

Bonding Modes in Palladium(II) Enolates: Consequences for Dynamic Behavior and Reactivity

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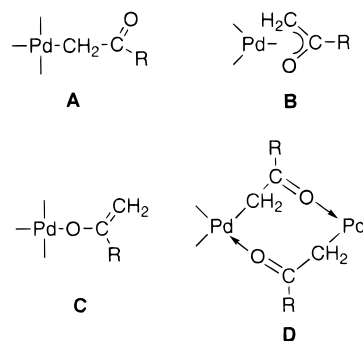
Received August 2, 1999

The behavior of palladium C-bound enolates $[\text{Pd}(\text{CH}_2\text{C}(\text{O})\text{CR}_3)\text{Cl}(\text{PPh}_3)_2]$ ($\text{R} = \text{H}$, **1**; $\text{R} = \text{Me}$, **2**) and $[\text{Pd}(\text{CH}_2\text{C}(\text{O})\text{CR}_3)(\text{PPh}_3)_2(\text{NCMe})](\text{BF}_4)$ ($\text{R} = \text{H}$, **5**; $\text{R} = \text{Me}$, **6**) has been studied. Dimeric species with bridging enolate moieties are formed in solution when a coordination site on the metal is made available, either with $\text{Pd}_2\{\mu\text{-}\kappa^2\text{-C,O-CH}_2\text{C}(\text{O})\text{CR}_3\}_2$ or with mixed $\text{Pd}_2\{\mu\text{-}\kappa^2\text{-C,O-CH}_2\text{C}(\text{O})\text{CR}_3\}(\mu\text{-X})$ ($\text{X} = \text{Cl}, \text{OH}$) bridges. It is proposed that π back-donation is important to stabilize oxygen bonding. Complexes **1** and **2** undergo exchange between free and coordinated phosphine in solution. Kinetic experiments support an intramolecular associative mechanism which could involve an oxoallyl-like transition state. The reactivity of the complexes has been explored. Some reactions typical of Pd-alkyls have been observed such as insertion of CO to give $\text{CR}_3\text{C}(\text{O})\text{CH}_2\text{COOH}$. Electrophilic attack on oxygen is very important: the hydrolysis of the enolate complexes has been studied and also the reaction with ClSiMe_3 to give silyl enol ethers.

Introduction

Many organic reactions of enol-type substrates are catalyzed by palladium.¹ Examples are the mild synthesis of unsaturated ketones from silyl enol ethers,² the coupling of in situ generated tin enolates with aryl or vinyl bromides,³ and the enantioselective aldol⁴ and Manich-type reactions.⁵ In those processes palladium enolate intermediates are believed to play a fundamental role. Some Pd-enolate complexes have been synthesized, but they are still scarce. As expected for a late transition metal, enolates prefer to coordinate to palladium either through the carbon atom (σ -alkyl type, **A**, Chart 1)⁶ or in the more elusive chelating η^3 -oxoallyl fashion (**B**, Chart 1).^{2a,4,7} The oxygen-bound type **C** (Chart 1), common for early transition metals, is not

Chart 1



easily found for palladium, and only one example has been proposed.⁸ Bridging C–O enolates (**D**, Chart 1) have also been isolated.^{6b}

C-bound palladium enolates undergo typical reactions of metal alkyls, such as insertion of isocyanides.^{6b,g} In addition, the presence of a nucleophilic site (oxygen) may also make them prone to electrophilic attack, and in fact they are more susceptible to protonolysis than unfunctionalized Pd-alkyls.^{6c}

To gain more insight into the behavior of this special and important type of palladium alkyls, we have studied in detail two palladium C-enolates synthesized by oxidative addition of halo ketones to $[\text{Pd}(\text{PPh}_3)_4]$. This is the most convenient way of preparation of these derivatives and has been used previously.⁶ The reactions and solution behavior described in this work show the importance of the different coordination modes of the enolate moiety (**A**, **B**, and **D**, Chart 1) and how the presence of the nucleophilic site makes enolates a distinct type of palladium alkyl.

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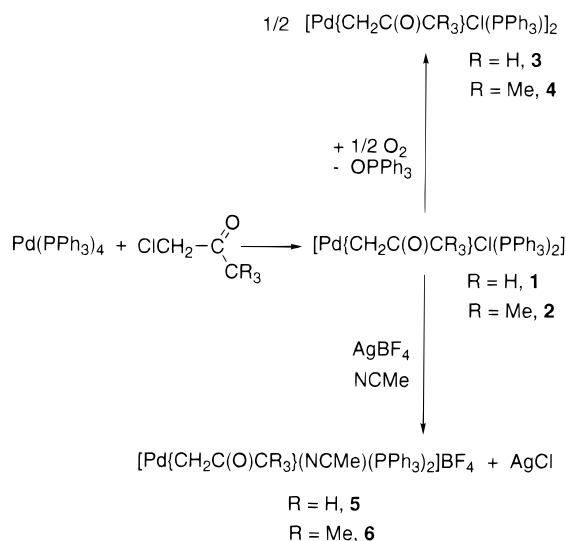
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Scheme 1**Results****Synthesis and Characterization of Pd-Enolates.**

The oxidative addition of $\text{ClCH}_2\text{C}(\text{O})\text{CR}_3$ ($\text{R} = \text{H}, \text{Me}$) to the zerovalent palladium complex $[\text{Pd}(\text{PPh}_3)_4]$ in toluene or THF gives the enolate derivatives $[\text{Pd}(\text{CH}_2\text{C}(\text{O})\text{CR}_3)\text{Cl}(\text{PPh}_3)_2]$ ($\text{R} = \text{H}, \mathbf{1}$; $\text{R} = \text{Me}, \mathbf{2}$) as air-stable white solids (Scheme 1).⁹ Complex **1** has been synthesized previously, and some of its reactions have been analyzed.^{6c,g} The bromo analogue of complex **2** has also been described,^{6f} but in either case some features of the solution behavior and reactivity of the complexes remained unexplored. **1** and **2** are an equilibrium mixture of *cis* and *trans* isomers in solution, the *trans* being the major one in both cases, as shown by their $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra. *Cis* and *trans* isomers had been detected for **1** before.^{6c} The percentages found in CDCl_3 at room temperature are *trans-1:cis-1* = 85:15 and *trans-2:cis-2* = 94:6. A ^1H NOESY experiment on **1** reveals chemical exchange between the methylene protons of both isomers.

