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

Ana C. Albéniz, N. Marta Catalina, Pablo Espinet,* and Rocío Redón

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, Prado de la Magdalena s/n, 47005 Valladolid, Spain

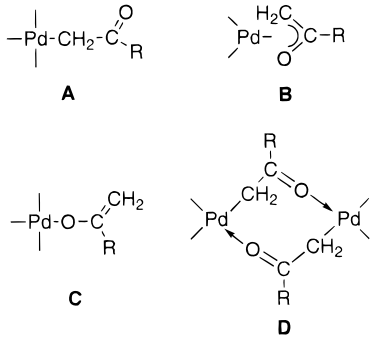
Received August 2, 1999

The behavior of palladium C-bound enolates $[Pd(CH_2C(O)CR_3)Cl(PPh_3)_2]$ (R = H, **1**; R = Me, **2**) and $[Pd(CH_2C(O)CR_3)(PPh_3)_2(NCMe)](BF_4)$ (R = H, **5**; R = 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 $Pd_2\{\mu\text{-}\kappa^2\text{-C,O-}CH_2C(O)CR_3\}_2$ or with mixed $Pd_2\{\mu\text{-}\kappa^2\text{-C,O-}CH_2C(O)CR_3\}(\mu\text{-X})$ (X = Cl, 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 $CR_3C(O)CH_2COOH$. 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 aldol[4] 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 easily found for palladium, and only one example has been proposed.[8] Bridging C−O enolates (**D**, Chart 1) have also been isolated.[6b]

Chart 1



C-bound palladium enolates undergo typical reactions of metal alkyls, such as insertion of isonitriles.[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 haloketones to $[Pd(PPh_3)_4]$. 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.

* E-mail: espinet@qi.uva.es. Fax: 34-983-423013.

(1) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, p 838.

(2) (a) Ito, Y.; Aoyama, H.; Hirao, T.; Mochizuki, A.; Saegusa, T. *J. Am. Chem. Soc.* **1979**, *101*, 494−496. (b) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011−1013.

(3) Farina, V.; Krishnamurthy, V.; Scott, W. J. *The Stille Reaction*; Wiley: New York, 1998.

(4) Sodeoka, M.; Ohrai, K.; Shibasaki, M. *J. Org. Chem.* **1995**, *60*, 2648−2649.

(5) Fujii, A.; Hagiwara, E.; Sodeoka, M. *J. Am. Chem. Soc.* **1999**, *121*, 5450−5458.

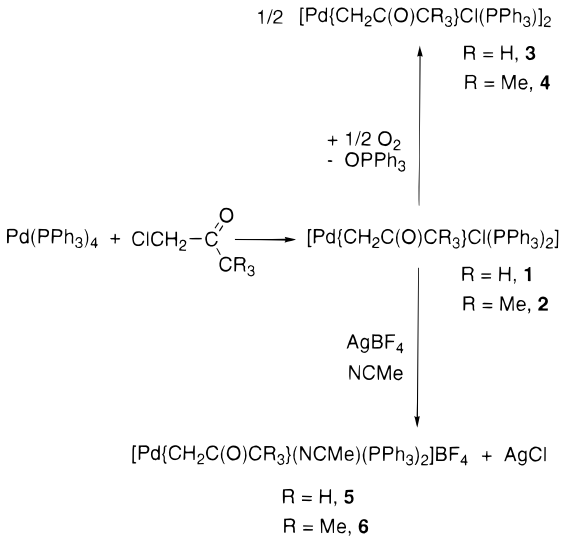
(6) (a) Vicente, J.; Abad, J. A.; Chicote, M. T.; Abrisqueta, M. D.; Lorca, J. A.; Ramírez de Arellano, M. C. *Organometallics* **1998**, *17*, 1564−1568. (b) Veya, P.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 4899−4907. (c) Suzuki, K.; Yamamoto, H. *Inorg. Chim. Acta* **1993**, *208*, 225−229. (d) Byers, P. K.; Canty, A. J.; Skelton, B. W.; Traill, P. R.; Watson, A. A.; White, A. H. *Organometallics* **1992**, *11*, 3085−3088. (e) Burkhardt, E.; Bergman, R. G.; Heathcock, C. H. *Organometallics* **1990**, *9*, 30−44. (f) Wanat, R. A.; Collum, D. B. *Organometallics* **1986**, *5*, 120−127. (g) Bertani, R.; Castellani, C. B.; Crociani, B. *J. Organomet. Chem.* **1984**, *269*, C15−C18.

