Characterization and Dynamics of $[Pd(L-L)H(solv)]^+$, $[Pd(L-L)(CH_2CH_3)]^+$, and $[Pd(L-L)(C(O)Et)(THF)]^+$ (L−L = 1,2-$(CH_2PBu^t_2)_2C_6H_4$): Key Intermediates in the Catalytic Methoxycarbonylation of Ethene to Methylpropanoate

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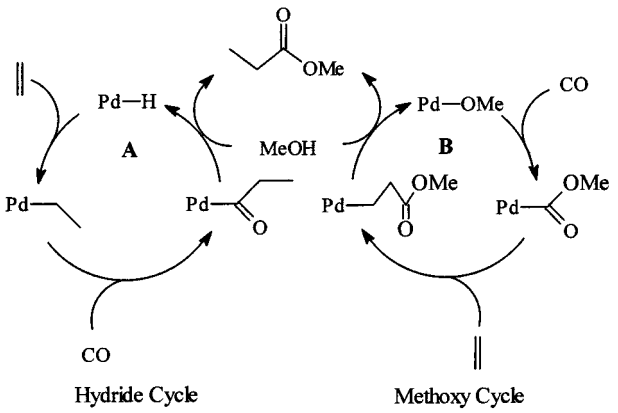
A detailed spectroscopic study has allowed the solution structure and dynamic properties of *all* the intermediates in the Pd-catalyzed methoxycarbonylation of ethene to be established. $[Pd(L-L)H(solv)]^+$ **1** (L−L = 1,2-$(CH_2PBu^t_2)_2C_6H_4$; solv = MeOH, **1a**; Pr^nOH, **1b**; THF, **1c**; EtCN, **1d**) is static, and the two inequivalent P atoms do *not* become equivalent through solvent exchange over all the temperatures studied. $[Pd(L-L)(CH_2CH_3)]^+$, **2**, contains a strong β-agostic C−H interaction which is remarkably stable and is not displaced even in strongly coordinating solvents such as EtCN. C_α and C_β of the ethyl group in **2** become equivalent via a stereospecific interchange involving $[Pd(L-L)H(\eta^2\text{-}C_2H_4)]^+$ without making the two P atoms equivalent; at higher temperatures these two inequivalent P atoms do become equivalent probably via a T-shaped intermediate. For $[Pd(L-L)(C(O)Et)(solv)]^+$, **6**, there is *no* β-agostic C−H interaction and multiple ^{13}C-labeling of the C(O)Et group shows that the inequivalent P atoms become equivalent via movement of the *intact* C(O)Et group. The crystal structure of the related complex [Pd(L−L)(C(O)Et)Cl] cocrystallized with dibenzylacetone has been determined.

Introduction

The methoxycarbonylation of ethene to form methylpropanoate (MP), using a palladium phosphine catalyst, is currently being developed by Ineos Acrylics as part of a novel two-stage route to methyl methacrylate (MMA).[1] This process employs a highly sterically hindered diphosphine ligand and results in the formation of MP with high turnover and selectivity (99.98%).[2] We have shown previously that the formation of MP employing this novel bis-phosphine ligand occurs via a catalytic mechanism involving a Pd(II) hydride (**A**) rather than the "methoxycarbonyl" cycle (**B**) [3] (see Scheme 1). Herein, we report a detailed spectroscopic analysis of the structure and dynamics of *all* the intermediates $[Pd(L-L)H(solv)]^+$, $[Pd(L-L)(CH_2CH_3)]^+$, and $[Pd(L-L)(C(O)Et)(THF)]^+$ involved in the catalytic cycle.

Scheme 1



Results and Discussion

Synthesis and Characterization of $[Pd(L-L)(CH_2CH_3)]^+$, 2a. Previous work [3] showed that $[Pd(L-L)H(MeOH)]^+$, **1a**, is formed on oxidation of [Pd(L−L)(dba)] [dba = *trans,trans*-$(PhCH{=}CH)_2CO$; L−L = 1,2-$(CH_2PBu^t_2)_2C_6H_4$, d^tbpx] in MeOH in the presence of an acid; the *quantitative* preparation of other analogues, containing different solvent molecules, may be

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(1) New MMA Technology, European Chemical News, Oct 30−Nov 5, 2000; p 20.
(2) Clegg, W.; Eastham, G. R.; Elsegood, M. R. J.; Tooze, R. P.; Wang, X. L.; Whiston, K. W. *Chem. Commun.* **1999**, 1877.
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Table 1. ^{31}P NMR Data for [Pd(L−L)H(solv)]$^+$ and [Pd(L−L)CH$_2$CH$_3$]$^+$ at 193 K

	[Pd(L−L)H(solv)]$^+$ **1**			[Pd(L−L)CH$_2$CH$_3$]$^+$ **2a**		
solvent	$\delta_{P(A)}$	$\delta_{P(B)}$	$^2J_{PP}$	$\delta_{P(A)}$	$\delta_{P(B)}$	$^2J_{PP}$
MeOH	75.5	21.8	16.1	67.7	36.3	31.0
^{n}PrOH	68.5	19.4	17	67.5	36.1	br
THF	72.8	21.6	18.1	67.9	37.1	31.5
EtCN	67.1	21.1	19.8	67.1	36.4	31.5

more easily accomplished via the reaction shown in eq 1.

$$[Pd(L{-}L)(O_3SCF_3)_2] \xrightarrow[(ii)]{(i)} [Pd(L{-}L)H(solv)]^+ + HO_3SCF_3 \quad (1)$$

solv = Pr^{n}OH, **1b**

= THF, **1c**

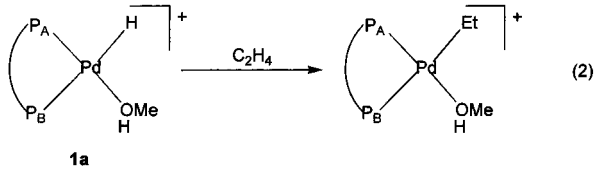
= EtCN, **1d**

(i) + MeOH followed by evacuation

(ii) + solv (Pr^{n}OH, THF or EtCN)

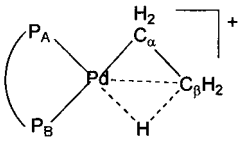
Consistent with our previous assignment of the inequivalent phosphorus atoms in **1a**,[3] there is a significant change in the value of $\delta_{P(A)}$ (trans to solvent) on varying the solvent in **1a**−**d** (see Table 1), whereas $\delta_{P(B)}$ remains relatively unchanged. In all cases, on the NMR time scale, there is *no* evidence for solvent exchange, which would allow P_A and P_B to become equivalent, until well above room temperature.