Complex **1** shows a static ^1H spectrum at room temperature (at 300 MHz) with the characteristic methylene proton signals: a triplet (δ 2.18, $^3J_{\text{H-P}} = 6.7$ Hz) for the *trans* isomer and a doublet of doublets (δ 2.85, $^3J_{\text{H-P}} = 11.6$, 5 Hz) for the *cis* isomer, in agreement with a previous report. However, complex **2** shows a fluxional behavior (see below), and the resonance for the methylene protons, $-\text{CH}_2\text{C}(\text{O})\text{CMe}_3$, of the *trans* isomer appears as a broad peak (δ 2.35). The corresponding signal for the *cis* isomer is a broad doublet of doublets (δ 2.50, $^3J_{\text{H-P}} = 10$ Hz, 5 Hz). The ^{13}C NMR spectra show the characteristic signals for the major *trans* isomers in both cases, and the carbonyl resonances appear at δ 211.2 (*trans-1*) and δ 220.9 (*trans-2*).

When a solution of complex **1** in THF was stirred for 1.5 h in the air, the dimeric product $[\text{Pd}_2\{\mu-\kappa^2\text{-C}, \text{O}-\text{CH}_2\text{C}(\text{O})\text{CH}_3\}_2\text{Cl}_2(\text{PPh}_3)_2]$ (**3**) and OPPh_3 were obtained (Scheme 1). When the same experiment was carried out under nitrogen, **1** was recovered unchanged. The presence of a bridging enolate is shown by the value of the

Table 1. First-Order Rate Constants for the Exchange of **1 and Free PPh_3 in CDCl_3 at Different Phosphine Concentrations^a**

PPh_3 conc (M)	$k_{\text{obs}} (\mathbf{1} \rightarrow \text{P}) (\text{s}^{-1})$
0.022	1.84 ± 0.06
0.046	1.896 ± 0.09
0.067	2.76 ± 0.06
0.085	2.44 ± 0.04
0.121	3.08 ± 0.06
0.127	3.59 ± 0.08
0.205	4.256 ± 0.016

^a $T = 298$ K; concentration of **1**, 0.02 M.

$\nu(\text{CO})$ band in the IR spectrum of **3** (1654 cm^{-1}), lower than $\nu(\text{CO})$ for complex **1** (1685 cm^{-1}). Similarly **2** also gives OPPh_3 and a complex of stoichiometry $[\text{Pd}(\text{CH}_2\text{C}(\text{O})\text{CMe}_3)\text{Cl}(\text{PPh}_3)]$ (**4**, Scheme 1). In this case the dimer seems to have chloro bridges in the solid state, since the presence of a bridging enolate is ruled out by the high value of $\nu(\text{CO})$ (1687 cm^{-1}). **3** and **4** can also be obtained by addition of a phosphine trap, such as $[\text{PdCl}_2(\text{PhCN})_2]$, to a solution of **1** or **2**. Complexes **3** and **4** are fluxional in solution, as discussed below.

Complexes **1** and **2** reacted with AgBF_4 in CH_3CN to give the cationic enolate derivatives $[\text{Pd}(\text{CH}_2\text{C}(\text{O})\text{CR}_3)(\text{PPh}_3)_2(\text{NCMe})](\text{BF}_4)$ ($\text{R} = \text{H}, \mathbf{5}$; $\text{R} = \text{Me}, \mathbf{6}$) (Scheme 1). The IR spectra of **5** and **6** in the solid state show the characteristic bands of coordinated MeCN (2319 and 2286 cm^{-1} for **5** and 2317 and 2287 cm^{-1} for **6**) and the $\nu(\text{CO})$ bands at 1680 cm^{-1} (**5**) and 1667 cm^{-1} (**6**), similar to the values found for complexes **1** (1685 cm^{-1}) and **2** (1669 cm^{-1}). This indicates that both complexes are monomeric, in contrast with an analogous cationic derivative prepared in the same way which crystallizes as a dimer $[\text{Pd}_2\{\mu-\kappa^2\text{-C}, \text{O}-\text{CH}_2\text{C}(\text{O})\text{Ph}\}_2(\text{PPh}_3)_4](\text{BF}_4)_2$.^{6b} In CD_3CN solution they show fluxional NMR spectra, as will be described below.

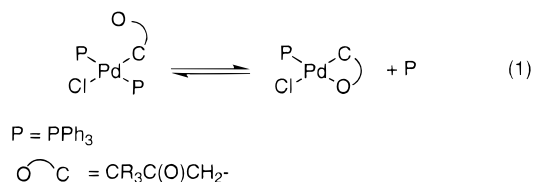
Dynamic Behavior of the Enolate Pd-Complexes. The presence of the enolate oxygen leads to several dynamic processes that affect the derivatives synthesized. Variable-temperature NMR experiments were performed on CDCl_3 solutions of **1** and/or **2**. Small amounts of the *cis* isomers are present in solution in each case, but only the major *trans* derivatives were studied in detail. Static ^1H NMR spectra are observed up to 313 K for complex **1** or 283 K for complex **2** (at 300 MHz). They both show a triplet for the methylene protons coupled to two equivalent phosphines and a singlet for the methyl groups. As the temperature is raised, the methylene triplet loses resolution and eventually becomes a broad singlet. The loss of H–P coupling can be explained by fast decoordination–recoordination of the phosphine ligands. In fact phosphine exchange is observed when free PPh_3 is added to a solution of either complex **1** or **2** in CDCl_3 , as shown by magnetization transfer experiments between the ^{31}P signals corresponding to free and coordinated phosphine. At least in these conditions PPh_3 exchange occurs by an associative pathway, the usual mechanism of ligand substitution on Pd(II) complexes, and a linear increase in k_{obs} is observed when the phosphine concentration increases (Table 1). The data in Table 1 fit the equation $k_{\text{obs}} = (1.50 \pm 0.2) + (13.9 \pm 1.8)[\text{PPh}_3]$, and the positive intercept for $[\text{PPh}_3] = 0$ suggests the simultaneous occurrence of a phosphine-independent pathway.

