienes with ethylene.[11] Therefore, this reaction has received considerable interest. Powell and co-workers[12] and others[13] were able to isolate 4-enyl insertion products. The mechanism depicted in eq 4 was proposed. However, most of these studies employed strained olefins, and direct observation of insertion of a simple, unactivated olefin such as ethylene has not been reported.[14]



Upon saturation of a solution of **2** with ethylene at room temperature, the carbonyl band of **2** disappears; instead, a strong band at ν(CO) 1732 cm^{-1} and a weaker band at ν(CO) 1664 cm^{-1} are observed. In the further course of the experiment, the intensity of the latter band increases, while the band at 1732 cm^{-1} decreases in intensity. Within 1 h, the band at ν 1664 cm^{-1} becomes the most intense. If the solution is purged with argon during the initial stages of the experiment, the band at ν(CO) 1732 cm^{-1} disappears, and **2** is recovered (ν(CO) 1655 cm^{-1}). By multinuclear NMR spectroscopy and 1D- and 2D-decoupling experiments, the species could be unambigiously identified as **2-E** and **5** (Scheme 3).

When ethylene is added to a CD_2Cl_2 solution of **2** at −30 °C, clean conversion to **2-E** occurs. Due to rapid exchange of coordinated with excess free ethylene, only one broad averaged signal is observed (δ 5.1, total 3 equiv of ethylene; free ethylene in blank experiment δ 5.4). When the solution is warmed, allyl−ethylene coupling occurs to yield the pent-4-en-1-yl complex **5**.[15] This complex is stabilized by recoordination of the oxygen donor of the hemilabile ligand; obviously, the ester function is not displaced by the excess ethylene,

(9) The ^{1}H NMR spectra display broad, averaged signals of less diagnostic value.

(10) (a) Keim, W.; Behr, A.; Röper, M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 8; pp 371−462. (b) Jolly, P. W. In ref 10a, pp 671−711. (c) Taube, R.; Wache, S.; Sieler, J. *J. Organomet. Chem.* **1993**, *459*, 335−347 and references cited therein. (d) Durand, J. P.; Dawans, F.; Teyssie, P. *J. Polym. Sci., Part A: Polym. Chem.* **1970**, *8*, 979−990.

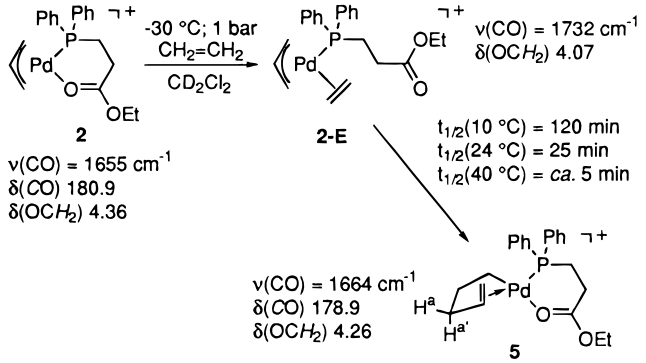
(11) (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley-Interscience: New York, 1992; pp 76−78. (b) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 6777−6784, 6785−6790.

(12) Hughes, R. P.; Powell, J. *J. Organomet. Chem.* **1973**, *60*, 387−407.

(13) (a) Gallazzi, M. C.; Hanlon, T. L.; Vittuli, G.; Porri, L. *J. Organomet. Chem.* **1971**, *33*, C45−C46. (b) Sadownick, J. A.; Lippard, S. L. *Inorg. Chem.* **1973**, *12*, 2659−2665. (c) Taube, R.; Böhme, P.; Gehrke, J.-P. *Z. Anorg. Allg. Chem.* **1989**, *578*, 89−98.

(14) Very recently, the reaction of similar palladium allyl complexes with various olefins was directly observed by NMR spectroscopy: DiRenzo, G. M.; Brookhart, M. *J. Am. Chem. Soc.*, in press.