Previous work showed that **1a** reacts immediately with ethene and the product was formulated as shown in eq 2. Using mono-^{13}C-labeled ethene, it was possible



1a (2)

to assign unambiguously the two inequivalent phosphorus resonances, and a reasonable assumption was to assign the fourth coordination site in the palladium−ethyl complex to MeOH. However, subsequent work on analogous reactions with **1b**−**d** suggests that the formulation of the ethyl complex in eq 2 should be revised. Thus, unlike **1a**−**d**, there is little variation in the chemical shifts of P_A and P_B with different solvents (see Table 1), and this behavior is more consistent with occupancy of the fourth coordination site in **2a** being due to a β-C−H interaction as shown below:



2a

Protonation of [Pd(L−L)(C$_2$H$_4$)] to give **2a** has been reported previously by Spencer et al.,[4] but, unfortunately, no NMR data were reported. Further support for this formulation of **2a** comes from examination of both the ^{13}C chemical shifts and C−H coupling constants, obtained by reacting **1a** with ^{13}CH$_2$=CH$_2$ (1 equiv) in MeOH when two different isotopomers are formed in the ratio 1:1, i.e., [Pd(L−L)(CH$_2{}^{13}$CH$_3$)]$^+$, **2b**, and [Pd(L−L)(^{13}CH$_2$CH$_3$)]$^+$, **2c**. In the isotopomer **2b**, P_A couples only with P_B (the coupling with C_β is too small to be resolved), and, hence, the expected signal is a doublet with $^2J_{P(A)P(B)}$ = 31 Hz, as found in the unenriched compound, **2a**. For the isotopomer **2c**, P_B couples with both P_A [$^2J_{P(A)P(B)}$ = 31 Hz] and the trans ^{13}C atom [$^2J_{P(B)C(\alpha)}$ = 38 Hz], resulting in a doublet of doublets. In solution, there is an equal amount of the two isotopomers **2b** and **2c**, but, because **2c** gives four equally intense resonances and **2b** only two, the intensity of each of the resonances due to **2c** is one-half the intensity of each of the resonances due to **2b**. Hence, the resulting signal for P_B is a multiplet consisting of six lines, with relative intensities 1:2:1:1:2:1, as observed in the experimental spectrum. In the ^{13}C{^{1}H} NMR spectrum at 193 K, C_α resonates at 31 ppm as a doublet of doublets [$^2J_{C(\alpha)P(B)}$ = 38 Hz, $^2J_{C(\alpha)P(A)}$ = 5 Hz], whereas C_β gives a singlet at 8 ppm. Finally, in the proton-coupled ^{13}C NMR spectrum at 193 K, the resonance at 8 ppm appears as a quartet [$^1J_{C(\beta)H}$ = 124 Hz], and that at 31 ppm as a triplet of doublets [$^1J_{C(\alpha)H}$ = 158 Hz, $^2J_{C(\alpha)P(B)}$ = 38 Hz], in perfect agreement with our assignments. In classical Pd−ethyl complexes,[5] $\delta(CH_3) > \delta(CH_2)$, but for **2a**−**c** $\delta(CH_2)$ and $\delta(CH_3)$ are at 31 and 8 ppm, respectively; this reversal of the CH_2 and CH_3 chemical shifts between classical and nonclassical metal−ethyl complexes is also found for [Pt(L−L)(CH$_2$-CH$_3$)]$^+$, which also contains a C_β−H agostic interaction.[6] In this case [δ_{CH2}, 22.0; δ_{CH3}, 8.2], it was possible to freeze out (145 K) the rotation of the $C_\beta H_3$ group and obtain two different values of $^1J_{C(\beta)H}$ in the ^{13}C NMR spectrum. In the ^{13}C NMR of **2b**−**c**, it was not possible, even at 145 K, to freeze out the $C_\beta H_3$ rotation to obtain the static isomer of **2**. Nevertheless, this agostic interaction is also supported by consideration of the values of $^1J_{C(\alpha)H}$, which are normally ca. 130 Hz for classical ethyl complexes but increase to ca. 155 Hz when there is an agostic interaction.[7]

The NMR data reported in Table 1 also suggest that the agostic interaction is retained in all the solvents examined, even in a strongly coordinating solvent such as EtCN. To confirm this, the reaction between [Pd(L−L)H(EtCN)]$^+$, **1d**, and ^{13}CH$_2$=CH$_2$ in EtCN has been studied. The data in EtCN are very similar to those obtained in MeOH (see Table 2), confirming the

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(6) Mole, L.; Spencer, J. L.; Carr, N.; G. Orpen, A. *Organometallics* **1991**, *10*, 49. Carr, N.; Mole, L.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Dalton Trans.* **1992**, 2653.

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Table 2. NMR Data at 193 K for [Pd(d^{t}bpx)(CH_2CH_3)]$^+$, 2a, in MeOH and EtCN

	MeOH	EtCN
$\delta_{P(A)}$	36.3	36.4
$\delta_{P(B)}$	67.7	67.1
$\delta_{C(\alpha)}$	31.0	31.8
$\delta_{C(\beta)}$	7.9	9.3
$^2J_{P(A)P(B)}$	31.1	31.5
$^2J_{P(A)C(\alpha)}$	38.0	39.8
$^2J_{P(B)C(\alpha)}$	5	5.5
$^1J_{C(\alpha)H}$	158	157
$^1J_{C(\beta)H}$	124	*a*

[a] Obscured by the solvent.

presence of the agostic interaction. This behavior is unexpected, since agostic interactions are usually relatively weak.

Dynamics of [Pd(L−L)(CH_2CH_3)]$^+$, 2a. It has been shown above that the methyl protons of the ethyl substituent in **2a**−**c** are equivalent on the NMR time scale, even at 145 K, due to the very low-energy barrier for the rotation of the methyl group. A similar behavior has been observed by Spencer in the study of analogous platinum complexes.[6] The rotation can occur with or without full dissociation of the agostic interaction, as described by Green and Wong.[8]

In addition to the low-energy $C_\beta H_3$ rotation described above, **2a**−**c** undergo a higher energy exchange process which still occurs below room temperature. The $^{31}P\{^1H\}$ NMR spectra of a 1:1 mixture of **2b** and **2c** in MeOH from 183 to 293 K are shown in Figure 1, and it is important to note that the two resonances due to P_A and P_B (see Scheme 2) change in a different way.

The resonance due to P_A is always a well-resolved doublet from 183 to 283 K and only starts to broaden at 293 K. This should be contrasted with the behavior of the resonance due to P_B; from 183 to 233 K, it is clearly a 1:2:1:1:2:1 multiplet, which starts to broaden at 243 K. At 248 K there is complete coalescence, and from 253 to 283 K, it becomes a doublet of doublets, with $^2J_{PP} = 31$ Hz and $^{av}J_{PC} = 19$ Hz. Finally, at 293 K, the resonance due to P_B starts to broaden again. The mechanism responsible for the room-temperature broadening will be discussed later. Consider now the mechanism responsible for the process occurring between 248 and 283 K, which clearly only affects the resonance due to P_B. It is possible to explain the observed changes by an exchange process which scrambles the two carbons of the ethyl group (see Scheme 2).