(9) The organometallic ligand $-\text{CH}_2\text{C}(\text{O})\text{CR}_3$ is referred to as enolate or C-enolate throughout this work. The alternative name ketonyl (acetyl when $\text{R} = \text{Me}$) is also used in the literature.

Table 2. First-Order Rate Constants for the Exchange of 1 and 2 at Different Complex Concentrations and Temperatures

<i>T</i> (K)	conc 1 (M)	conc 2 (M)	<i>k</i> _{obs} (2→1) (s ⁻¹)
273.2	0.024	0.030	0.045 ± 0.003
282.9			0.175 ± 0.006
283.3	0.012	0.012	0.201 ± 0.004
	0.023	0.028	0.211 ± 0.005
	0.096	0.096	0.204 ± 0.003
288.3	0.024	0.030	0.440 ± 0.019
293.0			0.62 ± 0.02
298.3			0.99 ± 0.04
303.5			1.49 ± 0.16
308.9			3.1 ± 0.2

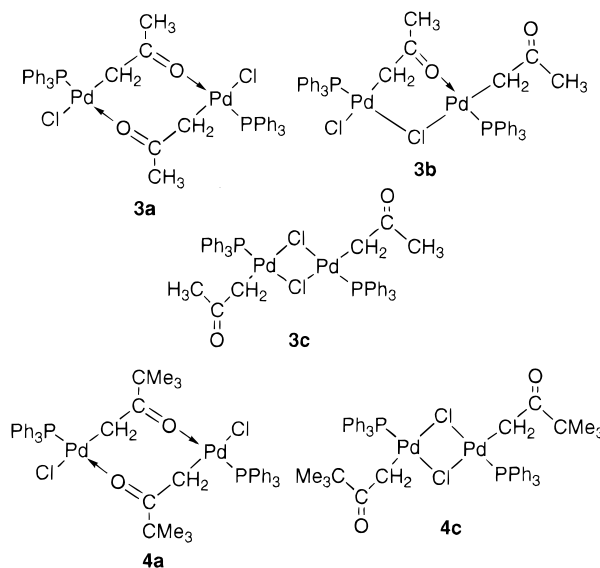
In the absence of free phosphine and in a noncoordinating solvent such as CDCl₃, the enolate oxygen atom could play the role of the entering ligand, either in an intramolecular (η^3 -oxoallyl transition state) or intermolecular way (enolate bridge transition state). A bridging chloro ligand could also trigger the substitution. ³¹P magnetization transfer experiments using equimolar solutions of complexes 1 and 2 in CDCl₃ were performed, and the exchange rate between the signals of both complexes was measured. The exchange rate does not change with concentration, according to the results found at 283.3 K for several-fold increase in complex concentration (Table 2). Rates were also measured in the temperature range 273–308 K (Table 2), and an Eyring plot gave the following activation parameters: $\Delta H^\ddagger = 77 \pm 4$ kJ mol⁻¹; $\Delta S^\ddagger = 15 \pm 13$ J K⁻¹ mol⁻¹. Although subjected to a large error, the value of ΔS^\ddagger is significantly small, and these results rule out an intermolecular mechanism for phosphine exchange. An intramolecular coordination of the enolate oxygen in an η^3 -oxoallyl fashion would account for the small ΔS^\ddagger value and the concentration-independent rate (eq 1).



This oxygen-triggered substitution may account for the phosphine-independent contribution observed in the exchange in the presence of phosphine.

Complexes 5 and 6 also show fluxional NMR spectra in CD₃CN solution: broad ¹H NMR signals, the methylene resonances appearing as broad singlets. Slow exchange spectra are obtained at about 243 K, and a triplet is observed for the CH₂C(O)CR₃ protons. The lack of H–P coupling at room temperature can be attributed to PPh₃ decoordination–recoordination, the same process observed for the neutral precursors 1 and 2. However, since acetonitrile is a coordinating solvent, we cannot rule out that the ligand exchange is solvent assisted in this case with little involvement of the enolate oxygen.

The dimeric complexes 3 and 4 also display a dynamic behavior in solution which can be attributed to rapid interconversion of different isomers. Their ¹H NMR spectra at room temperature show broad signals for both the methylene and the methyl protons and only one broad resonance in the ³¹P{¹H} NMR spectra (3, δ 36.2, 4 δ 36.7). The ³¹P resonances split at 223 K into four

Chart 2

(3) or two (4) major signals. The assignment of the ¹H NMR signals for each species at this temperature is based on their relative intensity and on a heteronuclear ¹H–³¹P inverse correlation. According to the NMR data the structures depicted in Chart 2 are proposed. Complex 3 at 223 K seems to be a mixture of μ -enol-*trans*-P (3a), μ -enol- μ -Cl-*trans*-P (3b), and μ -Cl-*trans*-P (3c), in a ratio 3a:3b:3c = 50:30:20, which undergo fast interconversion as the temperature is raised. The chemical shifts for the ³¹P{¹H} NMR resonances found indicate that the phosphines are *trans* to either Cl or O (δ 36.4, 3a; δ 36.5 and 37, 3b; δ 36.9, 3c) but not to C (expected δ around 20 ppm) or another phosphine (expected δ around 25–28 ppm). When complex 3 is dissolved in CDCl₃ at 223 K, the same mixture of isomers is found, which means that even at this temperature the equilibrium is established quickly. Complex 4 is a mixture of two isomers, μ -enol-*trans*-P (4a) and μ -Cl-*trans*-P (4c), in a ratio 4a:4c = 24:76 at 223 K (Chart 2). It seems that a bridging enolate is preferred for 3 versus a chloro bridge at low temperatures and in the solid state, whereas the opposite is found for 4.