(7) (a) Lemke, F. R.; Kubiak, C. P. *J. Organomet. Chem.* **1989**, *373*, 391−400. (b) Yoshimura, N.; Murahashi, S.-I.; Moritani, I. *J. Organomet. Chem.* **1973**, *52*, C58−C60.

(8) Sodeoka, M.; Tokunoh, R.; Miyazaki, F.; Hagiwara, E.; Shibasaki, M. *Synlett* **1997**, 463−466.

10.1021/om990613o CCC: $18.00
Publication on Web 11/25/1999

Scheme 1



Results

Synthesis and Characterization of Pd-Enolates. The oxidative addition of $ClCH_2C(O)CR_3$ (R = H, Me) to the zerovalent palladium complex $[Pd(PPh_3)_4]$ in toluene or THF gives the enolate derivatives $[Pd(CH_2C(O)CR_3)Cl(PPh_3)_2]$ (R = H, **1**; R = Me, **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 $^{31}P\{^1H\}$ 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, $^3J_{H-P}$ = 6.7 Hz) for the trans isomer and a doublet of doublets (δ 2.85, $^3J_{H-P}$ = 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, $-CH_2C(O)CMe_3$, 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, $^3J_{H-P}$ = 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 $[Pd_2\{\mu\text{-}\kappa^2\text{-C,O-}CH_2C(O)CH_3\}_2Cl_2(PPh_3)_2]$ (**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 ν(CO) band in the IR spectrum of **3** (1654 cm^{-1}), lower than ν(CO) for complex **1** (1685 cm^{-1}). Similarly **2** also gives $OPPh_3$ and a complex of stoichiometry $[Pd(CH_2C(O)CMe_3)Cl(PPh_3)]$ (**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 ν(CO) (1687 cm^{-1}). **3** and **4** can also be obtained by addition of a phosphine trap, such as $[PdCl_2(PhCN)_2]$, to a solution of **1** or **2**. Complexes **3** and **4** are fluxional in solution, as discussed below.

(9) The organometallic ligand $-CH_2C(O)CR_3$ is referred to as enolate or C-enolate throughout this work. The alternative name ketonyl (acetonyl when R = Me) is also used in the literature.

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_{obs} (**1**→P) (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.

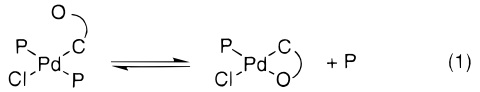
Complexes **1** and **2** reacted with $AgBF_4$ in CH_3CN to give the cationic enolate derivatives $[Pd(CH_2C(O)CR_3)(PPh_3)_2(NCMe)](BF_4)$ (R = H, **5**; R = Me, **6**) (Scheme 1). The IR spectra of **5** and **6** in the solid state show the characteristic bands of coordinated MeCN (2319 and 2286 cm^{-1} for **5** and 2317 and 2287 cm^{-1} for **6**) and the ν(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 $[Pd_2\{\mu\text{-}\kappa^2\text{-C,O-}CH_2C(O)Ph\}_2(PPh_3)_4](BF_4)_2$.[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 $k_{obs} = (1.50 \pm 0.2) + (13.9 \pm 1.8)[PPh_3]$, and the positive intercept for $[PPh_3] = 0$ suggests the simultaneous occurrence of a phosphine-independent pathway.

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

T (K)	conc **1** (M)	conc **2** (M)	k_{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 $CDCl_3$, 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. ^{31}P magnetization transfer experiments using equimolar solutions of complexes **1** and **2** in $CDCl_3$ 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 $\Delta S^{\ddagger}$ 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 $\Delta S^{\ddagger}$ value and the concentration-independent rate (eq 1).