Scheme 3

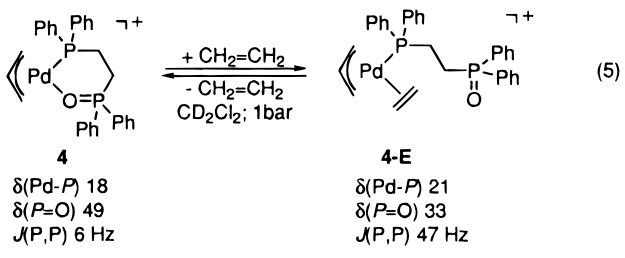


in contrast to the behavior of the corresponding allyl complex **2**.[16] Considering the NMR spectroscopic properties of the pentenyl ligand, the signals of the olefinic protons are shifted to lower field in comparison to a free α-olefin by $\Delta\delta = 0.5-1.4$. Coupling to the phosphine donor and the diastereotopy of the allylic protons H^a and $H^{a'}$ at low temperatures[17] also clearly indicate coordination to the metal center. The magnitudes of the P−C coupling constants of the $PdCH_2$− (no coupling observed) and the vinyl group of the pentenyl ligand (=CH_2, 10 Hz; =CH−, 5 Hz) support the stereochemistry at the square-planar palladium center depicted in Scheme 3.[18] In the NMR experiments, formation of **5** is accompanied by the conversion of ethylene, present in excess, to butenes. The cationic allyl complexes **2**−**4** are precursors to very active catalysts for the dimerization of ethylene,[5] and it is assumed that during the NMR experiment a small, and thus undetectable, amount of a catalytically active species is formed (*vide infra*). At higher temperatures, further conversion of **5** can occur. Following the reaction of **2-E** to give **5** at +40 °C ($CDCl_3$), after 1 h minor amounts of two new species with ^{31}P NMR resonances at δ 39.4 and δ 21.0, respectively, were observed. On the basis of H,H-COSY and ^{13}C NMR data, the species with δ 21.0 was tentatively assigned as the *syn*,*syn*-1,3-dimethylallyl complex analogous to **2**, which may form by rearrangement of **5**. Similar isomerizations of a pentenyl to an allyl complex have been described.[15b,c] Complex **5** was isolated as an off-white solid. Due to impurities of **2** (formed from unreacted **2-E** upon workup *in vacuo*) or by compounds formed by further reaction of **5**, an analytically pure sample could not be obtained. Attempted crystallizations were hampered by the inevitable formation of oils.

When the reaction **2-E** → **5** was monitored by ^1H NMR spectroscopy, the first-order rate constants were obtained for different temperatures: $k(10\ °C) = (9.6 \pm 0.5) \times 10^{-5}\ s^{-1}$, $k(17\ °C) = (2.27 \pm 0.11) \times 10^{-4}\ s^{-1}$ and $k(24\ °C) = (4.6 \pm 0.8) \times 10^{-4}\ s^{-1}$ (solvent CD_2Cl_2). At 40 °C the reaction was to fast to be followed accurately, a rate of *ca.* $2.3 \times 10^{-3}\ s^{-1}$ was estimated ($CDCl_3$). The exchange of H^3 and H^4 in the NMR spectra of **2**−**4** (*vide supra*) occurs via a η^1-allyl species.[7] In contrast, no analogous evidence for dynamic behavior was observed for **2-E**. Though it is by no means ruled out, no evidence for intermediacy of a η^1-allyl species in the conversion to **5** was found, and thus our data would also be in agreement with C−C linkage occurring between the ethylene and the η^3-bound allyl ligand. From the kinetic data a free enthalpy of activation $\Delta G^{\ddagger}(17\ °C) = (91.2 \pm 0.8)\ kJ\ mol^{-1}$ results.

Complex **3** seemed a more promising starting compound for formation of a crystalline pentenyl complex. Due to its aromatic backbone, **3** can readily be obtained as a solid by precipitation or crystallization, in contrast to **2**. Analogous to **2**, **3** reacts with excess ethylene at −30 °C to yield **3-E**. When the temperature is raised, insertion yielding the pentenyl complex occurs with rates similar to those for **2**. However, accompanying conversion of ethylene to butenes occurs much faster than with **2**/**5**. In accordance with this behavior, **3** is a precursor to much more active ethylene dimerization catalysts than **2**.[19] Thus, although mixtures of **3** and the pentenyl complex could be precipitated as solids from solution as anticipated, rapid depletion in ethylene prevented reasonable conversions to the pentenyl complex.

The phosphine−phosphine oxide complex **4** displays different properties toward ethylene than the phosphino−ester complexes. When ethylene is added at −30 °C, no substitution of the phosphine oxide donor is observed by ^1H and ^{31}P NMR spectroscopy. However, the signals are slightly broadened and shifted compared to the spectrum of **4** in the absence of ethylene. Variable-temperature ^{31}P NMR spectroscopy[9] (Figure 1) showed that **4** is in a dynamic equilibrium with the ethylene complex **4-E** (eq 5).[20] At temperatures higher



(5)

than −30 °C, only traces of **4-E** are present, whereas at temperatures lower than *ca.* −80 °C **4-E** is the major species (1 atm of ethylene).