This interesting stereospecific interchange process can only be detected in this case through the VT NMR measurements on the monolabeled ethyl complex, and in the fast exchange limit (ca. 263 K) between the two isotopomers in Scheme 2, $^{av}J_{PC} = (38 + 0)/2 = 19$ Hz, as observed experimentally. As expected for such a process, the $^{13}C\{^1H\}$ resonances due to the methyl and methylene groups both broaden and then coalesce (δ ca. 18) with increasing temperature. Spencer has shown that for analogous platinum complexes[6] the carbon atoms of the ethyl group, which are inequivalent at low temperature, also become equivalent on increasing the temperature. It is usually accepted that the C_α/C_β scrambling process occurs via an equilibrium between

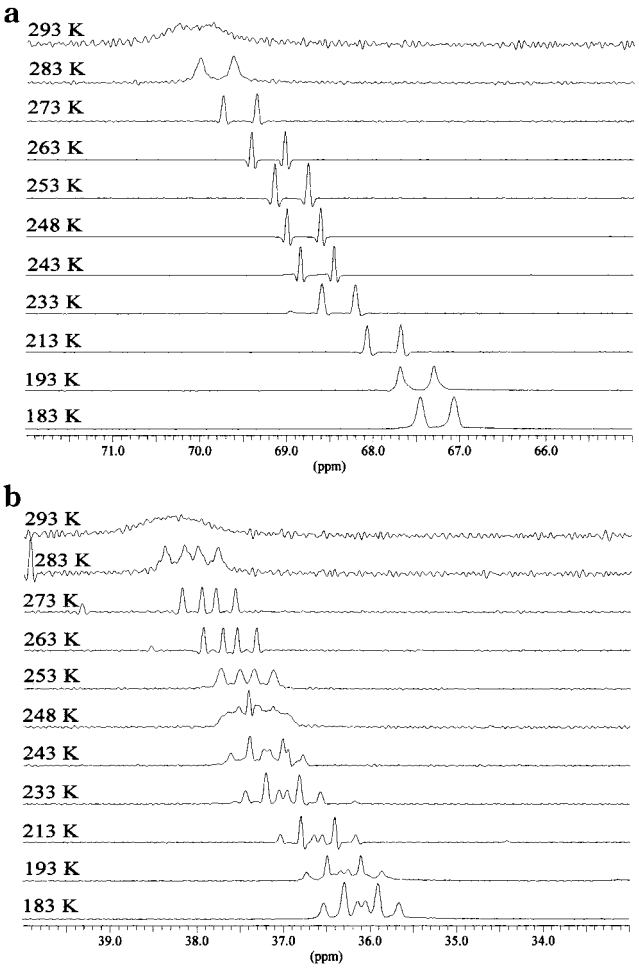


Figure 1. VT $^{31}P\{^1H\}$ NMR spectra of **2**, which has been prepared from **1a** + $^{13}CH_2{=}^{12}CH_2$ and contains 50% ^{13}C at both the C_α and C_β positions: (a) P_A resonance and (b) P_B resonance (see text for labeling scheme).

the ethyl−agostic complex and a hydride ethene complex, which readily undergoes ethene rotation (see Scheme 2). In some cases, the occurrence of such an equilibrium has been proved experimentally.[7,9] The electronic and steric properties of the ligand significantly influence the position of the equilibrium between the ethene hydride and the agostic−ethyl complex shown in Scheme 2, but the energy difference between the two forms is usually quite small, and this explains why the C_α/C_β scrambling of the ethyl group occurs at low temperature.

Above ca. 283 K, there is a gradual broadening of the resonances due to P_A and P_B in **2a** until at 353 K there is only one resonance at 54 ppm; this coalescence is concomitant with the appearance of resonances due to **1a** as a result of the equilibrium shown in eq 3.

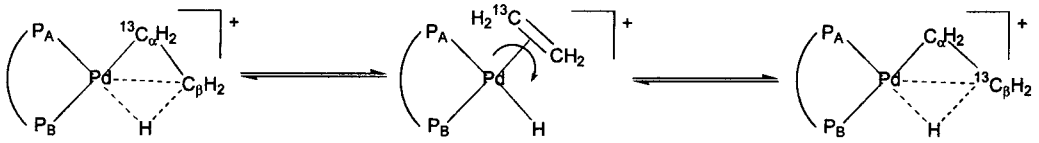
$$\underset{\textbf{2a}}{[Pd(L{-}L)CH_2CH_3]^+} \overset{MeOH}{\rightleftharpoons} \underset{\textbf{1a}}{[Pd(L{-}L)H(MeOH)]^+} + C_2H_4 \quad (3)$$

Nevertheless, there is a differential broadening of the resonances due to **1a** and **2a** in this temperature region, which suggests that P_A and P_B in **2a** may become

(8) Green, M. L. H.; Wong, L. L. *Chem. Commun.* **1988**, 677.

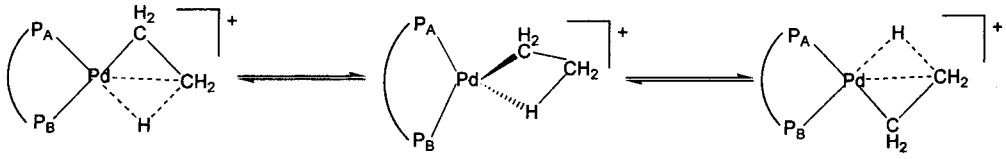
(9) Werner, H.; Feser, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 157.

Scheme 2

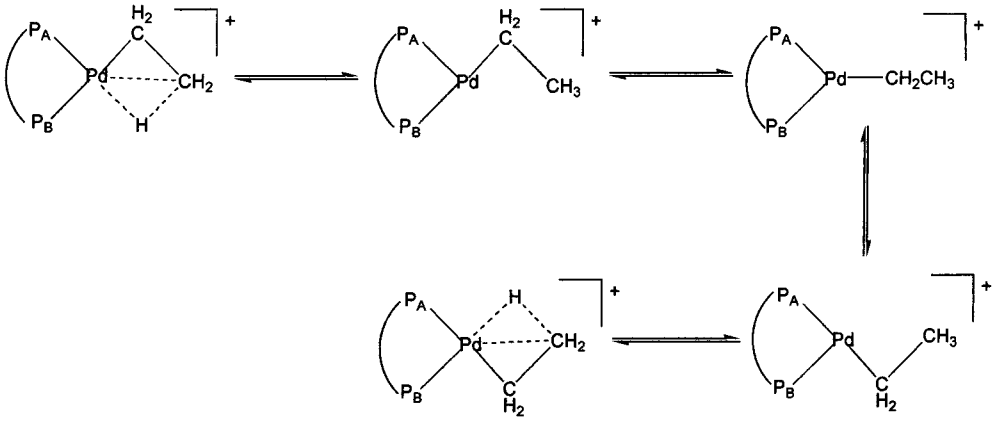


Scheme 3

A) Non-dissociative mechanism



B) Dissociative mechanism



equivalent. Two different mechanisms can be proposed in order to explain the equivalence of the P atoms of **2a** at high temperature (see Scheme 3). The first mechanism, A, involves a non-dissociative intramolecular rearrangement of **2a** via a tetrahedral intermediate, and the second mechanism, B, requires the reversible disruption of the strong agostic interaction to generate a 14-electron T-shaped intermediate, which allows interconversion via a Y-shaped species. Spencer[6] has proposed this second mechanism in order to explain a similar process in analogous platinum complexes. Romeo et al.[10] have claimed a dissociative mechanism involving internal rearrangement of T-shaped intermediates for explaining the cis−trans isomerization process in Pt(PR$_3$)$_2$(Me)$_2$. The theoretical possibility of this mechanism has been demonstrated by Thorn and Hoffman,[11] who made quantomechanical calculations on model platinum compounds. They calculated a very low activation energy for the T−Y interconversion, whereas all the experimental data suggest a higher value. This possibly stems from the very simplistic model adopted in the calculation (i.e., [PtH(PH$_3$)$_3$]$^+$), since Yamamoto's experimental work suggests a high activation energy for this process.[12]

It is also noteworthy that, on carrying out the same experiment on the ethyl complex **2a** in EtCN, the solvento hydride complex [Pd(L−L)H(EtCN)]$^+$, **1d**, is the main species present in solution even at 293 K, whereas in MeOH no hydride is present under the same conditions. This result clearly shows the importance of the solvent in determining the position of the equilibrium in eq 3. Moreover, the resonances due to **2a** are still well separated in both MeOH and EtCN at 293 K. This lends further support to the conclusion that the equilibrium in eq 3 and the process that makes the two P atoms equivalent in **2a** are independent.

