Mechanistic Studies of Catalytic Olefin Dimerization Reactions Using Electrophilic η^3-Allyl−Palladium(II) Complexes

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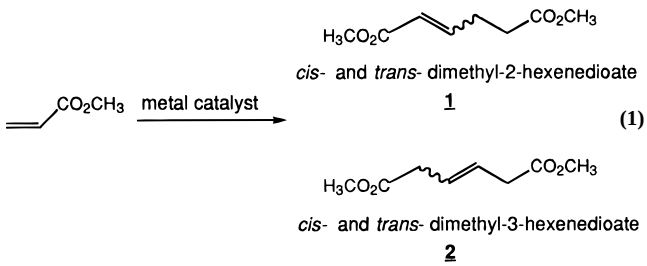
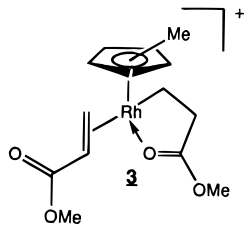
Abstract: The dimerization of olefins by well-defined cationic η^3-allyl−palladium complexes of the type $[(C_3H_5)Pd(L)(PR_3)]^+[BAr'_4]^-$ ($Ar' = [3,5\text{-}C_6H_3(CF_3)_2]$; L = OEt_2, H_2O; R = cyclohexyl (Cy), *n*-butyl (^{n}Bu)) has been studied. These complexes react with ethylene or methyl acrylate at −80 °C with loss of L to form the η^2-olefin complexes $[(C_3H_5)Pd(\eta^2\text{-olefin})(PR_3)]^+[BAr'_4]^-$ (olefin = $H_2C{=}CH_2$, $CH_2{=}CHC(O)OCH_3$). Upon warming, allyl−olefin coupling occurs. The dimerization of ethylene occurs rapidly at 0 °C with an observable ethyl−ethylene intermediate $[(C_2H_5)Pd(C_2H_4)_2(PCy_3)]^+[BAr'_4]^-$. Methyl acrylate reacts to form a stable acrylate chelate complex, $[(CH_3O(O)CCH_2CH_2)Pd(CH_2{=}CHC(O)OCH_3)(PR_3)]^+[BAr'_4]^-$, which is the catalyst resting state for methyl acrylate dimerization which occurs at room temperature to give predominantly *trans*-dimethyl-2-hexenedioate.

Introduction

Transition metal-catalyzed dimerization of functionalized olefins represents an attractive route to inexpensive difunctional monomers useful for polymer synthesis via condensation techniques. The regioselective tail-to-tail dimerization of methyl acrylate has been extensively examined as an alternative route to adipic acid, one of the monomers used in the production of Nylon 6,6.[1−29] As shown in eq 1, tail-to-tail dimerization yields the unsaturated, linear diesters which can be converted to adipic acid by hydrogenation and hydrolysis. Since acrylates are produced from oxidation of propene, this route provides an entry into adipic acid based on a C_3 feedstock which contrasts with the currently practiced methods based on C_6 feedstocks.[1,2]



Acrylate dimerization catalysts based on Rh, Ru, Pd, and Ni have all been reported.[3−29] The most efficient catalyst systems and those best understood mechanistically are cationic Rh(III) catalysts derived from protonation of bis-ethylene complexes of the type $C_5Me_5Rh(C_2H_4)_2$, (η^5-1,2,3-trimethylindenyl)Rh-$(C_2H_4)_2$, and (η^5-1,2,3,4,5,6,7-heptamethylindenyl)Rh$(C_2H_4)_2$. The resting state of the $C_5Me_5Rh^{III}$-based catalyst was shown to be the rhodium(III)−chelate complex **3** illustrated below, with the turnover-limiting step being the migratory insertion reaction of **3** with exclusive tail-to-tail coupling occurring.[9,11,12]



Extensive work on the economically more attractive Pd(II)-based systems has been reported. Four catalyst precursors, $(C_6H_5CN)_2PdCl_2$, $Pd(CH_3CN)_4^{2+}$, (η^3-CH_2CRCH_2)PdL_2, and $Pd(AcAc)_2$, have been investigated. Early work by Hazeldine[17] on $(C_6H_5CN)_2PdCl_2$ revealed dimerization activity at 113 °C

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1996.

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in pure methyl acrylate (60 turnovers, approximately 90% selectivity for linear dimers). Oehme and co-workers[18] discovered that activation of $(C_6H_5CN)_2PdCl_2$ with $AgBF_4$/benzoquinone resulted in a longer lived catalyst (340 turnovers) operating at room temperature while Nugent and McKinney[5] examined the influence of various Lewis and protic acid additives on the catalytic activity of this system. Nugent later reported a mild, highly selective route for the dimerization of methyl acrylate using the electrophilic, dicationic $[Pd(CH_3CN)_4]^{2+}[BF_4]_2^-$ and $LiBF_4$ (150 turnovers, 40 °C).[19,20] Tkatchenko and co-workers[24,30,31] have examined η^3-allyl−Pd(II) precursors for methyl acrylate dimerization. Typically, (η^3-allyl)$Pd(COD)^+$ salts were treated with phosphines in CH_2Cl_2 to generate active catalyst systems. Bu_3P was found to be particularly effective; addition of 0.5 equiv to (η^3-CH_2-CCH_3CH_2)$Pd(COD)^+$ resulted in an active catalyst system (300 turnovers, 20 h, 80 °C) with high selectivity for linear dimers. Methyl acrylate dimerization was also achieved by protonation of $Pd(AcAc)_2$ with HBF_4 in CH_2Cl_2.[25,31]

Several possible mechanisms have been suggested for these Pd(II)-catalyzed acrylate dimerizations including an oxidative addition pathway through a vinyl hydride intermediate,[23] a Cossee−Arlman insertion mechanism functioning through a palladium hydride intermediate,[17] and carbon−carbon bond coupling through formation of a Pd(II) metallacycle.[25] No thorough mechanistic studies have been carried out which firmly established the mechanistic details of these closely related Pd(II) catalytic systems. Thus, it was the goal of this work to prepare well-defined Pd(II)-catalyst precursors and examine working catalyst systems by NMR spectroscopy in order to establish the mechanism of acrylate dimerization.

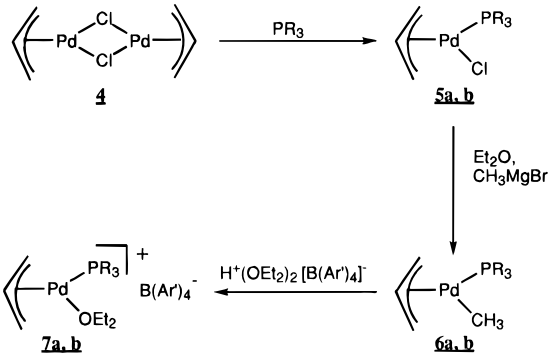
We report here the synthesis of monocationic η^3-allyl−palladium(II) complexes of the type (η^3-C_3H_5)$Pd(PR_3)(OEt_2)^+$-$(BAr'_4)^-$ (Ar′ = [3,5-$(CF_3)_2C_6H_3$]) and use of these complexes for both catalytic ethylene and methyl acrylate dimerization and low-temperature NMR studies which lend insight into the details of the catalytic cycle for these dimerization reactions.

Results and Discussion

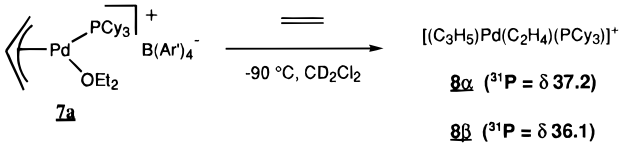
1. Synthesis of the η^3-Allyl−Palladium(II) Precatalysts $[(C_3H_5)Pd(OEt_2)(L)]^+[BAr'_4]^-$ (7: L = PCy_3 (a), PBu_3 (b)). The dimeric complex $[(C_3H_5)PdCl]_2$ (**4**)[32] reacts with PCy_3 or PBu_3 via chloride bridge-splitting to give the monomeric complexes $[(C_3H_5)Pd(Cl)(PR_3)]$ (**5a,b**).[33] Treatment of **5a,b** with CH_3MgBr gives $[(C_3H_5)Pd(CH_3)(PR_3)]$ (**6a,b**).[34] Complex **6a** (R = Cy) and complex **6b** (R = ^{n}Bu) are isolated as a pure crystalline solid and as an oil, respectively. Protonation of complexes **6a,b** with the oxonium acid, $(Et_2O)_2H^+(BAr'_4)^-$ (Ar′ = 3,5-$C_6H_3(CF_3)_2$), gives complexes **7a,b** in good yields (Scheme 1).

Complexes **7a,b** are highly electrophilic and the diethyl ether ligands are quite labile. In the presence of even traces of water, the ether ligand is readily displaced and thus complexes $[(C_3H_5)Pd(OEt_2)(PR_3)]^+[BAr'_4]^-$ (**7a,b**), which are isolated or are observed in solution, often contain small amounts of the corresponding aquo complexes. The noncoordinating counterion $[3,5\text{-}C_6H_3(CF_3)_2]_4B^-$ stabilizes these highly electrophilic complexes and increases their solubility, whereas traditional counterions, such as $[PF_6]^-$ and $[BF_4]^-$, often yield insoluble complexes that can decompose via halide ion abstraction.[35] The use of the noncoordinating counterion, together with the high purity of the crystalline tricyclohexylphosphine complex, enabled the detailed mechanism of reactions of these complexes with ethylene and methyl acrylate to be investigated by low-temperature NMR spectroscopy.