(1)

P = PPh_3

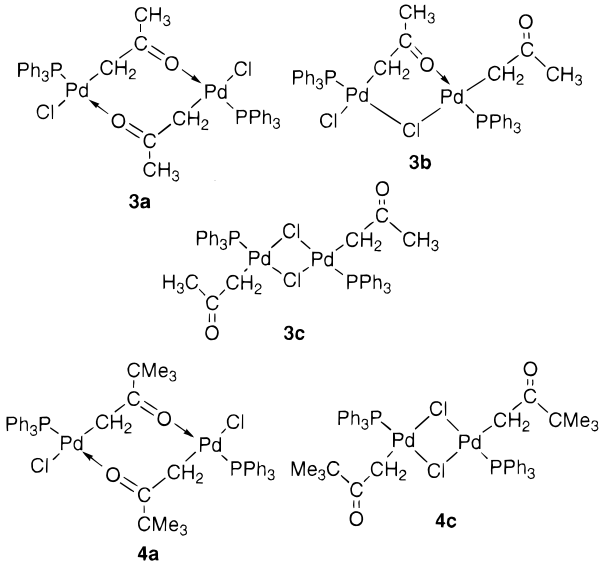
O⌒C = $CR_3C(O)CH_2$-

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 CD_3CN 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 $CH_2C(O)CR_3$ protons. The lack of H−P coupling at room temperature can be attributed to PPh_3 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 $^{31}P\{^1H\}$ NMR spectra (**3**, δ 36.2, **4** δ 36.7). The ^{31}P 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 $^1H-^{31}P$ 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 $^{31}P\{^1H\}$ 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 $CDCl_3$ 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≡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 $CDCl_3$ to give the carboxylic acid $CH_3C(O)CH_2COOH$ and acetone or $CMe_3C(O)CH_2$-COOH 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

(10) Bender, R.; Braunstein, P.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Chem. Commun.* **1984**, 42−43.

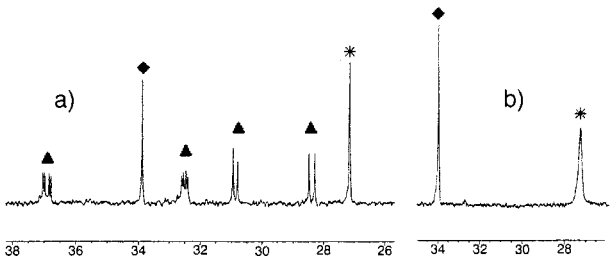
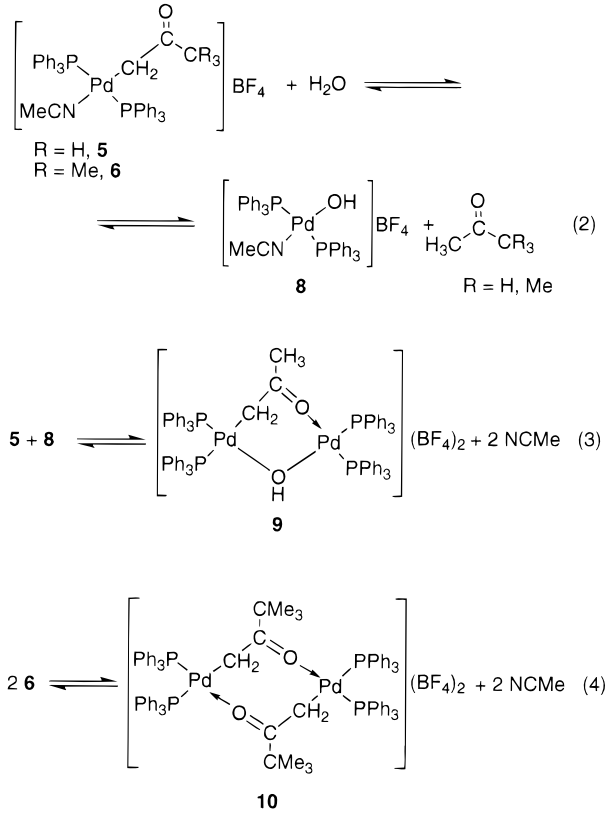


Figure 1. $^{31}P\{^{1}H\}$ NMR for the mixture of **5** (*), **8** (◆), and **9** (▲) in $CDCl_3$, (a) before and (b) after adding CD_3CN.