Correspondingly, when the temperature is raised to room temperature, no formation of a pentenyl complex is observed. However, after the NMR sample is stored

(15) For similar complexes, prepared by different routes, see: (a) Lehmkuhl, H.; Rufinska, A.; Benn, R.; Schroth, G.; Mynott, R. *Liebigs Ann. Chem.* **1981**, 317−332. (b) Parra-Hake, M.; Rettig, M. F.; Williams, J. L.; Wing, R. M. *Organometallics* **1986**, *5*, 1032−1040. (c) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795−1803. (d) Flood, T. C.; Bittler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076−6077. (e) Ermer, S. P.; Struck, G. E.; Bitler, S. P.; Richards, R.; Bau, R.; Flood, T. C. *Organometallics* **1993**, *12*, 2634−2643. (f) Pedone, C.; Benedetti, E. *J. Organomet. Chem.* **1971**, *31*, 403−414.

(16) This observation must be kept in mind, when estimating the coordination behavior of the P,O-ligand in an assumed intermediate in catalysis from the relative coordination strength of the oxygen donor in model compounds, such as **2**−**4**, as the other ligands coordinated to the metal center obviously have a strong impact.

(17) $T_c \approx 17$ °C (300 MHz). It is assumed that this exchange occurs between two species with opposite enantiotopic faces of the olefinic moiety binding to the metal center. This requires intermediate decoordination of the olefinic function.

(18) For comparative ^{13}C NMR data *cf.* ref 15e. The *J*(H,P) values provide no clear picture considering the stereochemistry in comparison to literature data: (a) de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907−2917. (b) Lindner, E.; Dettinger, J.; Fawzi, R.; Steimann, M. *Chem. Ber.* **1993**, *126*, 1347−1353.

(19) Mecking, S. Dissertation, RWTH Aachen, 1994.

(20) For a theoretical treatment of exchange between two nonequally populated sites *cf.*: Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; pp 25−29, 80−84.

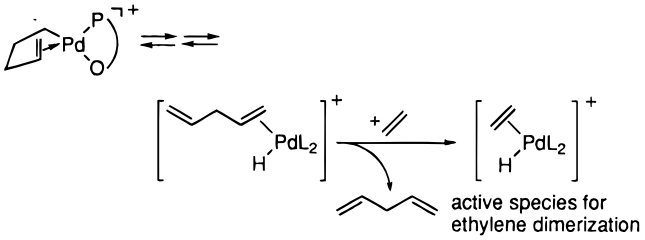
for 1 day at room temperature, in addition to the ^{1}H NMR signals of **4**, weak signals (integrating for *ca.* 10% relative to **4**) analogous to the pentenyl ligand in **5** are observed. All ethylene had been converted to butenes. Also, a new pair of ^{31}P resonances was observed (δ 43.6 and 26.2, J(P,P) = 4 Hz). Thus, it may be assumed that **4-E** displays the same reactivity as **2-E** and **3-E**.

The reactivity of the cationic allyl complexes toward ethylene/CO mixtures is of interest, as **2**−**4** have also been applied as well-defined catalyst precursors for the cooligomerization of ethylene and CO.[5] When a 1:1 ethylene/CO mixture is bubbled through a methylene chloride solution of **2**, despite the higher solubility of ethylene, the carbonyl complex **2-CO** (ν(CO ester) 1732 cm^{-1}, ν(CO) 2135 cm^{-1}) is the only species observed initially; small amounts of **2-E** (ν(CO ester) 1732 cm^{-1}) may have been obscured. Eventually, however, the pentenyl complex **5** (ν(CO ester) 1664 cm^{-1}) is formed, as in the absence of CO. No insertion of CO into the allyl moiety was observed with **2-CO**. Such reactions most often require harsh conditions, and to the best of our knowledge, only one example of formation of an isolable acyl complex has been reported.[21] Thus, it can be assumed that the first step in the activation of allyl catalyst precursors in the cooligomerization of ethylene and CO occurs by insertion of ethylene.