Scheme 1. Synthesis of Precatalysts $[(C_3H_5)Pd(OEt_2)(PR_3)]^+[BAr'_4]^-$ (**7a,b**: R = Cy (a) ^{n}Bu (b))



Scheme 2 *In Situ* Generation of Isomeric $[(C_3H_5)Pd(C_2H_4)(PCy_3)]^+[BAr'_4]^-$ (**8α** and **8*β***)



2. Reactivity of the η^3-Allyl Complex $[(C_3H_5)Pd(OEt_2)(PCy_3)]^+[BAr'_4]^-$ (7a) with Ethylene. Spectroscopic Detection of Reaction Intermediates. A. Initial Observation of Catalytic Ethylene Dimerization. Treatment of a CD_2Cl_2 solution of the η^3-allyl−palladium ether complex $[(C_3H_5)Pd(OEt_2)(PCy_3)]^+[BAr'_4]^-$ (**7a**) at −10 °C with excess ethylene results in catalytic ethylene dimerization to form butenes. The major butene isomer present was identified by ^{1}H NMR spectroscopy as *trans*-2-butene (cis:trans, ca. 1:6). Having demonstrated that **7a** dimerizes ethylene, a detailed analysis of the reaction mechanism was performed by monitoring this reaction by low temperature NMR spectroscopy. Two key intermediates in the catalytic formation of butenes have been observed. The characterization of these intermediates and the details of the initiation process and the subsequent dimerization reaction are described below.

B. Formation, Low-Temperature Spectroscopic Characterization, and Dynamic Behavior of $[(C_3H_5)Pd(C_2H_4)(PCy_3)]^+[BAr'_4]^-$ (8). Exposure of the η^3-allyl−palladium ether complex $[(C_3H_5)Pd(OEt_2)(PCy_3)]^+[BAr'_4]$ (**7a**) to 40 equiv of ethylene in CD_2Cl_2 at −90 °C results in the generation of two new species in approximately a 1:1 ratio with ^{31}P NMR signals at 37.2 and 36.1 ppm (Scheme 2 and Figure 1a). Warming this solution in the NMR probe results in broadening of these signals, coalescence at −74 °C, and sharpening to a singlet at −40 °C. Rate analysis ($k = \pi\Delta\upsilon/\sqrt{2}$) at the coalescence temperature (−74 °C) yields $k_{ex} = 300\ s^{-1}$ with $\Delta G^{\ddagger} = 9.3$ kcal mol^{-1}.

On the basis of ^{1}H NMR spectroscopy, these species are proposed to be two isomers of the η^3-allyl−palladium ethylene adduct $[(C_3H_5)Pd(C_2H_4)(PCy_3)]^+[BAr'_4]^-$ (**8**). At −20 °C a multiplet centered at 4.4 ppm (see Figure 1b) that can be

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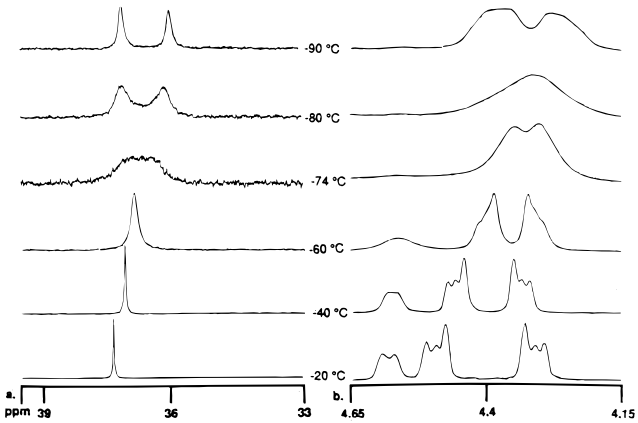
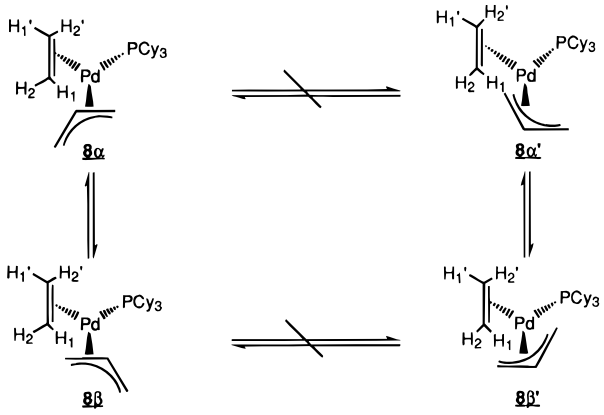


Figure 1. Variable-temperature ^{31}P (a) and ^{1}H (b) NMR spectra of **8**.

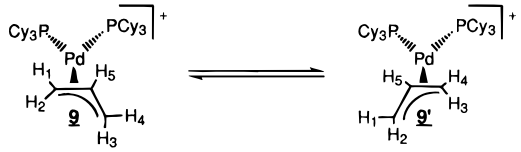
Scheme 3. Proposed Dynamic Behavior of $[(C_3H_5)Pd(C_2H_4)(PCy_3)]^+[BAr'_4]^-$ (**8**)



interpreted as an AA′BB′ pattern is observed, which corresponds to the four hydrogens of the palladium-bound ethylene ligand. In the presence of excess ethylene, these signals remain sharp, indicating that no exchange of bound ethylene with free ethylene is occurring on an NMR time scale at −20 °C. Three allyl resonances appear at 5.32 (multiplet), 4.58 (broad doublet), and 2.41 (broad) ppm. The two remaining allyl resonances are obscured by the resonances of Et_2O and the tricyclohexylphosphine. The ^{1}H NMR resonances of the bound ethylene exhibit complex behavior between −20 and −90 °C (Figure 1b). Clearly between −20 and −74 °C the chemical shift difference between H_A, H_A' and H_B, H_B' decreases. Below −74 °C the resonances again separate, and at −90 °C two very broad signals are observed which we propose to be two overlapping sets of AA′BB′ resonances (see below). While accurate rate data cannot be extracted from these spectra, it is clear that this dynamic process must be the same one responsible for the temperature dependence of the ^{31}P signals.

The dynamic behavior of **8** is proposed to occur through a "rocking" motion of the allyl ligand which interconverts isomers **8α** and **8*β*** (Scheme 3). Solid-state structures of certain η^3-allyl−palladium(II) complexes support the idea that the allyl unit can be rotated out of the square plane in such a way that the C_1-C_2 of the allyl ligand is nearly aligned with the plane formed by Pd and the remaining two ligands.[36] In analogy with other Pd(II) olefin complexes, we assume that ethylene rotation in **8α** and **8*β*** (which interconverts H_1 with H_1' and H_2 with H_2') is always rapid on an NMR time scale. At low temperatures two ^{31}P signals will be observed for **8α** and **8*β*** as well as two

Scheme 4. The Two Enantiomers of $[(C_3H_5)Pd(PCy_3)_2]^+[BAr'_4]^-$ (**9**)



sets of AA′BB′ signals for the ethylene hydrogens. Rapid allyl rocking will result in coalesence of the ^{31}P signals as well as averaging the two sets of AA′BB′ patterns to a single AA′BB′ pattern as observed at −20 °C. The fact that the ethylene ^{1}H signals do not coalesce to a single resonance indicates that enantiomers **8α**, and **8α′** (and **8*β***, and **8*β′***) do not interconvert on an NMR time scale. Such a process could have occurred by the normal $\pi \rightarrow \sigma$ allyl mechanism,[37−42] but the narrow ^{1}H line widths at −20 °C indicate such a process must have a free energy of activation greater than ca. 14 kcal/mol.

C. Dynamic Behavior of $[(C_3H_5)Pd(PCy_3)_2]^+[BAr'_4]^-$ (9). To provide further support for the allyl rocking mechanism, the cationic allyl complex $[(C_3H_5)Pd(PCy_3)_2]^+[BAr'_4]^-$ (**9**) was examined in which the two cis ligands (PCy_3) are identical. If the allyl unit is unsymmetrically bound to Pd an allyl rocking would result in a degenerate exchange between the two enantiomers **9** and **9′** (Scheme 4). Complex **9** was prepared by addition of 1 equiv of PCy_3 to a CD_2Cl_2 solution of $[(C_3H_5)Pd(OEt_2)(PCy_3)]^+[BAr'_4]^-$ (**7a**). The ^{31}P NMR spectrum at −82 °C showed nonequivalent ^{31}P signals as an AB quartet centered at 36.6 ppm (J_{pp} = 29.3 Hz). Warming resulted in broadening and coalescence of the ^{31}P signals to a singlet above −50 °C. As expected, at −20 °C the ^{1}H NMR spectrum showed only three signals for the five allyl hydrogens at δ 5.36 (m, 1H, H_5), 4.47 (bs, 2H, H_1 and H_4), and 2.91 (bs, 2H, H_2 and H_3).[43]

The rates for allyl-rocking are most conveniently measured by line shape analysis of the ^{31}P NMR resonances of P_A and P_B. The experimental line shapes were compared to calculated line shapes using the DNMR3 simulation program.[44−47] Figure 2 illustrates the set of observed and calculated spectra for complex **9**. Using this technique, rate constants could be

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(43) A reviewer has suggested that the dynamic behavior we ascribe to allyl rocking may be due to interconversion of two conformational isomers of the tricyclohexylphosphine ligand. This cannot be ruled out for the mono-tricyclohexylphosphine complexes. In the case of the bis-tricyclohexylphosphine complex **9**, only two ^{31}P resonances are observed under slow exchange conditions. These signals are coupled to one another showing they belong to a single isomer undergoing a degenerate isomerization which interconverts the two ^{31}P sites. This is consistent with the allyl rocking proposal (**9** ⇌ **9′**). If two conformations of the tricyclohexylphosphine ligand were possible, then three isomers would be expected for **9**. Only one isomer of the three would exhibit inequivalent phosphorus nuclei. It seems unlikely that this would be the sole isomer detectable. Thus we favor allyl rocking to account for the dynamics of **9** and, by analogy, for the dynamics of the other allyl complexes.

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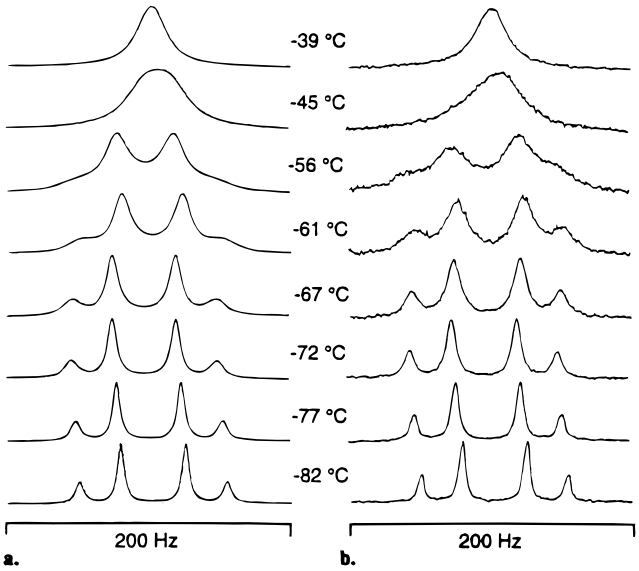


Figure 2. Calculated (a) and observed (b) variable-temperature ^{31}P NMR spectra for **9**.