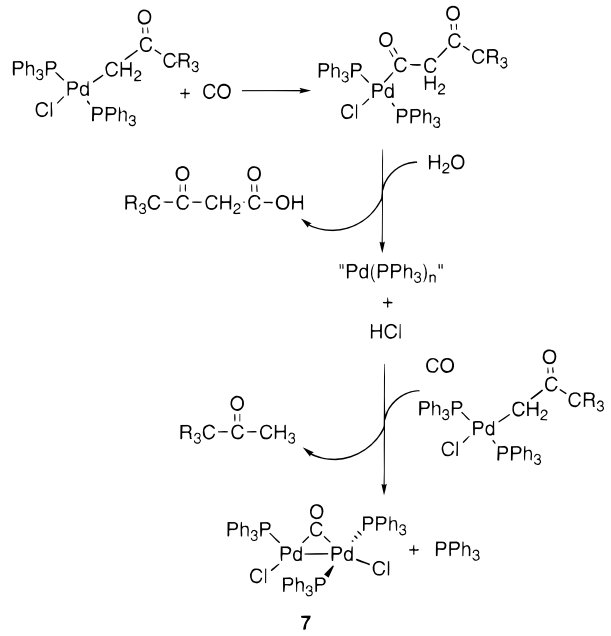
indeed hydrolysis reactions are observed in noncoordinating solvents. Complexes **1** and **2** slowly decompose in $CDCl_3$ by protonolysis of the enolate moiety to give the corresponding ketone and $[PdCl_2(PPh_3)_2]$. The same products are observed when HCl(aq) is added to **1** or **2** in chloroform. 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 $[Pd(OH)(PPh_3)_2(NCMe)](BF_4)$ (**8**), and a dimer $[Pd_2\{\mu\text{-}\kappa^2\text{-C,O-}CH_2C(O)CH_3\}(\mu\text{-}OH)(PPh_3)_4](BF_4)_2$ (**9**) is found (eqs 2 and 3). A solution of **6** in $CDCl_3$ contains complexes **6**, **8,** and the enolate-bridged $[Pd_2\{\mu\text{-}\kappa^2\text{-C,O}-CH_2C(O)CMe_3\}_2(PPh_3)_4](BF_4)_2$ (**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).

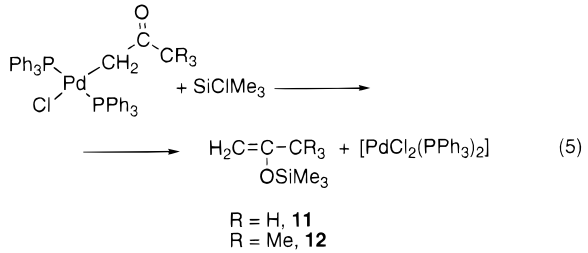
Cationic hydroxo derivatives (**8**, **9**) are the straightforward products of the hydrolysis of **5** and **6**. The

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 $[PdCl_2(PPh_3)_2]$, 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 $CH_2{=}C(OSiMe_3){-}CR_3$ (**11**, R = H; **12**, R = Me) and $[PdCl_2(PPh_3)_2]$ (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 $-CH_2(CO)R$ moiety. We observe that the preference for the dimeric enolate bridge follows the trend Ph > Me > ^{t}Bu 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 (R = Me, ^{t}Bu) or dimeric C−O bridging Pd enolates for R = 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 ν(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 R = ^{t}Bu > 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 R = Me, ^{t}Bu than when R = 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. ^{1}H, ^{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 ^{1}H 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. $[Pd(PPh_3)_4]$ was prepared as described elsewhere.[13]