Reactivity of [Pd(L−L)H(MeOH)]$^+$, 1a, with Higher α-Olefins. The hydride, **1a**, reacts in MeOH with other α-olefins, i.e., propene, 1-hexene, and 1-hexadecene. All these olefins insert at low temperature into the Pd−H bond and NMR spectroscopic experiments clearly indicate that only one insertion product is formed. By analogy with the reaction with ethene, these compounds can be formulated as [Pd(L−L)(CH$_2$C-H$_2$(CH$_2$)$_n$CH$_3$)]$^+$ (n = 0, **3**; 3, **4**; 13, **5**); only the linear isomer is formed, and this is obviously preferred for steric reasons. It is noteworthy that the catalytic system based on [Pd(L−L)(dba)], using conditions similar to those used for the methoxycarbonylation of ethene, is also active for the methoxycarbonylation of these higher α-olefins; significantly, only the linear ester is formed.

As found for the ethyl complex, **2a**, the alkyl−agostic complexes **3**−**5** exist in equilibrium with the hydride **1a**:

$$[\mathrm{Pd(L{-}L)(CH_2CH_2(CH_2)_nCH_3)}]^+ \overset{\mathrm{MeOH}}{\rightleftharpoons} [\mathrm{Pd(L{-}L)H(MeOH)}]^+ + \mathrm{C}_m\mathrm{H}_{2m} \quad (4)$$

n = 0, **3**; 3, **4**; 13, **5**; **1a**; m = 3, 6, 16

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(12) Yamamoto, A. *J. Chem. Soc., Dalton Trans.* **1999**, 1027.

Table 3. Equilibrium Constant (K_{eq}) for Different Linear α-Olefins (C_mH_{2m}) (see eqs 3 and 4)

m	K_{eq} at 193 K	K_{eq} at 293 K
2	0	0
3	0	7.5×10^{-3}
6	2.8×10^{-3}	0.56
16	0.77	∞

The values of K_{eq} calculated from the NMR data for the equilibria shown in eqs 3 and 4 at different temperatures are reported in Table 3. The position of the equilibrium strongly depends on the chain length of the olefin. At 293 K, the ethyl−agostic compound **2a** is the only product observed with ethene, whereas an appreciable amount of the hydride **1a** is present on using propene. $[Pd(L-L)H(MeOH)]^+$, **1a**, is the main product present in solution at 293 K with 1-hexene, and **1a** is the only product when 1-hexadecene is used. The fact that the position of this equilibrium strongly depends on the chain length of the alkyl substituent is probably connected with the fact that L−L is a highly sterically hindered ligand, which also contributes toward the very high selectivity for the formation of methyl propanoate. In the same context, it is noteworthy that **2a** does not react with excess ethene to give higher alkyl complexes. Moreover, it has been reported that the catalysts used for the formation of polyketones switch to the oligomerization of ethene when the reaction is carried out in the absence of CO;[13] in contrast, there is no evidence for ethene oligomerization using the catalytic system based on L−L under the same conditions.

Synthesis and Characterization of $[Pd(L-L)(C(O)Et)(THF)]^+$, 6b. $[Pd(L-L)(CH_2CH_3)]^+$, **2a**, reacts in MeOH under N_2 with 1 equiv of CO to give the hydride **1a** and MP. This results from reaction of **2a** with CO to give $[Pd(L-L)(C(O)Et)(MeOH)]^+$, **6a**, followed by rapid formation of the final products. This process is too fast to follow by NMR, even at low temperature, and thus it is not possible to distinguish between alternative mechanistic possibilities such as whether it proceeds by reductive elimination from the $[Pd(L-L)(C(O)Et)(MeOH)]^+$ complex, **6a**, to give a zerovalent palladium species first, and subsequently Pd−H by protonation at Pd(0), or whether reductive elimination and protonation proceed concertedly. Alternatively, it may be quite possible that the high basicity of the Pd(0) intermediate, as a consequence of the use of the very basic bis(di-*tert*-butylphosphine) ligand, is responsible for fast protonation at Pd(0) and the high stability of mononuclear Pd(L−L)H species.

To isolate and characterize the acyl complex, the reaction has been performed in nonalcoholic solvents. Thus, **2a** reacts in THF at low temperature with 1 equiv of CO, resulting in the formation of a new species which shows two doublets at δ 36.3 and 83.4 ($^2J_{PP} = 40$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum at 193 K. These NMR data indicate that the new species contains two cis inequivalent P atoms, in agreement with the formulation $[Pd(L-L)(C(O)Et)(THF)]^+$, **6b**. A related complex, [Pd(L−L)(C(O)Et)Cl], **7**, can be isolated from the reaction of [Pd(L−L)(dba)] with EtC(O)Cl in Et_2O, clearly showing

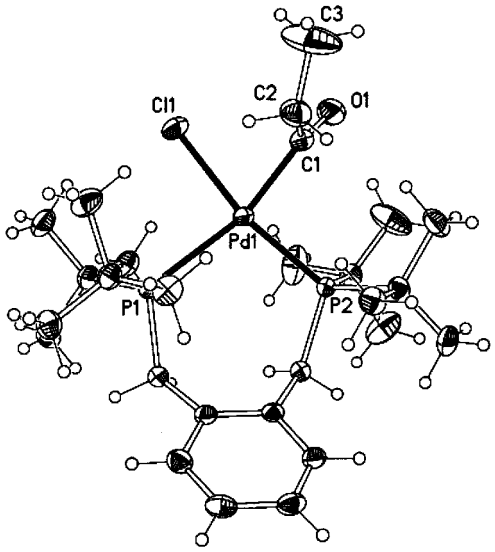

Figure 2. Molecular structure of [Pd(L−L)(C(O)Et)Cl], **7**, in its cocrystal with dba. Selected bond lengths (Å) and angles (deg): Pd1−P1 2.4812(9), Pd1−P2 2.3177(8), Pd1−Cl1 2.4135(9), Pd1−C1 2.010(4), P1−Pd1−P2 103.08(3), Cl1−Pd1−C1 77.42(10), P1−Pd1−C1 158.56(11), P2−Pd1−Cl1 158.37(3). Displacement ellipsoids are at the 50% probability level.