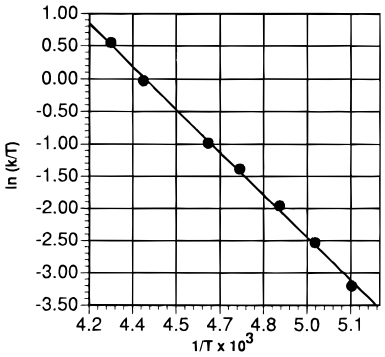


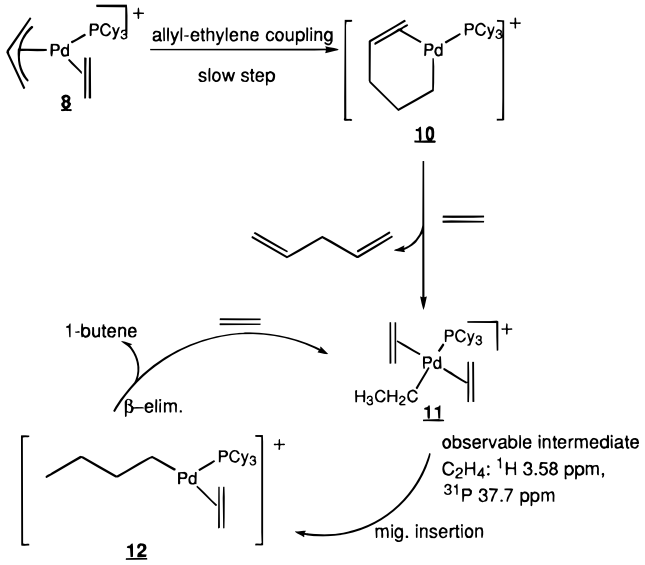
Figure 3. The Eyring plot of the rate data for intramolecular allyl rocking in complex **9**.

obtained over a 50 °C temperature range (−86 to −36 °C), which permits calculation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for this process. The Eyring plot of the data for intramolecular allyl rocking in complex **9** yields $\Delta H^{\ddagger} = 9.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -8.8$ eu and is shown in Figure 3.

D. Spectroscopic Studies of the Dimerization Cycle. The η^3-allyl−palladium ethylene complex $[(C_3H_5)Pd(C_2H_4)(PCy_3)]^+[BAr'_4]^-$ (**8**) is stable up to −20 °C in the presence of excess ethylene. Warming above −20 °C results in dimerization of ethylene to butenes (primarily *trans*-2-butene cis:trans, ca. 1:6). The major organometallic species remaining after ethylene dimerization is the *unreacted* allyl ethylene complex, **8**. This observation implies that complex **8**, in a slow step, undergoes a transformation which generates an active catalyst for ethylene dimerization which then rapidly dimerizes ethylene before appreciable depletion of starting complex **8**. Monitoring of this solution by variable-temperature ^{1}H and ^{31}P NMR spectroscopy yields additional information.

At −20 °C a new ^{31}P resonance grows in at 33.7 ppm at the same time that ethylene dimerization to predominantly the *trans*-2-butene isomer occurs. Its maximum intensity corresponds to only about 25% of that of resonances for **8α**, **8*β***. This species presumably corresponds to the catalyst resting state for ethylene dimerization. In addition to the production of butenes, the ^{1}H NMR spectrum reveals formation of a small amount of a species containing olefinic resonances (assigned as 1,4 pentadiene) along with the appearance of a new broad singlet at 3.58 ppm in the ^{1}H NMR spectrum.[48] Saturation of the resonance at 3.58 ppm

Scheme 5. Proposed Mechanistic Scheme for Catalytic Butene Formation



results in nearly complete disappearance of the signal at 5.41 ppm for free ethylene. Correspondingly, irradiating the free ethylene signal results in complete disappearance of the 3.58 ppm signal. This result indicates that the 3.58 ppm resonance belongs to a new palladium−ethylene complex in which the coordinated ethylene is exchanging with free ethylene at −20 °C. While the structure of this species is uncertain, a reasonable proposal is that this species corresponds to the ethyl−ethylene complex, **11**, which is the catalyst resting state in the dimerization cycle.[49,50] After complete dimerization of ethylene, the 3.58 ppm species disappears. Scheme 5 represents a tentative proposal for the reaction of $[(C_3H_5)Pd(OEt_2)(PCy_3)]^+[BAr'_4]^-$ (**7a**) with ethylene and entry into the catalytic ethylene dimerization cycle.

3. Reactivity of the Allyl Ether Complexes $[(C_3H_5)Pd(OEt_2)(L)]^+[BAr'_4]^-$ (7: L ,= PCy_3 (a), PBu_3) (b) with Methyl Acrylate. Spectroscopic Detection and Study of Reaction Intermediates. A. Initial Observation of Catalytic Methyl Acrylate Dimerization. Exposure of the η^3-allyl−palladium ether complexes $[(C_3H_5)Pd(OEt_2)(PR_3)]^+[BAr_4']^-$, (**7a,b**) to excess methyl acrylate results in catalytic methyl acrylate dimerization. For example, treatment of 1 mL of methyl acrylate (10 mmol) with 0.05 g (0.04 mmol) of the tri-*n*-butylphosphine complex, $[(C_3H_5)Pd(OEt_2)(P(^nBu_3))]^+[BAr_4']^-$ (**7b)** results in the formation of tail-to-tail methyl acrylate dimers (200 turnovers) after 24 h at 60 °C. The reactivity of methyl acrylate with complexes **7a** and **7b** has been studied by low-temperature NMR spectroscopy. These studies, which reveal the mechanistic details of the initiation step and the catalytic cycle, are described below.

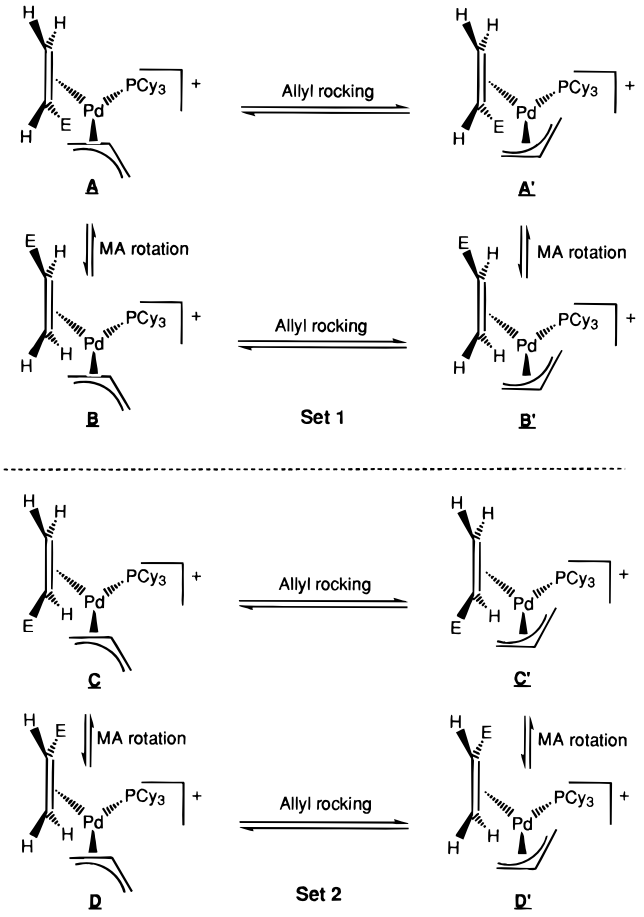
B. Low-Temperature NMR Spectroscopic Characterization of the Acrylate Complex $[(C_3H_5)Pd(CH_2{=}CHC(O)OCH_3)(PCy_3)]^+[BAr'_4]^-$ (13). Treatment of $[(C_3H_5)Pd(OEt_2)(PCy_3)]^+[BAr'_4]^-$ (**7a**) with 1 equiv of methyl acrylate in CD_2Cl_2 at −100 °C results in the formation of four new species with ^{31}P signals at 38.5, 37.5, 37.3, and 37.2 ppm

(48) Very recently, the reaction of similar allyl−palladium complexes with ethylene was directly observed: Mecking, S.; Keim, W. *Organometallics* In press.

(49) Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137.

(50) There is no evidence that this species is a bis-ethylene complex. However, since ethylene readily displaces diethyl ether in these cationic species, we believe a bis-ethylene complex is more likely than a solvated mono-ethylene complex.

Scheme 6. The Eight Stereoisomers of $[(C_3H_5)Pd(\eta^2\text{-}CH_2{=}CHC(O)OCH_3)(PCy_3)]^+[BAr'_4]^-$ (**13**)[a]

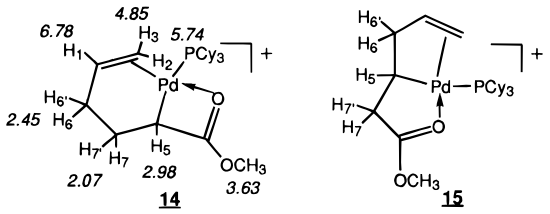


[a] Allyl rocking is shown from left to right and olefin rotation is shown from top to bottom. Sets **1** and **2** result from coordination of the two enantiofaces of the η^2-methyl acrylate ligand.

(approximate ratios, 1.5:2.5:1:2). Warming this solution results in broadening of the ^{31}P resonances, coalescence of two pairs of signals at ca. −70 °C, and sharpening to two singlets at 38.3 and 37.7 ppm at −50 °C. We postulate that these species are cationic η^3-allyl−palladium complexes of the type $[(C_3H_5)Pd(\eta^2\text{-}CH_2{=}CHC(O)OCH_3)(PCy_3)]^+[BAr'_4]^-$ (**13**). Eight isomers of complex **13** could possibly be observed if both allyl rocking and methyl acrylate rotation were slow on the NMR time scale (see Scheme 6).