Synthesis of $[Pd(CH_2C(O)CH_3)Cl(PPh_3)_2]$ (1). The preparation in the literature was slightly modified.[6c] To a slurry of $Pd(PPh_3)_4$ (2 g, 1.73 mmol) in toluene under a nitrogen atmosphere was added $ClCH_2C(O)CH_3$ (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 $C_{39}H_{35}ClOP_2Pd$: C, 64.74; H, 4.87. Found: C, 64.42; H, 4.84. IR, ν(C=O) 1685 cm^{-1}, ν(Pd−Cl) 262 cm^{-1}. ^{1}H NMR (300 MHz, δ, $CDCl_3$): *trans*-**1**, 7−7.9 (m, 30 H, Ph), 2.18 (t, 2 H, CH_2-, $^3J_{H-P}$ = 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}P{^{1}H} NMR (121 MHz, δ, $CDCl_3$): *trans*-**1**, 28.3 (s); *cis*-**1**, 21.3 (d, 1P, $^2J_{P-P}$ = 34 Hz), 38.1 (d, 1P, $^2J_{P-P}$ = 34 Hz). ^{13}C{^{1}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 tetrahydrofurane 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 $C_{42}H_{41}ClOP_2Pd$: C, 65.89; H, 5.40. Found: C, 65.49; H, 5.54. IR, ν(C=O) 1669 cm^{-1}, ν(Pd−Cl) 284 cm^{-1}. ^{1}H 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−, $^3J_{H-P}$ = 10.5 Hz, 5.4 Hz), 1.06 (s, 9H, 3Me). ^{1}H NMR (300 MHz, δ, $CDCl_3$, 243 K): *trans*-**2**, 2.32 (t, $^3J_{H-P}$ = 7.6 Hz, CH_2, 2 H), 0.13 (s, 9 H, 3Me), 7.4−7.75 (m, 30 H, Ph). ^{31}P{^{1}H} NMR (121 MHz, δ, $CDCl_3$, 293 K): *trans*-**2**, 28.9 (bs), *cis*-**2**, 19.9 (d, 1P, $^2J_{P-P}$ = 34 Hz), 39.9 (d, 1P, $^2J_{P-P}$ = 34 Hz). ^{13}C{^{1}H} NMR (74.5 MHz, δ, $CDCl_3$, 243 K): 26.7 (s, 3 CH_3), 29.1 (s, CH_2−), 44.2 (s, *C*Me$_3$), 220.87 (s, C=O), 128.1−135.1 (Ph).

Synthesis of $[Pd_2(\mu\text{-}CH_2C(O)CH_3)_2Cl_2(PPh_3)_2]$ (3). Complex **1** (0.1 g, 0.138 mmol) was dissolved in tetrahydrofurane (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 $C_{42}H_{40}Cl_2O_2P_2Pd_2$: C, 54.68; H, 4.37. Found: C, 54.24; H, 4.33. IR, ν(C=O) 1654 cm^{-1}, ν(Pd−Cl) 279 cm^{-1}. ^{1}H 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}P{^{1}H} NMR (121 MHz, δ, $CDCl_3$, 293 K): 36.2 (s). ^{13}C{^{1}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). ^{1}H 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}P{^{1}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 $C_{48}H_{52}Cl_2O_2P_2Pd_2$: C, 57.27; H, 5.21. Found: C, 56.94; H, 5.07. IR, ν(C=O) 1687 cm^{-1}, ν(Pd−Cl) 275 cm^{-1}. ^{1}H 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}P{^{1}H} NMR (121 MHz, δ, $CDCl_3$, 293 K): 36.7 (s). ^{1}H 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}P{^{1}H} NMR (121 MHz, δ, $CDCl_3$, 223 K): 38.1 (s, **4c**), 37.4 (s, **4a**).

Preparation of $[Pd(CH_2C(O)CH_3)(PPh_3)_2(NCMe)](BF_4)$ (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

(11) Campbell, H. J.; Edward, J. T. *Can. J. Chem.* **1960**, *38*, 2109.