Activation of Allyl Complexes in Olefin Oligomerization Reactions. A generally accepted mechanism for the oligomerization of olefins by late transition metals involves subsequent insertions of the substrate into a metal hydride complex as the active species.[22] Considering the activation of allyl catalyst precursors to the active species, from oligomerization reactions of olefins 1:1 coupling products of the allyl moiety with the olefinic substrate have been isolated, which provide indirect evidence for formation of a hydride complex.[23] Other mechanisms for oligomerization of olefins with allyl complexes as catalysts have been proposed[24] but have received little support.

As mentioned in the previous section, NMR experiments were accompanied by dimerization of ethylene, without observation of an active species, presumably due to its low concentration. Although this dimerization can cause depletion in ethylene, it occurs at a much lower rate than in a typical catalytic oligomerization experiment.[5b,19] For instance, exposing a dilute solution of **3** (0.05 mmol in 20 mL of CH_2Cl_2) to 30 atm of ethylene at room temperature results in dimerization at a rate of 6000 mol/(mol h).[19] This dramatic increase in activity at higher ethylene concentrations may in part be due to more rapid activation of the catalyst precursor. A possible mechanism for the formation of a hydride species is shown in Scheme 4. In this context it is interesting that very recent results by Brookhart *et al.* support that olefin exchange of such complexes is an

Scheme 4



associative process;[25] this would result in an enhancement of the liberation of pentadiene by higher ethylene concentrations. On basis of the above assumption, experiments aimed at clarifying the final fate of the allyl moiety during activation were carried out under ethylene pressure.

A THF solution of **2** (*ca.* 0.5 mmol in 10 mL) was stirred under 5 atm of ethylene, and samples were drawn periodically and analyzed by GC. In samples taken within the first 3 h, 1,4-pentadiene was identified by gas chromatography by enrichment with a genuine sample, and by GC−MS. Small peaks with retention times corresponding to *cis*- and *trans*-1,3-pentadiene were also observed. After 24 h, no more 1,4-pentadiene was observed. The use of the weakly coordinating solvent THF is necessary to generally slow down the dimerization and isomerization reactions occurring. Using CH_2Cl_2, no pentadienes could be detected, presumably due to rapid isomerization of the initially formed 1,4-pentadiene to the reactive 1,3-isomers and subsequent cooligomerization with ethylene, resulting in distribution of the allyl group over a large number of different products.

Conclusion

Cationic palladium allyl complexes with a scope of bidentate P,O-ligands can be prepared conveniently. These compounds are well-defined precursors to very active catalysts for C−C linkage reactions of olefins. The P,O-ligands in these complexes are hemilabile; the oxygen donor can be displaced by other ligands such as carbon monoxide and ethylene. The O-donor of a phosphino−ester ligand is displaced much more readily than with a phosphine−phosphine oxide, and the results imply that the former behaves as a monodentate P-coordinated ligand under the conditions of catalysis. The hemilability of the P,O-ligands allowed the direct observation of coupling of ethylene with an allyl ligand to yield a σ,π-η^3-pent-4-en-1-yl complex. In ethylene dimerization experiments using an allyl complex as a catalyst precursor, 1,4-pentadiene was identified. These observations provide support for a palladium hydride as the catalytically active species, formed by activation of the allyl precursor through insertion of ethylene and subsequent β-hydride elimination.

Experimental Section

All manipulations were carried out under a dry argon atmosphere by standard Schlenk techniques. For reactions above atmospheric pressure a heavy-walled 100 mL round-bottom glass tube with two necks equipped with glass threads was used. NMR spectra were acquired on a Bruker CXP-200,

(21) Ozawa, F.; Son, T.; Osakada, K.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1989**, 1067−1068.
(22) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; pp 577−617.
(23) (a) Bogdanovic, B.; Henc, B.; Karmann, H.-G.; Nüssel, H.-G.; Walter, D.; Wilke, G. *Ind. Eng. Chem.* **1970**, *62*, 34−44. (b) Bogdanovic, B. *Adv. Organomet. Chem.* **1979**, *17*, 105−140. (c) Grenouillet, P.; Neibecker, D.; Tkatchenko, I. *Organometallics* **1984**, *3*, 1130−1132.
(24) Sen, A.; Lai, T.-W. *Organometallics* **1983**, *2*, 1059−1060.
(25) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414−6415.