Based on experiments described above, it is reasonable to assume that at −100 °C allyl rocking is slow but acrylate rotation is rapid. This would lead to the appearance of four ^{31}P signals as is observed for the sets **13A** ⇌ **13B**, **13A′** ⇌ **13B′**, **13C** ⇌ **13D**, **13C′** ⇌ **13D′**. At higher temperatures rapid allyl rocking would lead to interconversion of the isomers of set 1, **13A**, **13B**, **13A′**, **13B′**, and, likewise, of set 2, **13C**, **13D**, **13C′**, **13D′**, and observation of two ^{31}P signals. Averaging of the two sets would have to occur by migration of Pd from one enantioface of methyl acrylate to the other or from one enantioface to the other of the allyl ligand. These processes apparently have higher activation energies than the methyl acrylate rotation and allyl rocking as supported by the dynamic behavior of **8**.

The isomeric η^3-allyl−palladium acrylate complexes $[(C_3H_5)Pd(CH_2{=}CHC(O)OCH_3)(PCy_3)]^+[BAr'_4]^-$ (**13**) are stable up to −30 °C in the presence of excess methyl acrylate. Warming the solution in the NMR probe to −25 °C results in the formation of a *single* new species with a ^{31}P resonance at 35.1 ppm. The ^1H NMR spectrum of this species exhibits a methoxy resonance at 3.63 ppm, olefinic resonances at δ 6.78 (m, 1H), 5.74 (d, 1H), and 4.85 (d, 1H), and upfield multiplets at δ 2.98 (m, 1H), 2.45 (m, 2H), and 2.07 (m, partially obscured by PCy_3). This species is proposed to be the four-membered chelate **14**, the result of coupling the allyl unit to C_β of the acrylate ligand. ^1H NMR assignments are shown below. The pattern of the resonances at 6.78, 5.74, and 4.85 ppm clearly corresponds to a terminal olefinic unit $-CH_2-CH{=}CH_2$, but the shifts are quite different from an uncomplexed α-olefin. Decoupling experiments establish that H_1 (δ 6.78) is coupled to both H_2 (δ 5.74, J_{12} = 16.7 Hz) and H_3 (δ 4.85, J_{13} = 9.4 Hz), consistent with the proposed structure. H_1 (δ 6.78) is also coupled to the resonance at δ 2.45 and provides support for this assignment as H_6, H_6'. The 1H band at δ 2.98 couples only to the 2H, δ 2.07 band and suggests that δ 2.98 is H_5 and δ 2.07 corresponds to H_7, $H_{7'}$. An alternate structure for **14** is the five-membered chelate complex **15** which could result from β-hydride elimination and reinsertion in **14**. However, **14** is preferred based on the observation that H_5 is coupled only to H_7, $H_{7'}$, and not H_6, $H_{6'}$. Also, being α to a carbonyl group H_7, $H_{7'}$ would be expected to appear further downfield than δ 2.07. These results show that allyl−acrylate coupling occurs at −25 °C to initially give the four-membered chelate **14**. The rate of allyl−acrylate coupling was measured at −25 °C ($k = 1.1 \times 10^{-3}$ s^{-1}, $\Delta G^\ddagger$ = 17.8 kcal mol^{-1}). A typical first-order rate plot is shown in the Experimental Section.

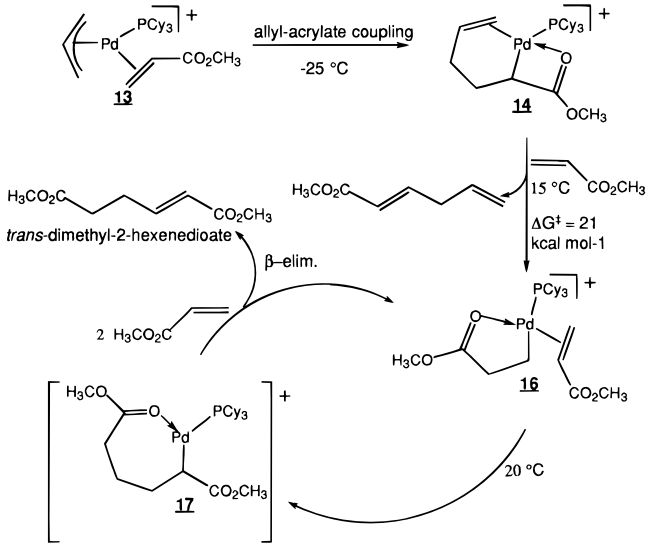


Warming the solution of **14** to 15 °C results in elimination of $CH_2{=}CHCH_2CH{=}CHCO_2CH_3$ and the formation of a new palladium species. The assignment of the elimination product as methyl 2,5-hexadieneoate is based on comparison of the ^1H NMR data with known values.[51] Particularly characteristic is the shift and pattern of the γ-methylene protons (H_3), a triplet of quartets at δ 2.96, due to vicinal coupling with H_2, H_4 (6.5 Hz), and long-range allylic coupling to H_1, H_5, H_6 (ca. 1.5 Hz). The first-order rate constant for elimination of $CH_2{=}CHCH_2CH{=}CHCO_2CH_3$ was determined to be 5.7×10^{-4} s^{-1} at 15 °C ($\Delta G^\ddagger$ = 21.0 kcal mol^{-1}).

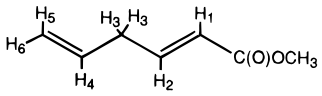
The new Pd species is assigned as the five-membered acrylate chelate complex $[(\eta^2\text{-}CH_2{=}CHCO_2CH_3)Pd(CH_2CH_2C(O)OCH_3)(PCy_3)]^+[BAr'_4]^-$ (**16**) based on ^1H, $^1H\{^{31}P\}$, ^{13}C, and ^{31}P NMR spectroscopy. A single ^{31}P band is observed at 49.5 ppm. The ^1H NMR shows a single methoxy resonance at δ 3.77 (s, 3H) and diagnostic of the chelate a 2H resonance at δ 2.72 (td, J_{HP} = 2.1 Hz) assigned to H_A and a 2H resonance at δ 1.77 (td, J_{HP} = 2.4 Hz) assigned to H_B. There is only a single broad resonance for methyl acrylate which suggests that free methyl acrylate is in rapid equilibrium with bound methyl acrylate. This was verified by cooling the solution to −60 °C which results in the appearance of signals for free methyl acrylate (δ 6.38, 6.13, and 5.81) as well as a second set for the bound methyl acrylate in **16** (δ 4.58, 4.31, and 4.12). The chelate structure is further confirmed by ^{13}C NMR data (20 °C) which show C_α at

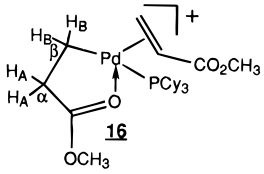
(51) Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833.

Scheme 7. Mechanism for Catalytic Methyl Acrylate Dimerization



δ 40.4, C_β at δ 15.2, $-OCH_3$ at δ 56.6, and the chelated carbonyl resonance at δ 240.6, a typical shift for such carbonyl groups.[52]





Holding the solution of **16** at 20 °C in the presence of methyl acrylate results in slow production of methyl acrylate dimers (predominantly *trans*-dimethyl 2-hexenedioate). No other palladium species appear. The expected palladium hydride intermediates in the reaction steps 14 → 16 and 17 → 16 are not observable under the reaction conditions. Thus, we assign 16 as the catalyst resting state. Scheme 7 summarizes the catalyst activation process and the overall catalytic cycle. The geometry assigned to **16** places the η^2-acrylate ligand cis to C_β of the chelate in the necessary geometry for migratory insertion. However, results described in the next section suggest that the alternative trans geometry must be considered.

C. Isolation and Crystallographic Characterization of a Palladium Chelate Complex from the Catalytic Reaction. To further verify the catalyst resting state as the chelate **16**, a derivative of this chelate has been isolated directly from the catalyst solution and structurally characterized by X-ray crystallography. Six equivalents of methyl acrylate were added to a dichloromethane solution of complex **7a** at −80 °C. The reaction was warmed to 0 °C and stirred for 3 h. The solvent was removed in vacuo, leaving a yellow oil. Single crystals were grown from a concentrated solution of Et_2O and hexane at −30 °C. ^{1}H NMR spectroscopy of this material reveals it to be the chelate complex **18** isolated as a mixture of the diethyl ether and aquo adducts. The crystal selected for X-ray analysis turned out to be the aquo complex. The ORTEP diagram of the aquo complex is shown in Figure 4 and selected bond lengths

(52) Brookhart, M.; Rix, F. C.; DeSimone, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 5894.

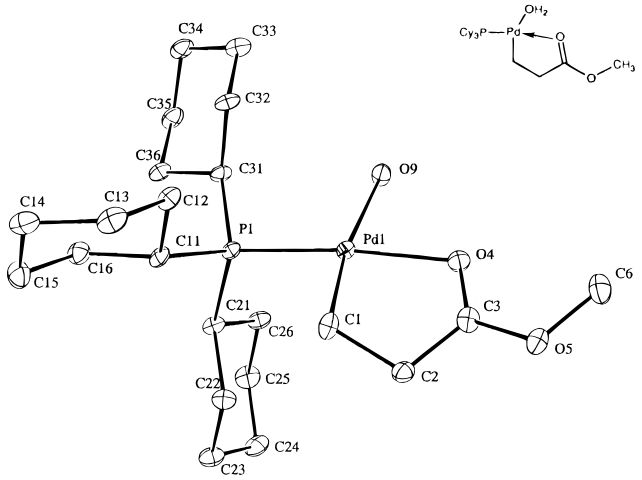


Figure 4. ORTEP diagram for $[(H_2O)Pd(CH_2CH_2C(O)OCH)(PCy_3)]^+[BAr'_4]^-$ (**18**).