Reactions with Unsaturated Substrates and Electrophiles. As a particular type of Pd-alkyls, insertion of some unsaturated substrates into the Pd–C bond of enolates can be anticipated. However 1 or 2 do not react with MeOOC–C \equiv C–COOMe, and neither the neutral nor the cationic derivatives undergo insertion of alkenes into the Pd–C bond. In contrast, CO reacts with 1 or 2 in CDCl₃ to give the carboxylic acid CH₃C(O)CH₂COOH and acetone or CMe₃C(O)CH₂COOH and pinacolone, respectively, plus a dimeric palladium derivative 7 (Scheme 2). 7 can be isolated as an orange solid in high yield when CO is bubbled through a solution of 1 or 2 in THF. It has been previously synthesized by comproportionation of Pd(0) and Pd(II) complexes, and in our case it may have been formed in a similar way, as depicted in Scheme 2.¹⁰

On the other hand, the oxygen center in the enolate moiety is susceptible to attack by electrophiles, and

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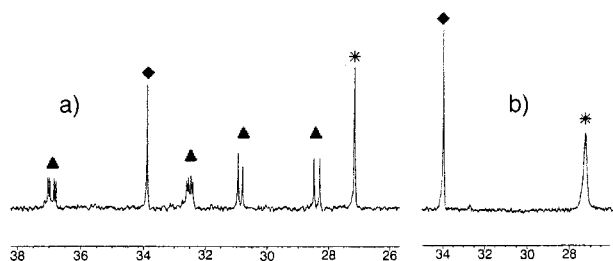
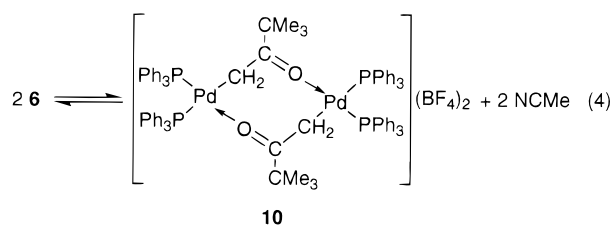
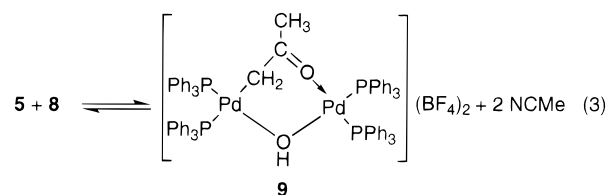
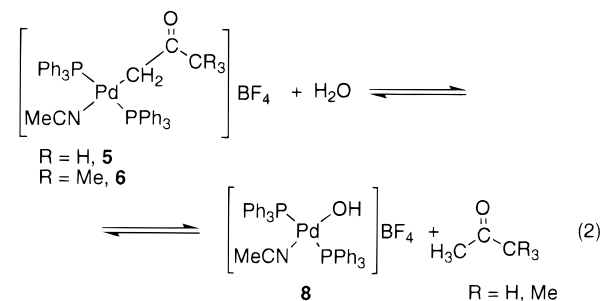


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR for the mixture of **5** (*), **8** (◆), and **9** (▲) in CDCl_3 , (a) before and (b) after adding CD_3CN .

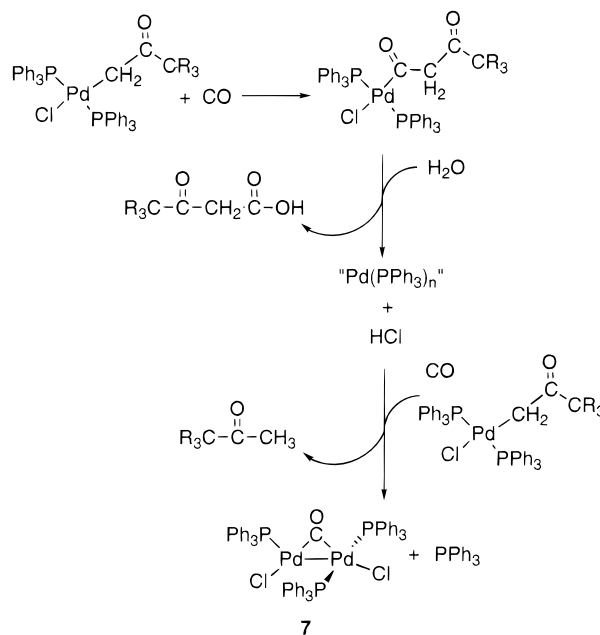
indeed hydrolysis reactions are observed in noncoordinating solvents. Complexes **1** and **2** slowly decompose in CDCl_3 by protonolysis of the enolate moiety to give the corresponding ketone and $[\text{PdCl}_2(\text{PPh}_3)_2]$. The same products are observed when $\text{HCl}(\text{aq})$ is added to **1** or **2** in chloroform. Solutions of the complexes in rigorously dried chlorinated solvents can be kept for longer periods of time if protected from light. The cationic complexes **5** and **6** are stable in acetonitrile solution, but when dissolved in CDCl_3 , they undergo hydrolysis reactions immediately. When **5** is dissolved in CDCl_3 , a mixture of **5**, the hydroxo derivative $[\text{Pd}(\text{OH})(\text{PPh}_3)_2(\text{NCMe})](\text{BF}_4)$ (**8**), and a dimer $[\text{Pd}_2\{\mu\text{-}\kappa^2\text{-C,O-CH}_2\text{C}(\text{O})\text{CH}_3\}(\mu\text{-OH})(\text{PPh}_3)_4](\text{BF}_4)_2$ (**9**) is found (eqs 2 and 3). A solution of **6** in CDCl_3 contains complexes **6**, **8**, and the enolate-bridged $[\text{Pd}_2\{\mu\text{-}\kappa^2\text{-C,O-CH}_2\text{C}(\text{O})\text{CMe}_3\}_2(\text{PPh}_3)_4](\text{BF}_4)_2$ (**10**) (eqs 2 and 4). The addition of H_2O increases the



amount of **8** and **9** in the first case, or **8** in the second, as expected from the equilibrium in eq 2. Addition of CD_3CN produces bridge splitting and the disappearance of the dimeric derivatives, leaving **5/8** or **6/8** as the only species present (Figure 1 and eqs 3 and 4).