(12) Protonation of the enolate oxygen could take place either in a σ-ketonyl form or in an intermediate π-coordinated enolate to give a vinyl alcohol complex (see: Hillis, J.; Francis, J.; Ori, M.; Tsutsui, M. *J. Am. Chem. Soc.* **1974**, *96*, 4800−4804). We have no experimental evidence to favor one pathway or the other.

(13) Coulson, D. R. in *Inorg. Synth.* **1990**, *28*, 107−109.

added, yielding a pale yellow solid, which was filtered washed with Et_2O (2 × 10 mL) and air-dried: 0.15 g, 90% yield. Anal. Calcd for $C_{41}H_{38}BF_4NOP_2Pd$: 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, CD_3CN, 293 K): 7.2−7.8 (m, Ph, 30 H), 2.30 (bs, 2 H, CH_2), 1.20 (bs, 3 H, CH_3). ^1H NMR (300 MHz, δ, CD_3CN, 238 K): 7.1−7.7 (m, Ph, 30 H), 2.24 (t, 2 H, $^3J_{H-P}$ = 8 Hz, CH_2), 0.90 (s, 3 H, CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, δ, CD_3CN, 293 K): 28.0 (s). $^{13}C\{^1H\}$ NMR (74.5 MHz, δ, CD_3CN, 238 K): 211.8 (s, C═O), 129.0−135.1 (Ph), 32.2 (s, CH_2), 30.0 (s, CH_3).

Complex **6** was prepared following the same procedure. Anal. Calcd for $C_{44}H_{44}BF_4NOP_2Pd$: 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, CD_3CN, 293 K): 7.2−7.9 (m, 30 H, Ph), 2.55 (bs, 2 H, CH_2), 0.20 (bs, 9 H, CMe_3). ^1H NMR (300 MHz, δ, CD_3CN, 243 K): 7.2−7.8 (m, Ph, 30 H), 2.54 (t, 2 H, $^3J_{H-P}$ = 7.8 Hz, CH_2), 0.08 (s, 9 H, CMe_3). $^{31}P\{^1H\}$ NMR (121 MHz, δ, CD_3CN, 293 K): 28.3 (bs). $^{13}C\{^1H\}$ NMR (74.5 MHz, δ, CD_3CN, 293 K): 219.4 (s, C═O), 127.8−135.3 (Ph), 44.8 (s, *C*Me_3), 27.6 (s, CH_2), 26.4 (s, C*Me*$_3$).

When complex **5** was dissolved in $CDCl_3$, 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 $CDCl_3$.

5: ^1H NMR (300 MHz, δ, $CDCl_3$): 6.8−7.9 (m, Ph), 2.30 (t, 2 H, $^3J_{H-P}$ = 8 Hz, CH_2), 1.40 (bs, 3 H, CH_3CN), 1.00 (s, 3 H, CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, δ, $CDCl_3$): 27.1 (s).

6: ^1H NMR (300 MHz, δ, $CDCl_3$,): 7.0−8.0 (m, Ph), 2.57 (t, 2 H, $^3J_{H-P}$ = 7.8 Hz, CH_2), 0.18 (s, 9 H, CMe_3), 1.34 (s, 3 H, CH_3CN). $^{31}P\{^1H\}$ NMR (121 MHz, δ, $CDCl_3$): 27.4 (s).

8: ^1H NMR (300 MHz, δ, $CDCl_3$): 6.8−7.9 (m, Ph), 0.9 (bs, 3 H, CH_3CN), −2.3 (bs, OH). $^{31}P\{^1H\}$ NMR (121 MHz, δ, $CDCl_3$): 33.9 (s).

9: ^1H NMR (300 MHz, δ, $CDCl_3$): 6.8−7.9 (m, Ph), 4.1 (dd, 1 H, $^2J_{H-H}$ = 11 Hz, $^3J_{H-P}$ = 4.5 Hz, CH_2), 2.8 (m, 1 H, CH_2), 1.2 (s, 3 H, CH_3), −0.4 (bs, OH). $^{31}P\{^1H\}$ NMR (121 MHz, δ, $CDCl_3$): 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, $CDCl_3$): 7.0−8.0 (m, Ph), 3.08 (d, 2 H, $^3J_{H-P}$ = 6.5 Hz, CH_2), 1.09 (s, 9 H, CMe_3). $^{31}P\{^1H\}$ NMR (121 MHz, δ, $CDCl_3$): 33.9 (d, 2 P, J = 36.8 Hz), 21.2 (d, 2 P, J = 36.8 Hz).