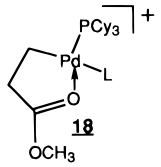
Table 1. Selected Interatomic Distances (in Å) for $[(H_2O)Pd(CH_2CH_2C(O)OCH)(PCy_3)]^+$ $[BAr'_4]^-$ (**18**)

Pd−P	2.2353(24)	P−C(11)	1.838(6)
Pd−C(1)	2.019(7)	P−C(21)	1.832(7)
Pd−C(2)	2.837(6)	P−C(31)	1.846(6)
Pd−C(3)	2.822(6)	C(1)−C(2)	1.531(8)
Pd−O(4)	2.150(4)	C(2)−C(3)	1.475(9)
Pd−O(9)	2.176(4)	C(3)−O(4)	1.243(8)

Table 2. Selected Bond Angles (in deg) for $[(H_2O)Pd(CH_2CH_2C(O)OCH)(PCy_3)]^+[BAr'_4]^-$ (**18**)

P(1)−Pd−C(1)	92.72(18)	C(1)−Pd−O(9)	170.30(20)
P(1)−Pd−O(9)	96.92(13)	Pd−P(1)−C(11)	114.91(21)
O(4)−Pd−O(9)	88.39(17)	Pd−P(1)−C(21)	111.34(20)
C(1)−Pd−O(4)	82.04(21)	Pd−P(1)−C(31)	107.72(21)
P(1)−Pd−O(4)	174.06(12)	Pd−O(4)−C(3)	109.6(4)

and angles are provided in Tables 1 and 2, respectively. A distorted square-planar geometry exists about the Pd(II) center with the carbonyl group chelated trans to tricyclohexylphosphine (Pd−O, 2.150(4) Å).



L = OH_2, OEt_2

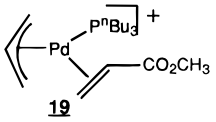
If the η^2-acrylate in **16** occupies the same coordination site as H_2O in **18**, then the catalyst resting state observed may actually be **16′** (with acrylate *trans* to C_β) rather than **16**. Since carbon−carbon bond formation requires a cis arrangement of the η^2-bound olefin and the alkyl group, an isomerization of complex **16′** from a trans geometry to a cis geometry would be necessary prior to alkyl migration and production of *trans*-dimethyl 2-hexenedioate.[53] This is illustrated in Scheme 8.

The palladium−acrylate chelate complex **18** (L = H_2O, Et_2O) shows identical coupling patterns but slightly different chemical shifts for the two methylene signals of the chelate (H_A: δ 2.75 for **18**, 2.72 for **16**; H_B: δ 1.96 for **18**, 1.77 for **16**). Treatment of **18** at 25 °C in CH_2Cl_2 with excess methyl acrylate

(53) We cannot rule out the presence of both **16** and **16′** in rapid equilibrium at 25 °C. Associative exchange of bound and free acrylate is rapid on the NMR time scale at 25 °C (see above); the five coordinate intermediate responsible for associative exchange thus could provide a mechanism for very rapid interconversion of **16** and **16′**.

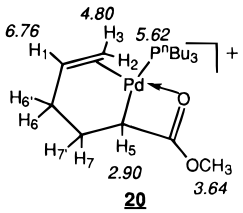
results in displacement of H_2O/Et_2O and formation of **16** (or **16′**) which at 25 °C catalytically produces *trans*-dimethyl 2-hexenedioate with a turnover frequency of 2.2 day^{-1}.

4. Reactivity of the η^3-Allyl−palladium Complex $[(C_3H_5)Pd(OEt_2)(P^nBu_3)]^+[BAr'_4]^-$ (7b) with Methyl Acrylate. Spectroscopic Detection and Study of Reaction Intermediates. Low -Temperature NMR Spectroscopic Studies. Treatment of $[(C_3H_5)Pd(OEt_2)(P^nBu_3)]^+[BAr'_4]^-$ (**7b**) with 1 equiv of methyl acrylate in CD_2Cl_2 results in the formation of η^2-acrylate complex **19** which exhibits two ^{31}P signals at −80 °C (13.5 and 13.0 ppm) in approximately a 2:1 ratio. We assume the ^{31}P spectrum of **19** at −80 °C is analogous to the spectrum of **13** at −60 °C and corresponds to rapid equilibration among isomers of set 1 and isomers of set 2 (see above) and the observation of only two ^{31}P signals. Warming this solution in the NMR probe results in broadening these signals, coalescence at −30 °C, and sharpening to a singlet at 11.4 ppm at −10 °C. Line shape analysis using the slow exchange approximation ($k = \pi\Delta\omega$) yields $k_1 = 30\ s^{-1}$ with $\Delta G^{\ddagger}_1 = 12.5$ kcal mol^{-1} and $k_{-1} = 14\ s^{-1}$ with $\Delta G^{\ddagger}_{-1} = 12.9$ kcal mol^{-1} at −40 °C. Consistent with the ^{31}P results, the ^1H NMR spectrum at −80 °C indicates the formation of two sets of bound acrylate resonances. Three of the six resonances are clearly visible at 5.12, 4.93, and 4.80 ppm. The three remaining resonances are observed at approximately 5.6, 5.4, and 4.6 ppm and are particularly obscured by the allyl resonances.



19

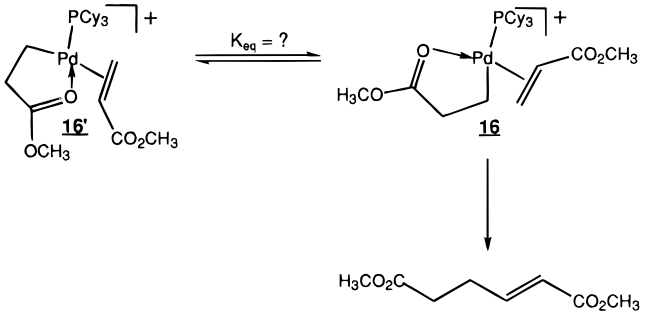
The allyl acrylate complex $[(C_3H_5)Pd(CH_2{=}CHC(O)OCH_3)(P^nBu_3)]^+[BAr'_4]^-$ (**19**) is stable up to −20 °C in the presence of excess methyl acrylate. Warming the solution in the NMR probe results in the formation of a new species with ^{31}P resonance at 18.6 ppm at −10 °C. On the basis of comparison with the ^1H NMR spectra of complex **14**, this new species, **20**, is assigned as the P^nBu_3 analog of the four-membered-chelate intermediate **14**, which results from allyl coupling to the β-carbon of the bound methyl acrylate ligand. Complex **20** shows similar coupling patterns to complex **14** but slightly different chemical shifts are observed. ^1H NMR (300 MHz, −10 °C, CD_2Cl_2) δ 7.72 (s, 8H, Ar′); 7.56 (s, 4H, Ar′); 6.78 (m, 1H, H_1); 5.62 (d, 1H, H_2); 3.64 (s, 3H, O*CH*$_3$); 4.80 (d, 1H, H_3); 2.90 (m, 1H, H_5).



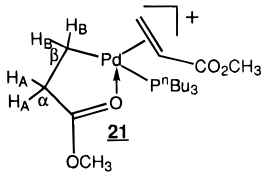
20

Warming the solution to 0 °C results in the elimination of $CH_2{=}CHCH_2CH{=}CHCO_2CH_3$ and the formation of a new species with ^1H resonances at 2.75 ppm (triplet-of-doublets) and 1.85 (triplet, partially obscured by the tricyclohexyl region). The new species is assigned as **21**, the $^nBu_3$ analogue of the five-membered acrylate chelate complex **16**, based on ^1H NMR comparisons with complex **16** and broad band phosphorous decoupling, which reduces the triplet-of-doublet pattern at 2.75 ppm to a triplet. After 2 h approximately a 1:1 ratio of **20**:**21** is observed which indicates that the elimination of methyl 2,5-hexadieneoate from **20** occurs at a much slower rate than from

Scheme 8



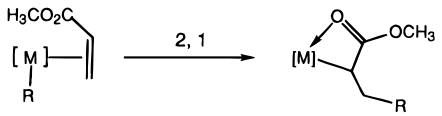
16.[54] $[(C_3H_5)Pd(CH_2CH_2C(O)OCH_3)(P^nBu_3)]^+[BAr'_4]]^-$ (**21**) dimerizes methyl acrylate at 60 °C to predominantly *trans*-dimethyl 2-hexenedioate (200 turnovers, 24 h).



Conclusions

The observations described here clearly show that a Cossee−Arlman type migratory insertion mechanism operates in the methyl acrylate dimerization cycle for the Pd(II) complexes studied here. It seems quite likely that a similar mechanism applies to all previously identified Pd(II)−methyl acrylate dimerization catalysts. Furthermore, the catalyst resting state in these Pd(II) systems, a chelate, η^2-acrylate complex, is quite similar to the catalyst resting state, **3**, previously established for the cationic Cp^*Rh^{III}-based system.

These observations, coupled with previous studies, provide a rationale for the highly regioselective tail-to-tail coupling normally observed for metal-catalyzed acrylate dimerization. It is well-established that migratory insertion of acrylate complexes of the general structure **22** (R = alkyl) occur in a highly regioselective 2,1 fashion to yield a species with the ester group α to the metal center. A chelate structure is observed in the cases where the first insertion product can be detected.[55]



22 **23**

Several factors may dictate such regioselectivity including the polarity of the double bond induced by the ester group, steric effects, and participation of the carbonyl oxygen in stabilizing the vacant coordination site which develops during migratory insertion.[56] In the case of hydride migration (R = H) the insertion reaction is *reversible* and, while kinetic 2,1 insertion is likely preferred,[57] reversibility allows for rapid formation of

(54) The NMR analysis of the sequence **19** → **20** → **21** is more complicated than the analogous transformations for the tricyclohexyl phosphine complexes **13** → **14** → **16**. The rate of **19** → **20** is only slightly faster than the **20** → **21** conversion and thus **20** never appears without substantial amounts of either **19** and/or **21** present.

(55) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.

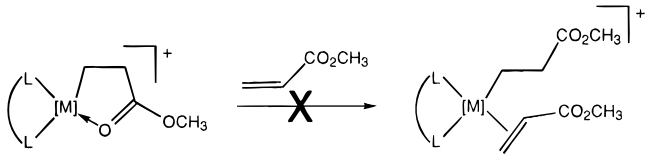
(56) Hauptman, E.; Brookhart, M.; Calabrese, J. C.; Fagan, P. J. *Organometallics* **1994**, *13*, 774.