the availability of the fourth coordination site of the complex for occupancy by another ligand. The $^{31}P\{^1H\}$ NMR spectrum of **7** consists of two doublets at δ 15.1 and 44.2 ($^2J_{PP} = 52.6$ Hz), and the shift to lower field observed for **6b** is in accord with the substitution of an anionic ligand, Cl^-, by a neutral less basic molecule, THF. Crystals of **7** suitable for X-ray analysis have been obtained directly from the reaction mixture (see Figure 2), and a noteworthy feature of the structure is that **7** contains one of the longest Pd−phosphine bonds (2.4812(9) Å) reported to date,[14,15] trans to the acyl ligand. The difference in the two Pd−P bond lengths, 0.163 Å, is due to the strong trans-influence of the acyl compared to the chloride ligand. A similar effect, not quite as marked, is seen in a previously reported series of diphosphine complexes of palladium with acyl and chloride ligands cis to each other, in which the Pd−P bond trans to Cl ranges from 2.228 to 2.254 Å, and the Pd−P bond trans to acyl ranges from 2.340 to 2.410 Å.[16] Most square-planar complexes of palladium and platinum containing acyl and phosphine ligands adopt a cis rather than a trans arrangement of these ligands, but in platinum complexes the value of d(Pt−P) when trans to acyl is always greater that the value of d(Pt−P) when trans to Cl, H, Me, or P.[17]

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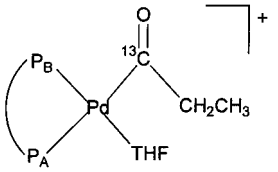
Table 4. NMR Data for the Isotopomers 6b−e of [Pd(d^{t}bpx)(C(O)Et)(THF)]$^+$ in THF at 193 K

	P_A	P_B	C_A	C_B	C_C
(a) NMR Chemical Shifts					
δ (ppm)	36.3	83.4	232	38.2	10.9
(b) Coupling Constants (Hz)					
P_A		40	84	23	
P_B	40		17	23	
C_A	84	17		23	3−4
C_B[a]	23	23	23		
C_C[a]			3−4		

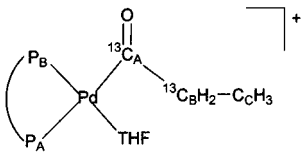
[a] $^1J_{C(B)H} = 133$, $^1J_{C(C)H} = 130$.

To establish unambiguously the structure and exchange processes occurring for **6b** in solution, ^{13}C-labeling of both the C(O) and/or Et groups within the acyl group have been carried out. For [Pd(L−L)(^{13}C(O)Et)(THF)]$^+$, **6c** (see below for labeling scheme) the two ^{31}P resonances at δ 36.3 and 83.4 can be assigned to P_A and P_B, respectively; both appear as doublets of doublets due to $^2J_{P(A)P(B)} = 40$ Hz, $^2J_{P(A)C} = 84$ Hz, and $^2J_{P(B)C} = 17$ Hz, and the much higher value of $^2J_{PC}$ clearly arises from the trans-coupling with P_A. The ^{13}C{^{1}H} NMR spectrum of **6c** has a resonance at δ ca. 232 due to the C(O) group.[18−20] The carbon spectrum is strongly temperature dependent, because of a dynamic process (see below). However, **6c** is completely static at 173 K and the C(O) resonance of the acyl group consists of a doublet of doublets, due to trans-$^2J_{P(A)C} = 84.0$ Hz and cis-$^2J_{P(B)C} = 17.0$ Hz.

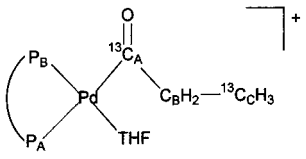


6c

A doubly ^{13}C-enriched acyl can be obtained in THF, THF/CH_2Cl_2, or EtCN on reaction of a 1:1 mixture of [Pd(L−L)($^{13}CH_2CH_3$)]$^+$, **2b**, and [Pd(L−L)($CH_2{}^{13}CH_3$)]$^+$, **2c**, with 1 equiv of ^{13}CO at 193 K. The products from this reaction are a 1:1 mixture of the two isotopomers [Pd(L−L)(^{13}C(O)$^{13}CH_2CH_3$)(THF)]$^+$, **6d**, and [Pd(d^{t}bpx)(^{13}C(O)$CH_2{}^{13}CH_3$)(THF)]$^+$, **6e** (see below for atom labeling).



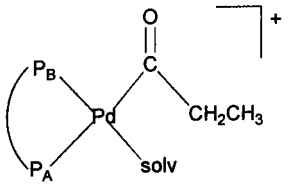
6d



6e

The NMR data of all the isotopomers **6a−e** at 193 K in THF are consistent with their static structures and are summarized in Table 4.

Table 5. NMR Data for [Pd(d^{t}bpx)(C(O)Et)(solv)]$^+$ (solv = THF, 6b; EtCN, 6f) and [Pd(L−L)(^{13}C(O)Et)(solv)]$^+$ (solv = THF, 6c; EtCN, 6g) at 193 K



	EtCN	THF
$\delta_{P(A)}$	20.2	36.4
$\delta_{P(B)}$	49.4	83.4
$\delta_{C(O)}$	233.2	232.0
$^2J_{P(A)P(B)}$	40	40
$^2J_{P(A)C}$	92	83.9
$^2J_{P(B)C}$	13	17.0

Noteworthy features include the following:

• The values for $^1J_{CH}$ are as expected for normal sp^3 carbons and are consistent with the absence of any significant β-C−H agostic interaction.

• Occupancy by THF of the fourth coordination site in [Pd(L−L)(C(O)Et)(THF)]$^+$ is supported by the large difference in ^{31}P chemical shifts at 193 K when THF is replaced by EtCN (see Table 5).

As far as we are aware, **6a−g** are the first examples in which a Pd−acyl complex containing a diphosphine and a labile solvent molecule have been unambiguously identified. Other authors have reported similar complexes, but they contain CO instead of solvent. For instance, Toth and Elsevier[19] have reported that the carbonylation of [Pd{(*S*,*S*′)-BDPP}(Me)(solv)]$^+$ [(*S*,*S*′)-BDPP = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane] results in the formation of [Pd{(*S*,*S*′)-BDPP}(C(O)Me)(CO)]$^+$ even on using a deficiency of CO. Moreover, they report that the reaction of [Pd{(*S*,*S*′)-BDPP}(C(O)Me)Cl] with $AgBF_4$ under N_2 results in a 1:1 mixture of [Pd{(*S*,*S*′)-BDPP}(C(O)Me)(CO)]$^+$ and [Pd{(*S*,*S*′)-BDPP}(Me)(solv)]$^+$. It is also interesting to note that carbonylation of [Pd(d^{i}ppe)(Me)(solv)]$^+$ results in the analogous species [Pd(d^{i}ppe)(C(O)Me)(CO)]$^+$;[21] in direct contrast, **6a−g** prefer solvent coordination rather than CO coordination, even in the presence of free CO. This is a very surprising experimental result, which is also interesting from a theoretical point of view, and one for which we have no obvious explanation.

Dynamics of [Pd(L−L)(C(O)Et)(THF)]$^+$. VT ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra of this complex show significant changes, and to obtain as much information as possible on the mechanism(s) responsible for these variations, we have examined the VT spectra of the isotopomers **6a−e**, which show consistent behavior.