Reactions with CO. Synthesis of [$Pd_2(\mu$-CO)$Cl_2(PPh_3)_3$] (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 $C_{55}H_{45}Cl_2OP_3Pd_2$: 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, $CDCl_3$): 7.15−7.8 (m, 45 H, Ph). $^{31}P\{^1H\}$ NMR (121 MHz, δ, $CDCl_3$): 22.4 (bs). $^{13}C\{^1H\}$ NMR (74.5 MHz, δ, $CDCl_3$, under a CO atmosphere): 210.4 (s, C═O), 128.0−135.1 (Ph).

CO was bubbled through solutions of **1** or **2** in $CDCl_3$ for 5 min. The yellow solutions turned orange, and **7** and the corresponding ketoacids, $CR_3C(O)CH_2COOH$, were observed by NMR.

R = H: ^1H NMR (300 MHz, δ, $CDCl_3$), 12.1 (bs, 1 H, COOH), 3.50 (s, 2 H, CH_2−), 2.17 (s, 3 H, CH_3).

R = Me: ^1H NMR (300 MHz, δ, $CDCl_3$), 12.3 (bs, 1 H, COOH), 3.58 (s, 2 H, CH_2−), 1.17 (s, 9 H, CMe_3).

Reaction of 1 with $SiClMe_3$. To a solution of **1** (0.0156 g, 0.022 mmol) in $CDCl_3$ (0.6 mL) was added $SiClMe_3$ (0.003 mL, 0.023 mmol). [$PdCl_2(PPh_3)_2$] and **11** appeared immediately as shown by ^1H and ^{31}P NMR.

11: ^1H NMR (300 MHz, δ, $CDCl_3$): 4.06 (m, 1 H, H^1), 4.05 (bs, 1 H, $H^{1'}$), 1.78 (d, J = 1 Hz, 3 H, Me^3), 0.21 (s, 9 H, $SiMe_3$).

Compound **12** was obtained in a similar way: ^1H NMR (300 MHz, δ, $CDCl_3$): 4.09 (d, J = 1 Hz, 1 H, H^1), 3.93 (bs, 1 H, $H^{1'}$), 1.05 (s, 9 H, 3 Me^3), 0.21 (s, 9 H, $SiMe_3$).

Kinetic Measurements. NMR tubes (5 mm) were charged with the appropriate amount of complexes **1** and **2** (or complex **1** and PPh_3), and $CDCl_3$ 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 ^{31}P resonance of complex **1** using a 90°−D_1−90°−t−90°−D_2 sequence, where $D_1 = 1/2\Delta\nu$, $\Delta\nu$ is the separation in Hz between both signals, t is the magnetization transfer delay, and D_2 is the relaxation delay. Values of 90° pulses and D_1 were determined at each temperature. After excitation, the signal areas of both signals (**1** and **2**, or **1** and PPh_3) were measured and processed to obtain the values of k_{obs}, as was reported before.[15] Values of k_{obs}(**1**→PPh_3) reported in Table 1 were calculated from the experimental k_{obs}(PPh_3→**1**) using the equilibrium equation [**1**]k_{obs}(**1**→PPh_3) = [PPh_3]k_{obs}(PPh_3→**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.

OM990613O

(14) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679−680.
(15) Albéniz, A. C.; Casado, A. L.; Espinet, P. *Inorg. Chem.* **1999**, *38*, 2510−2515.
(16) (a) Casado, A. L.; Casares, J. A.; Espinet, P. *Organometallics* **1997**, *16*, 5730−5736. (b) Kirkup, L. *Experimental Methods*; Wiley: Brisbane, 1994.