(57) Grant, B.; Brookhart, M. Unpublished results.

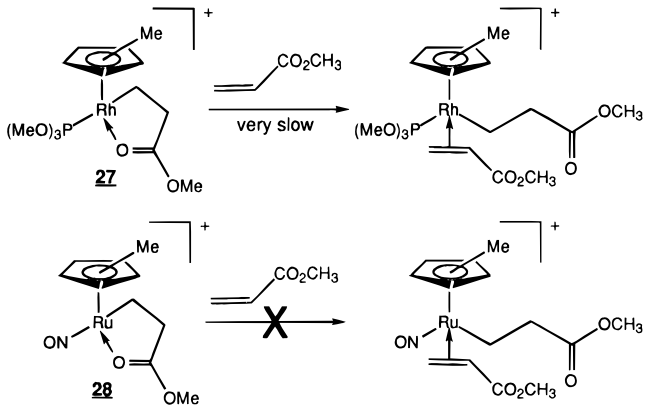
the thermodynamically more stable five-membered chelate. In support of this idea we have observed rapid isomerization of a four-membered chelate to a five-membered chelate at −80 °C, in related Pd(II) α-diimine systems.[55]

Based on these observations, the tail-to-tail selectivity can be explained using the following general scheme (Scheme 9). The metal hydride, [M]−H, generated in the catalytic cycle reacts with methyl acrylate to yield the more stable five-membered chelate **25** (the four-membered chelate, **24**, is likely the kinetically favored insertion product). Binding of methyl acrylate to **25** leads to the η^2-acrylate complex **26**. Species **26** then undergoes irreversible 2,1 insertion via migration of C_2 to C_β which results in tail-to-tail coupling. Small amounts of head-to-tail dimer are sometimes observed;[28] these isomers most likely result from trapping and insertion of a four-membered chelate of type **24**.

A second general feature of acrylate dimerization catalysts which operate by this mechanism is also apparent. The chelate occupies two coordination sites and the carbonyl oxygen is unable to be displaced by the weakly donating η^2-acrylate ligand. Thus, an additional coordination site *cis* to the [M]−C_2 bond must be available for coordination of acrylate to allow migratory insertion from the chelate. Consistent with this hypothesis, Pd(II) complexes possessing bidentate ligands such as phenanthroline are ineffective acrylate dimerization catalysts due to the unavailability of the third coordination site:



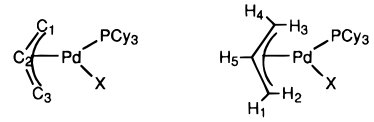
Similarly **27** is an extremely poor dimerization catalyst[9,11,12] and **28** exhibits no dimerization activity:[56]



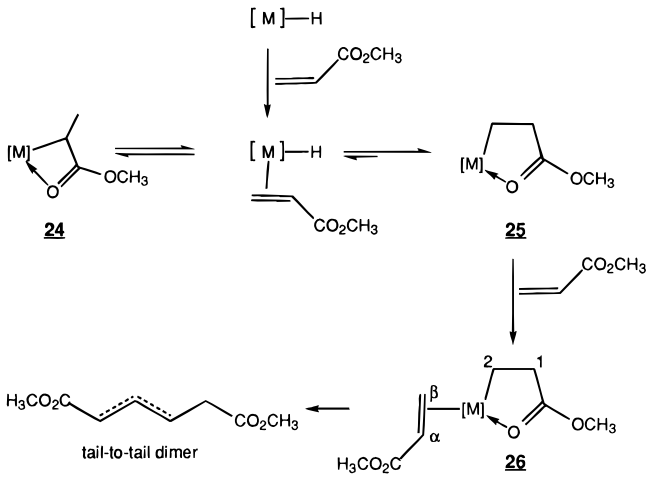
These general observations provide guidelines for design of other late-metal catalysts for dimerization of acrylates.

Experimental Section

General. All reactions were conducted under an atmosphere of dry, oxygen-free nitrogen or argon using standard drybox or Schlenk techniques. Air- and moisture-sensitive reagents were handled using standard syringe techniques. Diethyl ether and *n*-hexane were freshly distilled under a nitrogen atmosphere from sodium and benzophenone. Dichloromethane-d_2 was vacuum transferred from CaH_2 and degassed via several freeze−pump−thaw cycles prior to use. Methyl acrylate was purchased from Aldrich and stored over 4 Å molecular sieves. The following preparations were based on standard literature procedures: $[H^+(Et_2O)_2(BAr_4')^-]$,[35] $[(C_3H_5)PdCl]_2$,[32] $[(C_3H_5)Pd(Cl)(PCy_3)]$,[33] and $[(C_3H_5)Pd(CH_3)(PCy_3)]$.[34] ^1H, ^{13}C, and ^{31}P chemical shifts were referenced to protonated residues of solvents or 85% H_3PO_4. Elemental analyses were performed by Oneida Research Services, Inc. In reporting chemical shifts, allyl carbons and hydrogens are labeled as follows:



Scheme 9. A General Scheme for Selective Tail-to-Tail Acrylate Dimerization



$[(C_3H_5)PdCl]_2$ (4). This compound was prepared as previously reported.[32] ^1H NMR (300 MHz, 20 °C, CD_2Cl_2) δ 5.44 (m, 1H, H_5); 4.05 (d, 2H, H_1 and H_4); 2.97 (d, 2H, H_2 and H_3). ^{13}C NMR (75.4 MHz, −80 °C, CD_2Cl_2) δ 111.5 (C_2); 63.1 (C_1 and C_3).

$[(C_3H_5)Pd(Cl)(PCy_3)]$ (5a). The following procedure is a modification of that reported by Shaw.[33] A Schlenk flask was charged with 0.50 g (1.37 mmol) of $[Pd(C_3H_5)Cl]_2$ and 0.766 g (2.73 mmol) of PCy_3. The reaction flask was cooled to −78 °C. Ether (50 mL) was added and the suspension was warmed slightly to give a yellow solution, which was cooled to −78 °C and stirred for 1 h, at which time a beige powder precipitated. The solvent was reduced in vacuo. The reaction mixture was filtered and the product was washed with Et_2O. An off-white solid was recovered (1.08 g, 85%). ^1H NMR (300 MHz, −20 °C, CD_2Cl_2) δ 5.50 (m, 1H, H_5); 4.55 (q, 1H, H_1); 3.58 (dd, 1H, H_2); 3.50 (t, 1H, H_4); 2.78 (d, 1H, H_3). ^{13}C NMR (75.4 MHz, 20 °C, CD_2Cl_2) δ (allylic) 116.5 (d, J_{CP} = 4.7 Hz, C_2); 79.5 (d, J_{CP} = 28.8 Hz, C_3); 51.4 (d, J_{CP} = 1.8, C_1); (PCy_3) 34.5 (d, J_{CP} = 18.9 Hz, C_1); 27.9 (d, J_{CP} = 11.3 Hz, C_2); 30.4 (s, C_3); 26.7 (s, C_4). ^{31}P NMR (121.5 MHz, 20 °C, CD_2Cl_2) δ 41.2.

$[(C_3H_5)Pd(Cl)(P^nBu_3)]$ (5b). The following procedure is a modification of that reported by Shaw.[33] A Schlenk flask was charged with 0.50 g (1.37 mmol) of $[Pd(C_3H_5)Cl]_2$ and cooled to −78 °C. Diethyl ether (50 mL) was added and the suspension was stirred. P^nBu_3 (2.73 mmol) was added dropwise and the suspension was warmed slightly to give a yellow solution, which was cooled to −78 °C and stirred for 2 h, at which time a white solid precipitated. The reaction mixture was filtered and the product was washed with hexane. A white solid was recovered (1.05 g, 82%). ^1H NMR (250 MHz, 20 °C, C_6D_6) δ 4.8 (m, 1H, H_5); 4.45 (t, 1H, H_1); 3.3 (dd, 1H, H_2); 2.9 (bs, 1H, H_4); 2.05 (bd, 1H, H_3). ^{13}C NMR (75.4 MHz, 20 °C, CD_2Cl_2) δ (allylic) 117.1 (d, J_{CP} = 5.3 Hz, C_2); 78.7 (d, J_{CP} = 31.1 Hz, C_3); 51.1 (bd, J_{CP} = 1.8 Hz, C_1); (P^nBu_3) 26.7 (s, C_γ); 24.8 (d, J_{CP} = 1.2 Hz, C_β); 24.5 (d, J_{CP} = 8.8 Hz, C_α); 13.8 (s, CH_3). ^{31}P NMR (121.5 MHz, 20 °C, CD_2Cl_2) δ 15.1. Anal. Found: C, 47.28; H, 8.59. Calcd: C, 46.76; H, 8.37.

$[(C_3H_5)Pd(CH_3)(PCy_3)]$ (6a). The following procedure is a modification of that reported by Nakamura.[34] A Schlenk flask was charged with 0.400 g (0.86 mmol) of $[(C_3H_5)Pd(Cl)(PCy_3)]$ (**5a**) and Et_2O (15 mL) was added to give a suspension. The reaction mixture was cooled to −78 °C and 288 μL of a 3 M solution of MeMgBr in Et_2O was

added dropwise. The solution was stirred at −78 °C for 1 h and the solvent was removed in vacuo. The white solid was dissolved in hexane and filtered. The solution was reduced in vacuo and the flask was cooled to −30 °C. White crystals were isolated (0.28 g, 73%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 4.99 (m, 1H, H_5); 3.47 (dd, 1H, J_{HH} = 7.3 Hz, H_4); 3.30 (t, 1H, H_1); 2.38 (dd, 1H, J_{HH} = 12.9 Hz, H_2); 2.33 (d, 1H, J_{HH} = 13.2 Hz, H_3); 0.03 (d, 3H, J_{HP} = 4.7 Hz, CH_3). ^{13}C NMR (75.4 MHz, CD_2Cl_2) δ (allylic) 117.2 (d, J_{CP} = 4.2 Hz, C_2); 60.7 (s, C_1); 56.0 (d, J_{CP} = 36.8 Hz, C_3); (PCy_3) 35.3 (d, J_{CP} = 17.4 Hz, C_1); 30.6 (d, J_{CP} = 13.4 Hz, C_2) 28.1 (d, J_{CP} = 10.6 Hz, C_3); 27.0 (s, C_4); −17.9 (d, J_{CP} = 13.2 Hz, CH_3). ^{31}P NMR (121.5 MHz, 20 °C, CD_2Cl_2) δ 42.2.