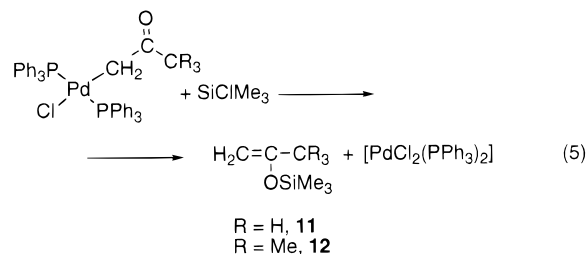
Cationic hydroxo derivatives (**8**, **9**) are the straightforward products of the hydrolysis of **5** and **6**. The

Scheme 2



protonolysis of the enolate derivatives **1** or **2** in the same way (water acting as a proton source) would produce a putative neutral hydroxo derivative, which in chlorinated solvents may give $[\text{PdCl}_2(\text{PPh}_3)_2]$, and this is the only palladium complex observed.

Complexes **1** and **2** react with electrophiles other than proton, and attack on oxygen is observed. Addition of ClSiMe_3 to solutions of **1** or **2** gives the silyl enol ethers $\text{CH}_2=\text{C}(\text{OSiMe}_3)\text{-CR}_3$ (**11**, $\text{R} = \text{H}$; **12**, $\text{R} = \text{Me}$) and $[\text{PdCl}_2(\text{PPh}_3)_2]$ (eq 5).



Discussion

Three different coordination modes to palladium have been shown to be important for the enolate ligands used in this work. Stable complexes display a C-bound enolate when there is only one coordination site on palladium. When a second coordination position is available, a bridging enolate is preferred to an oxoallyl chelating form, both in the neutral and cationic derivatives, and the stability of the bridge is finely tuned by the nature of the R group in the $-\text{CH}_2(\text{CO})\text{R}$ moiety. We observe that the preference for the dimeric enolate bridge follows the trend $\text{Ph} > \text{Me} > \text{tBu}$ as shown by the distribution of enolate versus Cl bridges in **3** and **4** and the isolation of cationic complexes from an acetonitrile solution which are monomeric C-bound Pd enolates in this work ($\text{R} = \text{Me}$, tBu) or dimeric C-O bridging Pd enolates for $\text{R} = \text{Ph}$.^{6b} Since the stability of the bridge decreases as the R group becomes a stronger donor, a π back-bonding interaction may be important in this bonding mode, which seems to be supported by

the important decrease in $\nu(\text{CO})$ upon bridge formation. A third bonding mode, chelating oxoallyl, is important in the fast intramolecular phosphine exchange observed for complexes **1** and **2**. The rates observed parallel the basicity of the enolate oxygen $\text{R} = \text{tBu} > \text{Me}$, as determined for the parent ketones.¹¹ Good σ donor properties for the entering ligand (O) seems to be a major factor that promotes the attainment of the transition state in the process. These apparently contradictory results show that the factors that favor the two C,O-enolate bonding modes (oxoallyl or bridging) are intrinsically different. The bridging mode is thermodynamically preferred, at least in the complexes described here, and is met in the isolated compounds. Nevertheless a chelating oxoallyl-like mode, with an incipient Pd–O bond (where π back-bonding could still be unimportant), seems to be a key transition state or intermediate in some reactions of the palladium enolates.

A few reactions undergone by the complexes prepared parallel the reactivity of Pd-alkyls. Thus insertion of CO into the Pd–C(enol) bond is observed, and β -ketoacids are obtained, in contrast with a previous report on the palladium enolate analogue derived from acetophenone.^{6b} Since phosphine substitution by CO is needed for insertion, the higher reactivity of the complexes used here seems to be a consequence of the easier phosphine decoordination promoted by the more strongly donating enolate when $\text{R} = \text{Me}$, tBu than when $\text{R} = \text{Ph}$. Also, reactions of **1** and other Pd-enolates with isonitriles have been described elsewhere, and insertion into the Pd–C bond has been observed.^{6b,g} However, one important difference with Pd-alkyls concerns the easy cleavage of the Pd–C(enolate) bond. Hydrolysis of the enolate ligand occurs for **1** and **2** and more easily for the cationic derivatives **5** and **6** in noncoordinating solvents. The cleavage probably occurs by intramolecular deprotonation of a coordinated water molecule by the enolate oxygen, since H_2O coordination seems to be a crucial step, as shown by the factors that favor the reaction: noncoordinating solvents and ligands that can be easily substituted (NCMe).¹² Other electrophiles also attack the enolate oxygen with cleavage of the Pd–C bond. The reaction of **1** or **2** with SiClMe_3 affords, by clean trimethylsilyl attack on the O, the corresponding silyl enol ethers, and this is relevant to the Pd-catalyzed syntheses that use silyl enol ethers, since it is the reverse reaction of the first step in the catalytic cycle.^{2,4,5}