Bruker AC300, or Varian Unity 500 spectrometer. Chemical shifts are referenced to internal or external TMS (^{1}H, ^{13}C), respectively, or to external 85% H_3PO_4 (^{31}P). NMR probe temperatures were measured using an external anhydrous methanol sample. In experiments using non-deuterated solvents, a coaxial tube with the deuterated compound was inserted as a lock, or a small amount was added directly to the sample solution. Assignments were confirmed by H,H-COSY and selective ^{1}H and ^{31}P decoupling of ^{1}H NMR spectra. Numbering of the allyl ligand in NMR data: H^1(syn)H^2(anti)-$C^1C^2H^5C^3H^4$(syn)H^3(anti); C^1 is *trans* to P. Gas chromatographic analyses were performed on a Siemens Sichromat with a 50 m Pona HP column. For GC−MS analyses a Varian 3700 gas chromatograph combined with a Varian MAT 112S mass spectrometer was used. IR spectra were recorded on a Nicolet 510 P FT spectrometer. Solvents were distilled from a drying agent under argon (methylene chloride, CaH_2; pentane and THF, sodium benzophenone ketyl). Ethylene (purity >99.5%) and carbon monoxide (purity >99.99%) were used as received. Genuine samples of 1,4-pentadiene, *trans*-1,3-pentadiene, and *cis*-1,3-pentadiene were purchased from Fluka. $[(C_3H_5)PdI]_2$ was obtained from $[(C_3H_5)PdCl]_2$[26] by halide exchange with NaI.[27]

Functionalized Phosphine Ligands. Phosphino carboxylic acid esters $Ph_2P(CH_2)_nC(O)OR$ were prepared by the procedure reported by Meijboom and van Doorn for the acids.[28] After evaporation of the ammonia solvent, the reaction mixture was worked up with methylene chloride/water, and the products were distilled through a 5 cm column at 0.01 mbar (bp 120−130 °C). Ethyl *o*-(diphenylphosphino)benzoate was prepared by esterification of the corresponding acid,[29] using DCC.[30] (2-(Diphenylphosphino)ethyl)diphenylphosphine oxide was prepared similarly to reported procedures.[31] NMR and IR data of the ligands have previously been reported.[31,32]

General Procedure for Preparation of Cationic P^O-Coordinated Allyl Complexes. A solution of 1.00 equiv of the P,O-ligand in methylene chloride (*ca.* 10 mL) was added to a methylene chloride solution (*ca.* 10 mL) of 1−2 mmol of $[(C_3H_5)PdI]_2$. After it was stirred for 30 min, the solution was transferred to a round-bottom flask containing 1.01 equiv of $AgSbF_6$. After it was stirred vigorously for 5 min, the mixture was filtered through celite on a frit into a flask kept at −20 °C. The succeeding workups are given below for the individual compounds; alternately, all compounds could be obtained in satisfying purity by removing the solvent from the filtrate *in vacuo*. The complexes were stored at −20 °C.

(η³-Allyl)[ethyl 3-(diphenylphosphino)propionate-κ²*P*,*O*]palladium(II) Hexafluoroantimonate (2[SbF₆]). A 1.0116 g amount of $[(C_3H_5)PdI]_2$ (1.843 mmol), 1.0546 g of $Ph_2P(CH_2)_2C(O)OEt$ (3.683 mmol), and 1.2776 g of $AgSbF_6$ (3.718 mmol) were reacted by the general procedure given above. The filtrate was concentrated *in vacuo* and layered with 20 mL of pentane. Upon storage at −78 °C, a yellow oil formed, which slowly crystallized. The supernatant was decanted, and the crystals were washed with pentane. Drying *in vacuo* at −10 °C yielded 2.31 g (94%) of yellow, microcrystalline powder. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.2−7.6 (m, 10 H; H_{arom}), 5.88−5.98 (m, 1H; H^5), 5.15 (t, $^3J(H^1,H^5) = {}^3J(H^1,P) = 7$ Hz, 1H; H^1), 4.36 (q, $^3J(H,H) = 7$ Hz, 2H; OCH_2), 4.28 (dd, $^3J(H^2,H^5) = 14$ Hz, $^3J(H^2,P) = 9$ Hz, 1H; H^2), 3.66 (br s, 1H; H^4), 2.90 (br s, 1H; H^3), 2.57−2.83 (br m, 4H; CH_2CH_2), 1.34 (t, $^3J(H,H) = 7$ Hz, 3H; CH_3). ^{13}C NMR (50 MHz, CH_2Cl_2): 180.9 (CO), 130.1−133.1 (C_{arom}), 121.8 (d, $^2J(C,P) = 5$ Hz; C^2_{allyl}), 88.2 (d, $^2J(C,P) = 26$ Hz; C^1_{allyl}), 65.8 (OCH_2), 50.5 (C^3_{allyl}), 29.3 (C^α), 20.8 (d, $^1J(C,P) = 25$ Hz; C^β), 13.9 (CH_3). ^{31}P NMR (81 MHz, CD_2Cl_2): δ +22.6 ppm. IR (CH_2Cl_2): ν 1655 cm^{-1} (CO), 660 cm^{-1} (ν_3 SbF_6^-). Anal. Calcd for $C_{20}H_{24}F_6O_2PPdSb$: C, 35.88; H, 3.61. Found: C, 35.81; H, 3.55.