[(C_3H_5)Pd(CH_3)(P^nBu_3)] (6b). The following procedure is a modification of that reported by Nakamura.[34] A Schlenk flask was charged with 0.866 g (2.25 mmol) of [(C_3H_5)Pd(Cl)(^{n}Bu$_3$)] (**5b**) and Et_2O (40 mL) was added to give a suspension. The reaction mixture was cooled to −78 °C and 750 μL of a 3 M solution of MeMgBr in Et_2O was added dropwise. The solution was stirred at −78 °C for 3 h. The resulting pale green solution was filtered, leaving a white solid (MgBrCl). The solution was reduced in vacuo and filtered again to remove additional MgBrCl. The solvent was then removed in vacuo and a yellow oil was isolated (1.430 g, 52%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.0 (m, 1H, H_5); 3.45 (m, 2H); 2.45 (dd, 1H); 2.3 (d, 1H); 0.05 (d, 3H, CH_3).

[(C_3H_5)Pd(OEt_2)(PCy_3)]$^+$[BAr′$_4$]$^-$ (7a: Ar′ = [3,5-$C_6H_3(CF_3)_2$]). A Schlenk flask was charged with 0.26 g (0.58 mmol) of [(C_3H_5)Pd(CH_3)(PCy_3)] (**6a**) and 0.59 g (0.58 mmol) of [H$^+$(OEt_2)$_2$(BAr′$_4$)$^-$]. The reaction flask was cooled to −78 °C and Et_2O (10 mL) was added. The reaction was warmed slightly to form a clear solution, which was cooled to −78 °C and stirred for 1 h. The solvent was reduced in vacuo to precipitate a beige powder, which was washed with hexane and isolated (0.58 g, 73%). In solution, an ether complex and an aquo complex of **7a** are observed in approximately a 7:3 ratio, respectively. ^{1}H NMR (300 MHz, −20 °C, CD_2Cl_2) δ 7.72 (s, 8H, Ar′); 7.56 (s, 4H, Ar′), 5.79 (m, 1H, H_5); 5.08 (bt, 1H, H_1); 4.01 (dd, 1H, H_2); 3.80 (b, 1H, H_4); 3.10 (bd, 1H, H_3). ^{13}C NMR (75.4 MHz, −20 °C, CD_2Cl_2) δ (BAr′$_4$) 161.7 (q, J_{CB} = 49.2, C_1); 134.7 (s, C_2); 128.7 (qq, J_{CF} = 32.2, C_3); 124.5 (q, 272.1, CF_3); 117.5 (bt, C_4); (PCy_3) 34.3 (d, 21.2, C_1); 30.1 (d, 16.1, C_2); 27.4 (d, 1.7, C_3); 26.0 (s, C_4); (allylic) 120.3 (b, C_2); 86.8 (d, J_{CP} = 22.9 Hz, C_3); (Et_2O) 66.9 (b, CH_2CH_3); 15.2 (s, CH_2CH_3). ^{31}P NMR (121.5 MHz, 20 °C, CD_2Cl_2) δ 39.7 (Et_2O complex); δ 41.3 (H_2O complex). Anal. Found: C, 50.30; H, 4.35. Calcd: C, 50.15; H, 4.43.

[(C_3H_5)Pd(OEt_2)(P^nBu_3)]$^+$[BAr′$_4$]$^-$ (7b: Ar′ = [3,5-$C_6H_3(CF_3)$]). A Schlenk flask was charged with 0.616 g (1.69 mmol) of [(C_3H_5)Pd(CH_3)(P^nBu_3)] (**6b**). The reaction flask was cooled to −78 °C and Et_2O (10 mL) was added. To the yellow palladium solution was added 1.71 g (1.69 mmol) of [H$^+$(OEt_2)$_2$(BAr′$_4$)$^-$]. The resulting yellow solution was stirred at −78 °C for 1 h. The reaction was filtered, leaving a small amount of insoluble material. Hexane was added to the filtrate to facilitate precipitation. The solvent was then reduced in vacuo and the resulting yellow solution was cooled to −30 °C. A yellow powder was isolated (0.320 g, 15%). ^{1}H NMR resonances (300 MHz, −80 °C, CD_2Cl_2) δ 7.72 (s, 8H, Ar′); 7.56 (s, 4H, Ar′); 5.65 (m, 1H, H_5); 4.75 (bt, 1H, H_1); 3.75 (dd, 1H, H_2); 2.6 (bd, 1H). ^{31}P NMR (121.5 MHz, −80 °C, CD_2Cl_2) δ 16 (Et_2O complex); 11 (H_2O complex).

[(C_3H_5)Pd(PCy_3)$_2$]$^+$[BAr′$_4$]$^-$ (9: Ar′ = 3,5-$C_6H_3(CF_3)_2$). A Schlenk flask was charged with 100 mg (0.073 mmol) of [(C_3H_5)Pd(OEt_2)(PCy_3)]$^+$[BAr′$_4$]$^-$ (**7a**) and 21 mg (0.073 mmol) of PCy_3. The reaction flask was cooled to −78 °C and 5 mL of CH_2Cl_2 was added. The solution was warmed to −40 °C and stirred for 3 h. The solvent was removed in vacuo, leaving a yellow oil, which was dissolved in a minimum amount of Et_2O/hexane and cooled to −78 °C. A white solid (0.06 g, 52%) was isolated. ^{1}H NMR (300 MHz, −20 °C, CD_2Cl_2) δ 7.72 (s, 8H, Ar′); 7.56 (s, 4H, Ar′); 5.36 (m, 1H, H_5); 4.47 (bs, 2H, H_1 and H_4); 2.91 (bs, 2H, H_2 and H_3). ^{13}C NMR (75.4 MHz, −20 °C, CD_2Cl_2) δ 119.5 (t, C_2); 70.6 (t, C_1 and C_3); (BAr′$_4$) 163.1 (q, C_1), 136.1 (C_2), 130.0 (m, C_3), 126.0 (q, CF_3), 118.8 (C_4); (PCy_3) 36.0 (b, C_1), 30.5 (C_2), 27.6 (d, C_3), 26.2 (C_4). ^{31}P NMR (121.5 MHz, −90 °C, CD_2Cl_2) δ 36.5 (dd).

[($H_3CO(O)CCH_2CH_2$)Pd(PCy_3)(L)]$^+$[BAr′$_4$]$^-$ (18: Ar′ = 3,5-$C_6H_3(CF_3)_2$; L = OEt_2, OH_2). A Schlenk flask was charged with 0.290 g (0.21 mmol) of [(C_3H_5)Pd(OEt_2)(PCy_3)]$^+$[BAr′$_4$]$^-$ (**7a**). The reaction flask was cooled to −78 °C and 10 mL of CH_2Cl_2 was added. Methyl acrylate (114 μL, 1.26 mmol) was added. The solution was warmed to 0 °C and stirred for 3 h. The solvent was removed in vacuo, leaving a yellow oil. The oil was dissolved in a minimum amount of Et_2O/hexane and cooled to −30 °C. Pale yellow crystals (0.90 g, 30%) were isolated. ^{1}H NMR (300 MHz, 20 °C, CD_2Cl_2) δ 7.72 (s, 8H, Ar′); 7.56 (s, 4H, Ar′); 3.87 (s, 3H, OCH_3); 2.75 (td, J_{HP} = 2.1 Hz, 2H); 1.96 (td, J_{HP} = 2.4 Hz, 2H); 1.0−2.0 (m, cyclohexyl). ^{13}C NMR (75.4 MHz, 20 °C, CD_2Cl_2) δ 240.6 (C=O), 56.6 (OCH_3), 40.4 (C_β), 15.2 (C_α); (BAr$_4$′) 163.1 (q, C_1), 136.1 (C_2), 130.0 (m, C_3), 126.0 (q, CF_3), 118.8 (C_4); (PCy_3) 35.3 (d, C_1), 31.4 (C_2), 28.7 (d, C_3), 27.4 (C_4). ^{31}P NMR (121.5 MHz, 20 °C, CD_2Cl_2) δ 49.54, 46.07. Anal. Found: C, 49.32; H, 4.43. Calcd: C, 49.36; H, 4.43.

X-ray Structural Analysis of [(H_2O)($H_3CO(O)CCH_2CH_2$)-Pd(PCy_3)]$^+$[BAr′$_4$]$^-$ (18). A single crystal of **18** (0.20 × 0.20 × 0.40 mm) was grown from a concentrated solution of Et_2O and hexane at −30 °C. The crystal was triclinic (*P*1, No. 2) with the following cell dimensions determined from 50 reflections (λ(Mo) = 0.71073 Å): a = 12.816(7) Å, b = 14.879(15) Å, c = 18.537(9) Å; α = 79.10(6)°, β = 89.28(4)°, γ = 85.72(6)°; z = 2; V = 3461(4) Å^3; F_w = 1503.40 ($PdC_{62}H_{74}BF_{24}O_5P$); D_c = 1.442 g m^{-3}.

Data were collected at −120 °C on a Rigaku diffractometer with a graphite monochromator using Mo Kα radiation. A total of 9559 data were collected of which 6187 unique reflections with $I \geq 2.5\sigma(I)$ were observed ($5° \leq 2\theta \leq 45°$; maximum h, k, l = 13, 16, 19; data octants = +/−h, +k, +/−l; ω scan method; scan speed = 2 deg min^{-1}). Three standards were collected every 100 reflections with no significant change in intensity. An absorption correction was applied using the ψ scan method[58] with a range of transmission factors of 0.85 to 0.94.

The structure was solved using direct methods. The asymmetric unit consists of one ion pair in a general position. Hydrogen atoms were idealized with C−H = 0.96 Å. The structure was refined by full-matrix least squares and corrected for anamolous dispersion. There are 847 parameters (data to parameter ratio of 7.30); final R = 0.055 (R_w = 0.063). The error of fit was 1.78 with a maximum $\Delta\sigma^{-1}$ of 0.021. The deepest hole was −0.93 e Å^{-3} and the highest peak was 1.52 e Å^{-3}. Selected interatomic distances and angles are summarized in Tables 1 and 2, respectively.