Experimental Section

General Procedures. C, H, and N elemental analyses were performed on a Perkin-Elmer 240 microanalyzer. ^1H , ^{13}C , and ^{31}P NMR spectra were recorded on Bruker AC-300 and ARX-300 spectrometers. Chemical shifts (in δ units, ppm) were referenced to TMS for ^1H and ^{13}C and to H_3PO_4 for ^{31}P . The spectral data were recorded at 293 K unless otherwise noted. IR spectra were recorded using Nujol mulls on a Perkin-Elmer 883 spectrophotometer. Organic products were analyzed using a HP-5890 gas chromatograph connected to a HP-5988 mass spectrometer at an ionizing voltage of 70 eV and a quadrupole

analyzer. Solvents were dried following standard procedures and distilled before use. Haloketones were purchased from Aldrich Chemical Co. and used without further purification. $[\text{Pd}(\text{PPh}_3)_4]$ was prepared as described elsewhere.¹³

Synthesis of $[\text{Pd}(\text{CH}_2\text{C}(\text{O})\text{CH}_3)\text{Cl}(\text{PPh}_3)_2]$ (1**).** The preparation in the literature was slightly modified.^{6c} To a slurry of $\text{Pd}(\text{PPh}_3)_4$ (2 g, 1.73 mmol) in toluene under a nitrogen atmosphere was added $\text{ClCH}_2\text{C}(\text{O})\text{CH}_3$ (0.1516 mL, 0.19 mmol). After 2 h a solution was formed, and it was stirred for one more hour, whereupon a white solid (**1**) appeared. It was filtered, washed with toluene, and air-dried: 0.93 g, 74% yield (mixture of *trans*-**1**:*cis*-**1** in a ratio 85:15 in CDCl_3 solution).

1: Anal. Calcd for $\text{C}_{39}\text{H}_{35}\text{ClO}_2\text{Pd}$: C, 64.74; H, 4.87. Found: C, 64.42; H, 4.84. IR, $\nu(\text{C}=\text{O})$ 1685 cm^{-1} , $\nu(\text{Pd}-\text{Cl})$ 262 cm^{-1} . ^1H NMR (300 MHz, δ , CDCl_3): *trans*-**1**, 7–7.9 (m, 30 H, Ph), 2.18 (t, 2 H, CH_2 -, $^3J_{\text{H-P}} = 6.7$ Hz), 1.3 (s, 3 H, Me); *cis*-**1**, 7–7.9 (m, Ph), 2.85 (dd, 2 H, CH_2 - $J = 4.5$, 11 Hz), 2.35 (s, 3H, Me). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, δ , CDCl_3): *trans*-**1**, 28.3 (s); *cis*-**1**, 21.3 (d, 1P, $^2J_{\text{P-P}} = 34$ Hz), 38.1 (d, 1P, $^2J_{\text{P-P}} = 34$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (74.5 MHz, δ , CDCl_3): *trans*-**1**, 211.2 (s, C=O), 30.7 (s, Me), 32.8 (s, CH_2), 127–135 (Ph).

Complex **2** was obtained following a similar procedure but using tetrahydrofuran as solvent and 1.5 h reaction time. A white solid was obtained (61% yield, mixture of *trans*-**2**:*cis*-**2** in a ratio 94:6 in CDCl_3 solution). Anal. Calcd for $\text{C}_{42}\text{H}_{41}\text{ClO}_2\text{Pd}$: C, 65.89; H, 5.40. Found: C, 65.49; H, 5.54. IR, $\nu(\text{C}=\text{O})$ 1669 cm^{-1} , $\nu(\text{Pd}-\text{Cl})$ 284 cm^{-1} . ^1H NMR (300 MHz, δ , CDCl_3 , 293 K): *trans*-**2**, 7.4–7.75 (m, 30 H, Ph), 2.35 (bs, 2 H, CH_2 -, 0.22 (bs, 9 H, 3Me), *cis*-**2**, 7.4–7.75 (m, Ph), 2.50 (dd, 2H, CH_2 -, $^3J_{\text{H-P}} = 10.5$ Hz, 5.4 Hz), 1.06 (s, 9H, 3Me). ^1H NMR (300 MHz, δ , CDCl_3 , 243 K): *trans*-**2**, 2.32 (t, $^3J_{\text{H-P}} = 7.6$ Hz, CH_2 , 2 H), 0.13 (s, 9 H, 3Me), 7.4–7.75 (m, 30 H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, δ , CDCl_3 , 293 K): *trans*-**2**, 28.9 (bs), *cis*-**2**, 19.9 (d, 1P, $^2J_{\text{P-P}} = 34$ Hz), 39.9 (d, 1P, $^2J_{\text{P-P}} = 34$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (74.5 MHz, δ , CDCl_3 , 243 K): 26.7 (s, 3 CH_3), 29.1 (s, CH_2 -), 44.2 (s, CMe₃), 220.87 (s, C=O), 128.1–135.1 (Ph).

Synthesis of $[\text{Pd}_2(\mu\text{-CH}_2\text{C}(\text{O})\text{CH}_3)_2\text{Cl}_2(\text{PPh}_3)_2]$ (3**).** Complex **1** (0.1 g, 0.138 mmol) was dissolved in tetrahydrofuran (20 mL), and the solution was stirred for 1.5 h in the air. The solution was evaporated to ca. 5 mL, and Et_2O (15 mL) was added. A light yellow solid appeared, which was filtered, washed with THF (2 mL) and then Et_2O (2×2 mL), and air-dried: 0.048 g, 75% yield. Anal. Calcd for $\text{C}_{42}\text{H}_{40}\text{Cl}_2\text{O}_2\text{P}_2\text{Pd}_2$: C, 54.68; H, 4.37. Found: C, 54.24; H, 4.33. IR, $\nu(\text{C}=\text{O})$ 1654 cm^{-1} , $\nu(\text{Pd}-\text{Cl})$ 279 cm^{-1} . ^1H NMR (300 MHz, δ , CDCl_3 , 293 K): 7.4–7.7 (m, Ph), 2.25 (bs, 2 H, CH_2 -), 1.95 (bs, 3 H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, δ , CDCl_3 , 293 K): 36.2 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (74.5 MHz, δ , CDCl_3 , 293 K): 31.6 (s, CH_2 -), 31.9 (s, CH_3), 211.2 (s, C=O), 128.3–134.8 (m, Ph). ^1H NMR (300 MHz, δ , CDCl_3 , 223 K): 7.3–7.8 (m, Ph), 2.25 (bs, CH_2 -, **3c**), 2.19 (bs, CH_2 -, **3a**), 2.14 (bs, CH_2 -, **3b**), 1.84 (s, CH_3 , **3a**, **3c**), 1.74 (s, CH_3 , **3b**), 1.69 (s, CH_3 , **3b**). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, δ , CDCl_3 , 223 K): 36.38 (s, **3a**), 36.45 (s, **3b**), 37.1 (s, **3b**), 36.9 (s, **3c**).