The VT ^{13}C{^{1}H} NMR spectra in THF of the carbonyl resonance in the acyl group of the mono-^{13}C-enriched isotopomer, **6c**, are shown in Figure 3. At 193 K, this resonance is a doublet of doublets ($^2J_{P(A)C(A)} = 84$ Hz and $^2J_{P(B)C(A)} = 17$ Hz) due to the static structure, whereas at 243 K it is a triplet; the triplet spacing (50 Hz) is unchanged at different magnetic fields and must therefore arise from a time-averaged intraexchange

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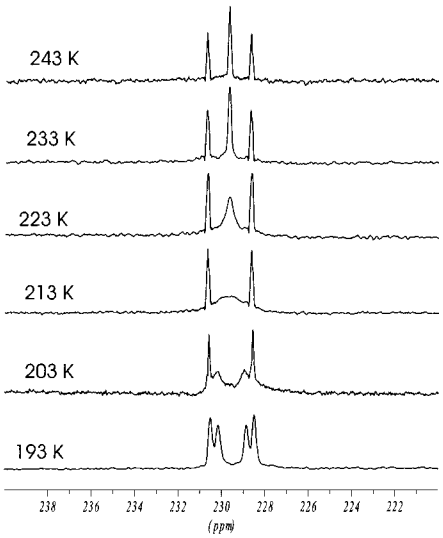


Figure 3. VT $^{13}C\{^1H\}$ NMR of $[Pd(L-L)(^{13}C(O)Et)(THF)]^+$, **6c,** in THF.

process which makes the cis- and trans-phosphorus atoms become equivalent. This is substantiated in the VT $^{31}P\{^1H\}$ NMR; the two sharp resonances at 173 K (δ 36.4 and 83.4) broaden and coalesce to give a single resonance (δ ca. 59, compare with $\delta_P{}^{mean}$ 60) at 256 K. In addition, with increasing temperature, resonances due to **2a** start to appear as a result of the equilibrium shown in eq 5.

$$[Pd(L-L)(C(O)Et)(THF)]^+ \rightleftharpoons \underset{\mathbf{6b}}{} \quad [\overbrace{Pd(L-L)(CH_2CH_3)}^{\mathbf{2a}}]^+ + CO + THF \qquad (5)$$

Nevertheless, over a wide temperature range (153−276 K) ^{31}P resonances due to the presence of both the acyl and ethyl complexes are clearly visible in all the isotopomers studied. For the reaction in eq 5, there is no spectroscopic evidence for the formation of $[Pd(L-L)Et(CO)]^+$ on variation of the ratio of Pd:CO ≤ 1:4 over the above temperature range.

VT $^{13}C\{^1H\}$ NMR spectra of a 1:1 mixture of **6d** and **6e** in CH_2Cl_2/THF are shown in Figure 4. These spectra are similar to those shown in Figure 3 and show additional couplings due to $^1J_{C(A)C(B)}$ and $^2J_{C(A)C(C)}$ (see Table 4). Of particular significance is the retention of these additional couplings over a wide temperature range. This shows that the intraexchange mechanism, which makes the two inequivalent P atoms become equivalent, must involve migration of the *intact* acyl group.

Two different mechanisms could account for the above spectroscopic changes. The first involves dissociation of the solvent and rearrangement of the T-shaped intermediate, and the second could involve an intraexchange of the square-planar complex via a tetrahedral intermediate. Reaction of [Pd(COD)(Me)Cl], **8**, with L−L and CO gives [Pd(L−L)(C(O)Me)Cl], **9** (eq 6). The $^{31}P\{^1H\}$ NMR spectrum of **9** at 196 K consists of two sharp doublets, whereas at 293 K they are broader but still separated. This suggests that the exchange process is

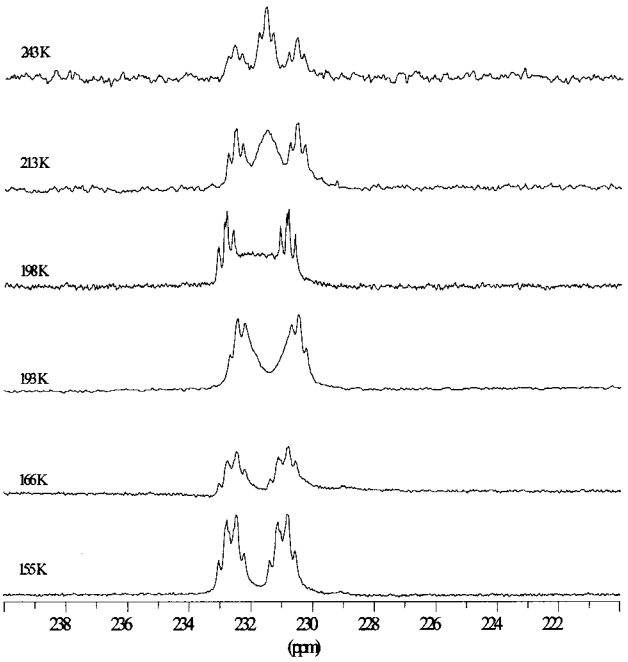
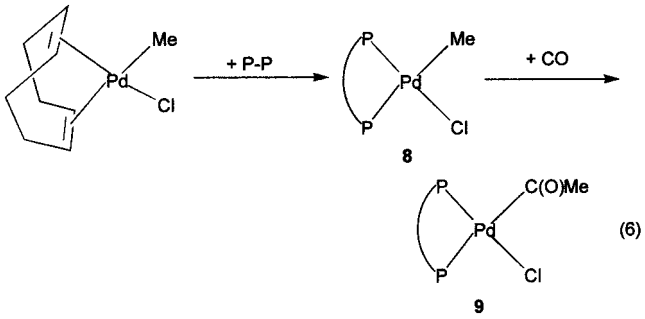


Figure 4. VT $^{13}C\{^1H\}$ NMR of a 1:1 mixture of $[Pd(L-L)(^{13}C(O)^{13}CH_2CH_3)(THF)]^+$, **6d**, and $[Pd(L-L)(^{13}C(O)CH_2{}^{13}CH_3)(THF)]^+$, **6e**, in CH_2Cl_2/THF.

slower for **9** than for **6b**−**e** and supports the dissociative mechanistic pathway.



Conclusions

In this paper, we have described different exchange processes of the intermediates involved in the hydride cycle of the catalytic methoxycarbonylation of ethene. Both the formation of $[\overbrace{Pd(L-L)(CH_2CH_3)}^{\mathbf{2a}}]^+$, **2a**, from $[Pd(L-L)H(MeOH)]^+$, **1a**, and the formation of $[Pd(L-L)(C(O)Et)(MeOH)]^+$, **6a**, involve facile equilibria, whereas the methanolysis of **6a** is an irreversible reaction and is probably the rate-determining step. This conclusion is supported by other authors who have studied the methoxycarbonylation of higher α-olefins.[22] Moreover, whereas the hydride complex **1a** is static over all the temperatures studied, the ethyl and the acyl complexes undergo a variety of intramolecular exchanges. In particular, for both the ethyl and acyl complexes there are exchange processes that equivalence the two P atoms, whereas the two P atoms in the hydride complex always remain inequivalent. Moreover, although this process occurs below room temperature in the acyl

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complex, it is not observed until 353 K in the ethyl complex. The reasons for these dramatic differences remain under investigation. In the case of exchange in the acyl complex, we have unambiguously shown that this process involves migration of the *intact* acyl group, a process that, as far as we are aware, has not been reported hitherto.

For the ethyl complex, two other low-temperature exchange processes have been characterized, i.e., the $C_\beta H_3$ rotation and the scrambling of the two C atoms of the ethyl group; the latter is stereospecific since the two P atoms remain inequivalent.