(η³-Allyl)[ethyl *o*-(diphenylphosphino)benzoate-κ²*P*,*O*]palladium(II) Hexafluoroantimonate (3[SbF₆]). 0.9646 g $[(C_3H_5)PdI]_2$ (1.758 mmol), 1.1750 g of *o*-$Ph_2PC_6H_4C(O)OEt$ (3.514 mmol), and 1.2145 g of $AgSbF_6$ (3.534 mmol) were reacted by the general procedure given above. The filtrate was concentrated *in vacuo*, and the product was then precipitated as a powder by slow addition of 40 mL of pentane. The supernatant was decanted, and the solid was washed with pentane. Drying *in vacuo* at −10 °C yielded 2.05 g (81%) of **3**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29, 7.69, 7.64, and 7.09 (m, 1H each; $PC_6H_4C(O)O$), 7.49−7.60 (m, 10 H; H_{Phenyl}), 5.95−6.04 (m, 1H; H^5), 5.11 (t, $^3J(H,H) = {}^3J(H,P) = 7$ Hz, 1H; H^1), 4.45 (q, $^3J(H,H) = 7$ Hz, additional 1 Hz coupling or diastereomeric conformations, 2H; OCH_2), 4.27 (dd, $^3J(H,H) = 14$ Hz, $^3J(H,P) = 9$ Hz, 1H; H^2), 3.51 (br s, 1H; H^4), 3.11 (br d, $^3J(H,H) = 10$ Hz, 1H; H^3), 1.33 (t, $^3J(H,H) = 7$ Hz, 3H; CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.3 (CO), 129.5−134.4 (C_{arom}), 121.7 (d, $^2J(C,P) = 5$ Hz; C^2_{allyl}), 86.3 (d, $^2J(C,P) = 27$ Hz; C^1_{allyl}), 65.8 (OCH_2), 52.5 (d, $^2J(C,P) = 2$ Hz; C^3_{allyl}), 13.6 (CH_3). ^{31}P NMR (202 MHz, $CDCl_3$): δ +22.3 ppm. IR (CH_2Cl_2): ν 1641 (C═O), 660 cm^{-1} (ν_3 SbF_6^-). Anal. Calcd for $C_{24}H_{24}F_6O_2PPdSb$: C, 40.17; H, 3.37. Found: C, 40.09; H, 3.51.

(η³-Allyl)[(2-(diphenylphosphino)ethyl)diphenylphosphine oxide-κ²*P*,*O*]palladium(II) Hexafluoroantimonate (4[SbF₆]). A 0.5266 g amount of $[(C_3H_5)PdI]_2$ (0.960 mmol), 0.7953 g of $Ph_2P(CH_2)_2P(═O)Ph_2$ (1.919 mmol), and 0.6633 g of $AgSbF_6$ (1.930 mmol) were reacted by the general procedure given above. The filtrate was concentrated *in vacuo* and layered with 20 mL of pentane. Storage at −78 °C yielded a microcrystalline solid. The supernatant was decanted, and the solid was washed with pentane. Drying *in vacuo* at −10 °C yielded 1.27 g (83%) of **4**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44−7.82 (m, 20 H; H_{arom}), 5.80−5.89 (m, 1H; H^5), 5.06 (t, $^3J(H^1,H^5) = {}^3J(H^1,P) = 7$ Hz, 1H; H^1), 4.16 (dd, $^3J(H^2,H^5) = 14$ Hz, $^3J(H^2,P) = 9$ Hz, 1H; H^2), 3.25 (br d, $^3J(H^4,H^5) = 5$ Hz, 1H; H^4), 2.66−2.82 (m, 5H; CH_2CH_2 and H^3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 127.6−133.5 (C_{arom}), 120.4 (d, $^2J(C,P) = 5$ Hz; C^2_{allyl}), 85.5 (d, $^2J(C,P) = 27$ Hz; C^1_{allyl}), 51.4 (d, $^2J(C,P) = 2$ Hz; C^3_{allyl}), 23.3 (dd, $^1J(C,P) = 70$ Hz, $^2J(C,P) = 2$ Hz; $CH_2P(═O)$), 19.8 (dd, $^1J(C,P) = 25$ Hz, $^2J(C,P) = 6$ Hz; CH_2PPh_2). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 48.6 (d, $^3J(P,P) = 7$ Hz; P═O), 19.8 (d, $^3J(P,P) = 7$ Hz; CH_2PPh_2). IR (CH_2Cl_2): ν 1127 (P═O), 660 cm^{-1} (ν_3 SbF_6^-). Anal. Calcd for $C_{29}H_{29}F_6OP_2PdSb$: C, 43.67; H, 3.66. Found: C, 43.90; H, 3.96.