Complex **4** was prepared in a similar way (50% yield). Anal. Calcd for $\text{C}_{48}\text{H}_{52}\text{Cl}_2\text{O}_2\text{P}_2\text{Pd}_2$: C, 57.27; H, 5.21. Found: C, 56.94; H, 5.07. IR, $\nu(\text{C}=\text{O})$ 1687 cm^{-1} , $\nu(\text{Pd}-\text{Cl})$ 275 cm^{-1} . ^1H NMR (300 MHz, δ , CDCl_3 , 293 K): 7.4–7.8 (m, Ph), 1.80 (bs, 2 H, CH_2 -), 1.30 (bs, 3 H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, δ , CDCl_3 , 293 K): 36.7 (s). ^1H NMR (300 MHz, δ , CDCl_3 , 223 K): 7.3–7.8 (m, Ph), 1.79 (b, CH_2 -, **4a**), 1.58 (b, CH_2 -, **4c**), 1.42 (bs, CH_3 , **4a**), 1.20 (s, CH_3 , **4c**). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, δ , CDCl_3 , 223 K): 38.1 (s, **4c**), 37.4 (s, **4a**).

Preparation of $[\text{Pd}(\text{CH}_2\text{C}(\text{O})\text{CH}_3)(\text{PPh}_3)_2(\text{NCMe})](\text{BF}_4)$ (5**).** Complex **1** (0.15 g, 0.207 mmol) was added to a solution of AgBF_4 (0.044 g, 0.227 mmol) in acetonitrile (20 mL). The mixture was stirred for 1.5 h in the dark, and then the suspension was filtered through Celite. The pale yellow solution was evaporated to ca. 2 mL, and Et_2O (10 mL) was

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added, yielding a pale yellow solid, which was filtered washed with Et₂O (2 × 10 mL) and air-dried: 0.15 g, 90% yield. Anal. Calcd for C₄₁H₃₈BF₄NOP₂Pd: C, 60.35; H, 4.69; N, 1.71. Found: C, 60.41; H, 5.02; N, 1.62. IR, 2319 and 2286 cm⁻¹ (NCMe), ν (C=O) 1680 cm⁻¹. ¹H NMR (300 MHz, δ , CD₃CN, 293 K): 7.2–7.8 (m, Ph, 30 H), 2.30 (bs, 2 H, CH₂), 1.20 (bs, 3 H, CH₃). ¹H NMR (300 MHz, δ , CD₃CN, 238 K): 7.1–7.7 (m, Ph, 30 H), 2.24 (t, 2 H, ³J_{H-P} = 8 Hz, CH₂), 0.90 (s, 3 H, CH₃). ³¹P{¹H} NMR (121 MHz, δ , CD₃CN, 293 K): 28.0 (s). ¹³C{¹H} NMR (74.5 MHz, δ , CD₃CN, 238 K): 211.8 (s, C=O), 129.0–135.1 (Ph), 32.2 (s, CH₂), 30.0 (s, CH₃).

Complex **6** was prepared following the same procedure. Anal. Calcd for C₄₄H₄₄BF₄NOP₂Pd: C, 61.59; H, 5.17; N, 1.63. Found: C, 61.18; H, 5.26; N, 1.58. IR: 2317 and 2287 cm⁻¹ (NCMe), ν (C=O) 1667 cm⁻¹. ¹H NMR (300 MHz, δ , CD₃CN, 293 K): 7.2–7.9 (m, 30 H, Ph), 2.55 (bs, 2 H, CH₂), 0.20 (bs, 9 H, CMe₃). ¹H NMR (300 MHz, δ , CD₃CN, 243 K): 7.2–7.8 (m, Ph, 30 H), 2.54 (t, 2 H, ³J_{H-P} = 7.8 Hz, CH₂), 0.08 (s, 9 H, CMe₃). ³¹P{¹H} NMR (121 MHz, δ , CD₃CN, 293 K): 28.3 (bs). ¹³C{¹H} NMR (74.5 MHz, δ , CD₃CN, 293 K): 219.4 (s, C=O), 127.8–135.3 (Ph), 44.8 (s, CMe₃), 27.6 (s, CH₂), 26.4 (s, CMe₃).

When complex **5** was dissolved in CDCl₃, a mixture of complexes **5**, **8**, and **9** was formed as shown by NMR. The addition of water to the mixture changed the ratio of products from **5**:**8**:**9** = 1.4:1:1.9 (referred to Pd) to **5**:**8**:**9** = 0.2:1:0.4.

Complex **6** gives a mixture of **6**, **8**, and **10** in CDCl₃.

5: ¹H NMR (300 MHz, δ , CDCl₃): 6.8–7.9 (m, Ph), 2.30 (t, 2 H, ³J_{H-P} = 8 Hz, CH₂), 1.40 (bs, 3 H, CH₃CN), 1.00 (s, 3 H, CH₃). ³¹P{¹H} NMR (121 MHz, δ , CDCl₃): 27.1 (s).