We have already shown[3] the importance of the nature of the bidentate ligand L−L in stabilizing the hydride species $[Pd(L-L)H(MeOH)]^+$, **1a**. Herein, we have fully characterized the first example of a stable acyl−solvento complex containing a bidentate phosphine ligand. Also, the formulation and dynamic behavior of the ethyl−agostic complex is of interest. Although related compounds have been characterized by Spencer,[4,6] using analogous ligands, our work shows that in $[\overline{Pd(L-L)(CH_2CH_3)}]^+$, the β-agostic interaction is maintained even in strongly coordinating solvents. The unique chemistry of these Pd/L−L complexes appears to be determined by the highly restrictive steric demands of L−L; this is also consistent with the reactivity of **1a** with higher olefins. Hence, the steric properties of L−L are of paramount importance in determining the high selectivity of the Ineos catalyst for the synthesis of MP.

Experimental Section

All reactions and sample manipulations were carried out using standard Schlenk techniques under nitrogen and in carefully dried solvents. ^{13}C-enriched samples were prepared using standard high vacuum line techniques. All NMR measurements were performed on Bruker AMX200 and AMX400 instruments using commercial probes. The chemical shifts were referenced to external H_3PO_4 (85% in D_2O) for phosphorus and to internal TMS for carbon. High-temperature NMR measurements were recorded using a 10 mm sapphire tube. All the chemical products were purchased from Aldrich Chemical Co., except $[Pd(L-L)(dba)]$,[2] [L−L],[23] and [Pd(COD)(Me)Cl],[24] which were prepared by published methods. ^{13}CO (99.8%) was purchased from Isotec Inc., and $^{13}CH_2{=}CH_2$ from Aldrich Chemical Co. Most of the compounds reported below have not been isolated because of their instability and/or because on attempted crystallization, only oils were obtained. Nevertheless, NMR measurements and detailed isotopic labeling experiments allow all of these compounds to be formulated unambiguously.

Synthesis of $[Pd(L-L)(O_3SCF_3)_2]$. $[Pd(L-L)Cl_2]$ (1.50 g, 2.62 mmol) was dissolved in CH_2Cl_2 (100 mL) in a 250 mL two-necked round-bottomed flask, and $Ag(O_3SCF_3)$ (1.35 g, 5.24 mmol) was added. A white precipitate of AgCl was immediately formed. The solution was further stirred for 1 h before removing the precipitate by filtration. The volume of the solution was, then, reduced in a vacuum to ca. 40 mL and the product precipitated by addition of *n*-hexane (100 mL). The solid was separated by filtration, washed with *n*-hexane (2 × 50 mL), and dried in a vacuum. Yield: 1.8 g (86%). Anal. Calcd for $C_{26}H_{44}F_6O_6P_2Pd\,S_2$: C, 39.08; H, 5.55. Found: C, 38.66; H, 5.67. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 293 K): 78.2 (s).

Synthesis of $[Pd(L-L)Cl_2]$. EtC(O)Cl (2.60 g, 27.2 mmol) was added via a syringe to a solution of $[Pd(L-L)(dba)]$ (2.00 g, 2.72 mmol) in Et_2O (100 mL). The solution turned from orange to yellow in color immediately, and a yellow precipitate began to form after 15 min. The reaction mixture was stirred for a further 2 h before the precipitate was separated by filtration and dried in a vacuum. Yield: 1.4 g (90%). Anal. Calcd for $C_{24}H_{44}Cl_2P_2Pd$: C, 50.43; H, 7.70. Found: C, 50.39; H, 7.65. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 293 K): 35.0 (s).

Synthesis of $[Pd(L-L)H(MeOH)]^+$, 1a. $[Pd(L-L)(dba)]$ (100 mg, 0.136 mmol) and benzoquinone, BQ (29.4 mg, 0.272 mmol) were mixed as solids and degassed under vacuum. The solids were partially dissolved under nitrogen in MeOH (2 mL), and then CF_3SO_3H (60.5 μL, 0.680 mmol) was added via a micropipet. The product was formed in a few minutes. $^{31}P\{^1H\}$ (MeOH, 293 K): 25.8 (d, $^2J_{PP}$ = 17 Hz), 77.5 (d, $^2J_{PP}$ = 17 Hz); ^{1}H (MeOH, 293 K) −10 (dd, $^2J_{PH}$ = 179.7 and 14.3 Hz).

Synthesis of $[Pd(L-L)H(solv)]^+$ (solv = Pr^{n}OH, 1b; THF, 1c; EtCN, 1d). $[Pd(L-L)(O_3SCF_3)_2]$ (100 mg, 0.125 mmol) was dissolved in MeOH (2 mL), and then, the solution was dried in vacuum and the residue was dissolved in the appropriate solvent (see Table 1).

Synthesis of $[\overline{Pd(L-L)(CH_2CH_3)}]^+$, 2a. Ethene was bubbled for a few seconds through a solution of $[Pd(L-L)H(MeOH)]^+$ (0.136 mmol) in MeOH (2 mL). The solution turned from brown-orange to brown-yellow immediately, and the product was detected via NMR spectroscopy. For the studies above room temperature, this sample was transferred to a 10 mm sapphire tube and pressurized with ethene (4 atm). $^{31}P\{^1H\}$ NMR (MeOH, 193 K): 36.3 (d, $^2J_{PP}$ = 31 Hz), 67.7 (d, $^2J_{PP}$ = 31 Hz).

Characterization of 2a via $^{13}CH_2{=}CH_2$ (synthesis of 2b and 2c). A brown-orange solution of $[Pd(L-L)H(MeOH)]^+$ (0.136 mmol) in MeOH (2.5 mL, 25% CD_3OD) was transferred to a 10 mm NMR tube equipped with a connection for the high-vacuum line. The tube was then frozen in liquid nitrogen and evacuated. The liquid nitrogen bath was then removed and the NMR tube put immediately into a dry ice/acetone bath, to avoid the condensation of ethene. To this solution was added 1 equiv of $^{13}CH_2{=}CH_2$ through the high-vacuum line, then frozen in the liquid nitrogen and sealed. $^{31}P\{^1H\}$ NMR (MeOH, 193 K): 36.3 (d + dd, $^2J_{PP}$ = 31 Hz, $^2J_{PC}$ = 38 Hz), 67.7 (d, $^2J_{PP}$ = 31 Hz). $^{13}C\{^1H\}$ NMR (MeOH, 193 K): 8 (s), 32 (dd, $^2J_{PC}$ = 38 and 5 Hz).

Synthesis of $[\overline{Pd(L-L)(CH_2CH_2CH_3)}]^+$, 3. A solution of $[Pd(L-L)H(MeOH)]^+$ (0.136 mmol) in MeOH (2.5 mL, 25% CD_3OD) in a 10 mm NMR tube equipped with a connection for the high-vacuum line was frozen in liquid nitrogen and evacuated. The liquid nitrogen bath was then removed and replaced with a dry ice/acetone bath. To this solution was added 2 equiv of propene through the high-vacuum line, followed by cooling in liquid nitrogen and sealing. $^{31}P\{^1H\}$ NMR (MeOH, 193 K): 37.8 (d, $^2J_{PP}$ = 30.5 Hz), 67.6 (d, $^2J_{PP}$ = 30.5 Hz).