IR Spectroscopic Experiments. The starting complex was placed in a Schlenk tube and dissolved in methylene chloride (1−3 mL) to yield a 0.03−0.06 M solution. After an IR spectrum was obtained, the reagent was added. Liquid substrates were dosed with an Eppendorf pipet. Gaseous reagents were bubbled through the solution; slow bubbling was continued during the entire experiment to maintain a sufficient concentration. During the experiment small samples were withdrawn and an IR spectrum was obtained immediately (using a normal cell with KBr windows).

NMR Spectroscopic Experiments. The allyl complex was dissolved in CD_2Cl_2 (0.8 mL) in an NMR tube capped with a septum to yield a 0.075 M solution. After a spectrum was acquired, ethylene or carbon monoxide was bubbled briefly

(26) Tatsuno, Y.; Yoshida, T.; Seiotsuka *Inorg. Synth.* **1979**, *19*, 220−221.

(27) Tibbetts, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1969**, *91*, 1108−1112.

(28) van Doorn, J. A.; Meijboom, N. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *42*, 211−222.

(29) Hoots, J. E.; Rauchfuss, T. B.; Wrobleski, D. A. *Inorg. Synth.* **1982**, *21*, 175−179.

(30) (a) Neises, B.; Steglich, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 522−524. (b) Trost, B. M.; van Vranken, D. L.; Bingel, C. *J. Am. Chem. Soc.* **1992**, *114*, 9327−9343.

(31) (a) Abatjoglou, A. G.; Kapicak, L. A. Eur. Pat. Spec. 72560, 1982. (b) Higgins, S. J.; Taylor, R.; Shaw, B. L. *J. Organomet. Chem.* **1987**, *325*, 285−292.

(32) Spectroscopic data for $Ph_2P(CH_2)_nC(O)OR$: (a) Podlaha, J.; Jegorov, A.; Budesinsky, M.; Hanus, V. *Phosphorus Sulfur Silicon Relat. Elem.* **1988**, *37*, 87−93. (b) Blinn, D. A.; Button, R. S.; Farazi, V.; Neeb, M. K.; Tapley, C. L.; Trehearne, T. E.; West, S. D.; Kruger, T. L.; Storhoff, B. N. *J. Organomet. Chem.* **1990**, *393*, 143−152. For complete ^{1}H, ^{13}C, and ^{31}P NMR data for all ligands, *cf.* ref 19.

through the solution at −30 °C *via* a cannula, and the sample was transferred to the precooled probe. For ^{13}C NMR, 0.1−0.2 M solutions in CH_2Cl_2 (4 mL, 10 mm NMR tube) were used. To confirm the identity of species observed in NMR- and IR-experiments, IR spectra of NMR reaction solutions were obtained.

(η^3-Allyl)(η^2-ethylene)[ethyl 3-(diphenylphosphino)-propionate-κ^1P]palladium(II) Hexafluoroantimonate (2-E[SbF_6]). ^1H NMR (500 MHz, CD_2Cl_2, −30 °C): δ 7.44−7.63 (m, 10H; H_{arom}), 5.57−5.66 (m, 2H; H^1 and H^5), 5.1 (br s; average of bound and free ethylene (total 3 equiv)), 4.60 (m, 1H; H^4), 4.07 (q, $^3J(H,H) = 7$ Hz, 2H; OCH_2), 3.68 (dd, $^3J(H^2,H^5) = 13$ Hz, $^3J(H^2,P) = 9$ Hz, 1H; H^2), 3.56 (d, $^3J(H^3,H^5) = 12$ Hz, 1H; H^3), 2.96 (q ≡ dt, $^3J(H,P) = {}^3J(H,H) = 8$ Hz, 2H; $C^\alpha H_2$), 2.50 (q ≡ dt, $^2J(H,P) = {}^3J(H,H) = 8$ Hz, 2H; $C^\beta H_2$), 1.21 (t, $^3J(H,H) = 7$ Hz, 3H; CH_3). ^{31}P NMR (202 MHz, CD_2Cl_2, −30 °C): δ +16.8. IR (CH_2Cl_2): ν 1732 cm^{-1} (CO).