6: ¹H NMR (300 MHz, δ , CDCl₃): 7.0–8.0 (m, Ph), 2.57 (t, 2 H, ³J_{H-P} = 7.8 Hz, CH₂), 0.18 (s, 9 H, CMe₃), 1.34 (s, 3 H, CH₃CN). ³¹P{¹H} NMR (121 MHz, δ , CDCl₃): 27.4 (s).

8: ¹H NMR (300 MHz, δ , CDCl₃): 6.8–7.9 (m, Ph), 0.9 (bs, 3 H, CH₃CN), -2.3 (bs, OH). ³¹P{¹H} NMR (121 MHz, δ , CDCl₃): 33.9 (s).

9: ¹H NMR (300 MHz, δ , CDCl₃): 6.8–7.9 (m, Ph), 4.1 (dd, 1 H, ²J_{H-H} = 11 Hz, ³J_{H-P} = 4.5 Hz, CH₂), 2.8 (m, 1 H, CH₂), 1.2 (s, 3 H, CH₃), -0.4 (bs, OH). ³¹P{¹H} NMR (121 MHz, δ , CDCl₃): 36.9 (dd, 1 P, *J* = 23, 7 Hz), 32.6 (dd, 1 P, *J* = 18, 7 Hz), 30.9 (d, 1 P, *J* = 18 Hz), 28.5 (d, 1 P, *J* = 23 Hz).

10: ¹H NMR (300 MHz, δ , CDCl₃): 7.0–8.0 (m, Ph), 3.08 (d, 2 H, ³J_{H-P} = 6.5 Hz, CH₂), 1.09 (s, 9 H, CMe₃). ³¹P{¹H} NMR (121 MHz, δ , CDCl₃): 33.9 (d, 2 P, *J* = 36.8 Hz), 21.2 (d, 2 P, *J* = 36.8 Hz).

Reactions with CO. Synthesis of [Pd₂(μ -CO)Cl₂(PPh₃)₃] (7**).¹⁰ CO was bubbled through a suspension of **1** (0.150 g, 0.207 mmol) in THF. The light yellow suspension turned into an orange solution. After 5 min an orange solid precipitated, which was filtered and air-dried: 0.1 g, 84% yield. Anal. Calcd for C₅₅H₄₅Cl₂OP₃Pd₂: C, 60.13; H, 4.13. Found: C, 59.75; H, 4.36. IR, ν (C=O) 1864 cm⁻¹. ¹H NMR (300 MHz, δ , CDCl₃): 7.15–7.8 (m, 45 H, Ph). ³¹P{¹H} NMR (121 MHz, δ , CDCl₃):**

22.4 (bs). ¹³C{¹H} NMR (74.5 MHz, δ , CDCl₃, under a CO atmosphere): 210.4 (s, C=O), 128.0–135.1 (Ph).

CO was bubbled through solutions of **1** or **2** in CDCl₃ for 5 min. The yellow solutions turned orange, and **7** and the corresponding ketoacids, CR₃C(O)CH₂COOH, were observed by NMR.

R = H: ¹H NMR (300 MHz, δ , CDCl₃): 12.1 (bs, 1 H, COOH), 3.50 (s, 2 H, CH₂-), 2.17 (s, 3 H, CH₃).

R = Me: ¹H NMR (300 MHz, δ , CDCl₃): 12.3 (bs, 1 H, COOH), 3.58 (s, 2 H, CH₂-), 1.17 (s, 9 H, CMe₃).

Reaction of 1 with SiClMe₃. To a solution of **1** (0.0156 g, 0.022 mmol) in CDCl₃ (0.6 mL) was added SiClMe₃ (0.003 mL, 0.023 mmol). [PdCl₂(PPh₃)₂] and **11** appeared immediately as shown by ¹H and ³¹P NMR.

11: ¹H NMR (300 MHz, δ , CDCl₃): 4.06 (m, 1 H, H¹), 4.05 (bs, 1 H, H¹), 1.78 (d, *J* = 1 Hz, 3 H, Me³), 0.21 (s, 9 H, SiMe₃).

Compound **12** was obtained in a similar way: ¹H NMR (300 MHz, δ , CDCl₃): 4.09 (d, *J* = 1 Hz, 1 H, H¹), 3.93 (bs, 1 H, H¹), 1.05 (s, 9 H, 3 Me³), 0.21 (s, 9 H, SiMe₃).

Kinetic Measurements. NMR tubes (5 mm) were charged with the appropriate amount of complexes **1** and **2** (or complex **1** and PPh₃), and CDCl₃ was added to a total volume of 0.6 mL to give solutions of the concentrations collected in Tables 1 and 2. The samples were placed in a probe provided with a B-VT-2000 temperature control unit. The temperature was calibrated measuring the difference between the chemical shifts of the MeOH signals at each temperature.¹⁴ Kinetics were carried out by magnetization transfer experiments, with selective inversion of the ³¹P resonance of complex **1** using a 90°–D₁–90°–*t*–90°–D₂ sequence, where D₁ = 1/2Δ*ν*, Δ*ν* is the separation in Hz between both signals, *t* is the magnetization transfer delay, and D₂ is the relaxation delay. Values of 90° pulses and D₁ were determined at each temperature. After excitation, the signal areas of both signals (**1** and **2**, or **1** and PPh₃) were measured and processed to obtain the values of *k*_{obs}, as was reported before.¹⁵ Values of *k*_{obs}(**1**→PPh₃) reported in Table 1 were calculated from the experimental *k*_{obs}(PPh₃→**1**) using the equilibrium equation [**1**]/*k*_{obs}(**1**→PPh₃) = [PPh₃]/*k*_{obs}-(PPh₃→**1**). Errors were calculated as reported before.¹⁶

Acknowledgment. We thank the Spanish Ministry of Education and Science (grant no. PB-96-0363) and the Junta de Castilla y León (grant no.VA18/97) for financial support.

OM9906130

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