Synthesis of $[\overline{Pd(L-L)(CH_2CH_2(CH_2)_3CH_3)}]^+$, 4. To a solution of $[Pd(L-L)H(MeOH)]^+$ (0.136 mmol) in MeOH (2 mL) was added 1-hexene (42.0 μL, 0.400 mmol) with a micropipet. $^{31}P\{^1H\}$ NMR (MeOH, 193 K): 38.6 (d, $^2J_{PP}$ = 30.2 Hz), 67.7 (d, $^2J_{PP}$ = 30.2 Hz).

Synthesis of $[Pd(L-L)(C(O)Et)(THF)]^+$, 6b. A solution of **2a** (0.136 mmol) in MeOH (2 mL) was prepared as described above and dried in a vacuum, and the residue was dissolved in THF (2 mL, 25% d_8-THF) under N_2. The resulting solution was stored in a dry ice/acetone bath, and its purity checked via NMR spectroscopy. The solution was then transferred to a 10 mm NMR tube equipped with a connection for the high-vacuum line, frozen in liquid nitrogen, and evacuated on a high-vacuum line. To this solution was added 1 equiv of CO and the mixture shaken prior to recording the NMR spectrum.

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$^{31}P\{^{1}H\}$ NMR (THF, 173 K): 32.5 (d, $^{2}J_{PP} = 40.0$ Hz), 79.9 (d, $^{2}J_{PP} = 40.0$ Hz).

Characterization of 6b via ^{13}C-Labeling (synthesis of 6c, 6d, and 6e). The monolabeled sample **6c** was prepared in the same way as **6b**, using ^{13}CO instead of ^{12}CO. The doubly ^{13}C-labeled samples **6d** and **6e** were prepared by addition of ^{13}CO (1 equiv) to a 1:1 mixture of **2c** and **2d**. **6c** $^{31}P\{^{1}H\}$ (THF, 173 K): 32.5 (dd, $^{2}J_{PP} = 40$ Hz, $^{2}J_{PC} = 82.9$ Hz), 79.9 (dd, $^{2}J_{PP} = 40$ Hz, $^{2}J_{PC} = 18.2$ Hz). $^{13}C\{^{1}H\}$ (THF, 173 K): 232 (dd, $^{2}J_{PC} = 82.9$ and 18.2 Hz). **6d** $^{31}P\{^{1}H\}$ (THF/CH_2Cl_2, 173 K): 33.5 (ddd, $^{2}J_{PP} = 39$ Hz, $^{2}J_{PC} = 83$ and 23 Hz), 82.0 (ddd, $^{2}J_{PP} = 39$ Hz, $^{2}J_{PC} = 18$ and 23 Hz). $^{13}C\{^{1}H\}$ (THF/CH_2Cl_2, 173 K): 231.9 (ddd, $^{2}J_{PC} = 83$ and 18 Hz, $^{1}J_{CC} = 23$ Hz), 38.2 (q, $^{2}J_{PC} = 23$ Hz, $^{1}J_{CC} = 23$ Hz). **6e** $^{31}P\{^{1}H\}$ (THF/CH_2Cl_2, 173 K): 33.5 (dd, $^{2}J_{PP} = 39$ Hz, $^{2}J_{PC} = 83$ Hz), 82.0 (dd, $^{2}J_{PP} = 39$ Hz, $^{2}J_{PC} = 18$ Hz). $^{13}C\{^{1}H\}$ (THF/CH_2Cl_2, 173 K): 231.9 (dd, $^{2}J_{PC} = 83$ and 18 Hz), 10.9 (d, $^{3}J_{CC}$ 3 Hz).

Synthesis of [Pd(L−L)(C(O)Et)(EtCN)]$^{+}$, 6f. 6f was prepared as for **6b**, using EtCN instead of THF as the solvent. $^{31}P\{^{1}H\}$ NMR (EtCN, 193 K): 20.2 (d, $^{2}J_{PP} = 40$ Hz), 49.4 (d, $^{2}J_{PP} = 40$ Hz).

Synthesis of [Pd(L−L)(^{13}C(O)Et)(EtCN)]$^{+}$, 6g. 6g was prepared as for **6c**, using EtCN instead of THF as the solvent. $^{31}P\{^{1}H\}$ (EtCN, 193 K): 20.2 (dd, $^{2}J_{PP} = 40$ Hz, $^{2}J_{PC} = 92$ Hz), 49.4 (dd, $^{2}J_{PP} = 40$ Hz, $^{2}J_{PC} = 13$ Hz). $^{13}C\{^{1}H\}$ (EtCN, 193 K): 233.2 (dd, $^{2}J_{PC} = 92$ and 13 Hz).

Synthesis of [Pd(L−L)(C(O)Et)Cl], 7. [Pd(L−L)(dba)] (30 mg, 0.04 mmol) was dissolved in Et_2O (2 mL), and EtC(O)Cl (3.8 mg, 0.04 mmol) was added via a micropipet. The solution immediately changed from orange to yellow; removal of the solvent followed by dissolution in Et_2O and layering with pentane gave yellow crystals, suitable for a single-crystal X-ray study. $^{31}P\{^{1}H\}$ NMR (THF, 193 K): 15.1 (d, $^{2}J_{PP} = 52.6$ Hz), 44.2 (d, $^{2}J_{PP} = 52.6$ Hz). Crystal data for **7**·dba: $C_{27}H_{49}ClOP_2Pd.C_{17}H_{14}O$, $M_r = 827.73$, triclinic, space group $P\bar{1}$, $a = 10.2985(7)$ Å, $b = 11.3708(7)$ Å, $c = 19.5555(13)$ Å, $\alpha = 90.228(2)°$, $\beta = 96.288(2)°$, $\gamma = 115.134(2)°$, $V = 2057.4(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.336$ g cm^{-3}, Mo Kα radiation, $\lambda = 0.71073$ Å, $\mu = 0.63$ mm^{-1}, $T = 160$ K; of 11 286 measured reflections corrected for absorption, 7934 were unique, $R_{int} = 0.0333$; $R = 0.0437$ ($I > 2\sigma$), $R_w = 0.1093$ (F^2, all data), GOF = 1.164, 465 parameters, final difference map extremes +0.92 and −1.06 e Å^{-3}.

Synthesis of [Pd(L−L)(Me)Cl], 9. To a solution of [Pd(COD)(Me)Cl] (1.00 g, 3.77 mmol) in CH_2Cl_2 (50 mL) was slowly added L−L (0.39 g, 3.8 mmol) in CH_2Cl_2 (50 mL). The solution was stirred at room temperature (4 h) and concentrated to ca. 30 mL. The product was precipitated by addition of *n*-hexane (100 mL), separated by filtration, washed with *n*-hexane (2 × 30 mL), and dried in a vacuum. Yield: 1.8 g (88%). Anal. Calcd for $C_{25}H_{47}ClPd$: C, 54.45; H, 8.59. Found: C, 54.39; H, 8.63. $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2, 293 K): 49.0 (d, $^{2}J_{PP} = 30.5$ Hz), 18.4 (d, $^{2}J_{PP} = 30.5$ Hz).

Synthesis of [Pd(L−L)(C(O)Me)Cl], 8. [Pd(L−L)(Me)Cl] (100 mg, 0.181 mmol) was dissolved in CH_2Cl_2 (2 mL) under CO (1 atm). In these conditions, **9** is partially converted into **8**. $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2, 293 K): 17.6 (br), 45.6 (br).

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Supporting Information Available: Crystallographic data for complex **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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