((1,2,5-η^3)-Pent-1-en-5-yl)[ethyl 3-(diphenylphosphino)-propionate-κ^2P,O]palladium(II) Hexafluoroantimonate (5[SbF_6]). ^1H NMR (500 MHz, CD_2Cl_2): δ 7.55−7.66 (m, 10H; H_{arom}), 7.06 (dddt, $^3J(H,H_{cis}) = 17$ Hz, $^3J(H,H_{trans}) = 9$ Hz, $^3J(H,H_{vic}) = 6$ Hz, $^3J(H,P) = 1.5$ Hz, 1H; =CH), 5.61 (br d, $^3J(H,H_{=CH}) = 17$ Hz, 1H; C=CHH_{cis}), 5.42 (ddd, $^3J(H,H_{=CH}) = 9$ Hz, $^3J(H,P) = 3$ Hz, $^2J(H,H) = 2$ Hz, 1H; C=CHH_{trans}), 4.26 (q, $^3J(H,H) = 7$ Hz, 2H; OCH_2), 2.54−2.64 (m, 4H; PCH_2CH_2), 2.2 (very br s, 2H; CH_2CH=), 1.86 (q ≡ dt, $^3J(H,H) = {}^3J(H,P) = 6$ Hz, 2H; Pd−CH_2), 1.74 (br, 2H; Pd−CH_2CH_2), 1.31 (t, $^3J(H,H) = 7$ Hz, 3H; CH_3). At −10 °C, two seperate broad signals at δ 2.41 and 1.96 are observed for the diasterotopic allylic protons. Coalescence occurs at *ca.* +17 °C (300 MHz). ^{13}C NMR (50 MHz, CH_2Cl_2−CD_2Cl_2): δ 178.9 (CO), 140.8 (d, $^2J(C,P) = 5$ Hz; −CH=), 130.0−134.4 (C_{arom}), 105.8 (d, $^2J(C,P) = 10$ Hz; =CH_2), 65.0 (OCH_2), 36.0, 35.1, and 32.8 (CH_2CH_2-CH_2), 28.8 (C^α), 22.0 (d, $^1J(C,P) = 28$ Hz; C^β), 13.9 (CH_3). ^{31}P NMR (202 MHz, CD_2Cl_2): δ +26.6. IR (CH_2Cl_2): ν 1664 cm^{-1} (CO).

The reaction **2-E** → **5** was monitored by IR spectroscopy by the general procedure given above. When the solvent was removed *in vacuo* or by precipitation with pentane, **5** was obtained as an off-white solid. The compound was dried *in vacuo* and stored at −20 °C. For attempted crystallization and purification *cf.* Results and Discussion.

(η^3-Allyl)(carbonyl)[ethyl 3-(diphenylphosphino)propionate-κ^1P]palladium(II) Hexafluoroantimonate (2-CO-[SbF_6]). Solutions of the complex were prepared by the above general procedures for spectroscopic experiments at room temperature, using 10% ^{13}CO-enriched carbon monoxide. ^{13}C NMR (50 MHz, CH_2Cl_2): δ 180.5 (Pd−CO), 171.6 (d, $^3J(C,P) = 14$ Hz; *C*(O)OEt), 129.4−132.9 (C_{arom}), 125.9 (d, $^2J(C,P) = 5$ Hz; C^2_{allyl}), 82.5 (d, $^2J(C,P) = 22$ Hz; C^1_{allyl}), 74.3 (C^3_{allyl}), 61.7 (OCH_2), 29.4 (C^α), 23.9 (d, $^1J(C,P) = 27$ Hz; C^β), 14.2 (CH_3). IR (CH_2Cl_2): ν 2135 (^{12}CO), 2087 (^{13}CO), 1732 cm^{-1} (CO of C(O)-OEt).

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Supporting Information Available: A plot showing data for kinetic experiments and the H,H-COSY spectrum of **5** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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