Measurement of the Rate of Interconversion between [(C_3H_5)-(PCy_3)Pd(C_2H_4)]$^+$[BAr′$_4$]$^-$ 8α and 8β. The sample was prepared in a drybox by charging the palladium complex [(C_3H_5)Pd(OEt_2)-(PCy_3)]$^+$[BAr′$_4$]$^-$ (**7a**) (12 mg, 0.009 mmol) and CD_2Cl_2 into an NMR tube at ambient temperature. The NMR tube was cooled to −78 °C under an argon atmosphere and ethylene was introduced via syringe (excess ethylene was removed by purging the solution with argon for approximately 30 min). The NMR tube was introduced into a precooled (−90 °C) NMR probe and gradually warmed. ^{1}H and ^{31}P NMR spectra were recorded. The rate of interconversion of **8α** and **8β** at the coalescent temperature (−74 °C, Bruker AMX-300 spectrometer) is calculated from the frequency seperation of the two PCy_3 resonances in the slow-exchange limit, $k = \pi(\upsilon_A - \upsilon_B)/\sqrt{2}$ (k = 300 s^{-1} at −74 °C). The free energy of activation obtained from the Eyring equation is 9.3 kcal mol^{-1}. ^{31}P NMR (121.5 MHz, −90 °C, CD_2Cl_2) δ 35.93, 37.04.

Measurement of the Rate of Interconversion (Allyl Rocking) between [(C_3H_5)(PCy_3)Pd(C_2H_4)]$^+$[BAr′$_4$]$^-$ 9 and 9′. The sample was prepared in a drybox by charging the palladium complex [(C_3H_5)Pd(PCy_3)$_2$]$^+$[BAr′$_4$]$^-$ (**9**) (10 mg, 0.006 mmol) and CD_2Cl_2 into an NMR tube at ambient temperature. The NMR tube was introduced into a precooled (−90 °C) NMR probe and gradually warmed. ^{31}P NMR spectra were recorded. Line broadening experiments were carried out for **9** and **9′** beginning at a temperature where the complexes were static (the phosphorus signals appeared as an AB quartet) to a temperature where the complexes were dynamic (the phosphorus signals appeared as a broad singlet). Experimental line shapes were compared to line shapes calculated using the DNMR3 program[43−46] (for an

(58) Gabe, E. J.; Le Page, Y. L.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

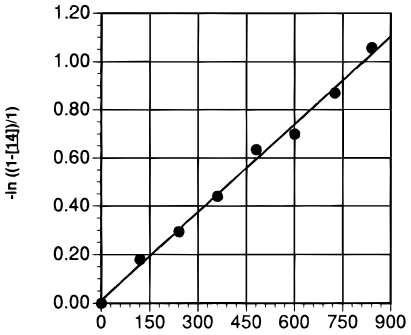


Figure 5. The $-\ln[(A_0 - B)]/A_0$ versus time data for allyl acrylate coupling of complex **13**.

illustration see Figure 4 in the Results and Discussion section). This dynamic NMR fitting program gave values of rate constants (k) which were used to calculate free energies of activation using the Eyring equation: 5 s^{-1} at −82 °C, $\Delta G^{\ddagger} = 10.4$; 8 s^{-1} at −77 °C, $\Delta G^{\ddagger} = 10.5$; 16 s^{-1} at −72 °C, $\Delta G^{\ddagger} = 10.5$; 29 s^{-1} at −67 °C, $\Delta G^{\ddagger} = 10.5$; 53 s^{-1} at −61 °C, $\Delta G^{\ddagger} = 10.6$; 81 s^{-1} at −56 °C, $\Delta G^{\ddagger} = 10.7$; 222 s^{-1} at −45 °C, $\Delta G^{\ddagger} = 10.8$; 405 s^{-1} at −39 °C, $\Delta G^{\ddagger} = 10.8$.

Spectroscopic Characterization of Catalytic Intermediates during Dimerization of Ethylene with $[(C_3H_5)Pd(OEt_2)(PCy_3)]^+[BAr'_4]^-$ (7a). In a typical experiment, the sample was prepared in a drybox by charging the palladium complex $[(C_3H_5)Pd(OEt_2)(PCy_3)]^+[BAr'_4]^-$ (**7a**) (10 mg, 0.007 mmol) and CD_2Cl_2 into an NMR tube at ambient temperature. The NMR tube was cooled to −78 °C under an argon atmosphere and ethylene was bubbled through the solution for 5 min. The NMR tube was then purged with argon for 30 min to remove excess ethylene and introduced into a precooled (−90 °C) NMR probe. Two isomers of complex **13** were immediately generated. ^{31}P NMR (121.5 MHz, −90 °C, CD_2Cl_2) δ 35.93, 37.04. Excess ethylene was added via syringe. The NMR tube was reintroduced into the NMR probe and gradually warmed to −20 °C, at which temperature a new species is observed which we propose to be the ethyl−ethylene complex **11**. ^{31}P NMR (121.5 MHz, −20 °C, CD_2Cl_2) δ 38.5. ^{1}H NMR (300 MHz, −20 °C, CD_2Cl_2) δ 3.58 (bs). The NMR probe was further warmed to −15 °C, at which temperature dimerization of ethylene to butenes (primarily *trans*-2-butene cis:trans, ca. 1:6) was observed.

Spectroscopic Characterization of Catalytic Intermediates during Dimerization of Methyl Acrylate with $[(C_3H_5)Pd(OEt_2)(PCy_3)]^+[BAr'_4]^-$ (7a). In a typical experiment, the sample was prepared in a drybox by charging the palladium complex $[(C_3H_5)Pd(OEt_2)(PCy_3)]^+[BAr'_4]^-$ (**7a**) (10 mg, 0.007 mmol) and CD_2Cl_2 into an NMR tube at ambient temperature. The NMR tube was cooled to −78 °C under an argon atmosphere and methyl acrylate was introduced via syringe. The NMR tube was introduced into a precooled (−100 °C) NMR probe. Four isomers of complex **13** were immediately generated (^{31}P NMR (121.5 MHz, −100 °C, CD_2Cl_2) δ 38.5, 37.5, 37.3, and 37.2). The NMR probe was gradually warmed to −25 °C, at which temperature the four-membered chelate complex **14** was observed. ^{1}H NMR (300 MHz, −25 °C, CD_2Cl_2) δ 7.72 (s, 8H, Ar′); 7.56 (s, 4H, Ar′); 6.78 (m, 1H, H_1); 5.74 (d, 1H, $J_{12} = 16.7$ Hz); 4.85 (d, 1H, $J_{13} = 9.4$ Hz); 2.98 (m, 1H, H_5); 2.45 (m, 2H, $H_{6,6'}$); 2.07 (m, partially obscured by cyclohexyl resonances). The rate of allyl acrylate coupling was measured at −25 °C ($k = 1.1 \times 10^{-3}$ s^{-1}, $\Delta G^{\ddagger} = 17.8$ kcal mol^{-1}) by monitoring the appearance of H_5 (2.98 ppm) of the four-membered chelate intermediate **14** (a typical first-order plot is shown in Figure 5). The NMR probe was further warmed to −15 °C, at which temperature methyl 2,5-hexadieneoate and the five-membered acrylate chelate complex **16** were observed. For best signal resolution the NMR probe was warmed to 25 °C. ^{1}H NMR (300 MHz, 25 °C, CD_2Cl_2) δ 7.72 (s, 8H, Ar′); 7.56 (s, 4H, Ar′); 3.78 (s, 3H, OCH_3); 2.72 (td, $J_{HP} = 2.1$ Hz, 2H); 1.77 (td, $J_{HP} = 2.4$ Hz, 2H); 1.0−2.0 (m, cyclohexyl). ^{31}P NMR (121.5 MHz, 20 °C, CD_2Cl_2) δ 49.5.

Spectroscopic Characterization of Catalytic Intermediates during Dimerization of Methyl Acrylate with $[(C_3H_5)Pd(OEt_2)(P^nBu_3)]^+[BAr'_4]^-$ (7b). In a typical experiment, the sample was prepared in a drybox by charging the palladium complex $[(C_3H_5)Pd(OEt_2)(P^nBu_3)]^+[BAr'_4]^-$ (**7b**) (10 mg, 0.008 mmol) and CD_2Cl_2 into an NMR tube at ambient temperature. The NMR tube was cooled to −78 °C under an argon atmosphere and methyl acrylate was introduced via syringe. The NMR tube was introduced into a precooled (−80 °C) NMR probe. Two isomers of complex **19** were immediately generated (^{31}P NMR (121.5 MHz, −100 °C, CD_2Cl_2) δ 13.5 and 13.0). The rate of interconversion of these isomers at the coalescent temperature (−40 °C, Bruker AMX-300 spectrometer) is calculated from line shape analysis of the two P^nBu_3 resonances using the slow-exchange approximation, $k = \pi\Delta\omega$ ($k_1 = 30$ s^{-1} and $k_{-1} = 14$ s^{-1}). The free energies of activation obtained from the Eyring equation are $\Delta G^{\ddagger}_1 = 12.5$ kcal mol^{-1} and $\Delta G^{\ddagger}_{-1} = 12.9$ kcal mol^{-1} at −40 °C. The NMR probe was gradually warmed to −10 °C, at which temperature the four-membered chelate complex **20** was observed. ^{1}H NMR (300 MHz, −10 °C, CD_2Cl_2) δ 7.72 (s, 8H, Ar′); 7.56 (s, 4H, Ar′); 6.78 (m, 1H, H_1); 5.62 (d, 1H, H_2); 3.64 (s, 3H, OCH_3); 4.80 (d, 1H, H_3); 2.90 (m, 1H, H_5). ^{31}P NMR (121.5 MHz, −10 °C, CD_2Cl_2) δ 18.6. The NMR probe was further warmed to 0 °C, at which temperature methyl 2,5-hexadieneoate (see above) and the five-membered acrylate chelate complex **21** were observed. ^{1}H NMR (300 MHz, 0 °C, CD_2Cl_2) δ 7.72 (s, 8H, Ar′); 7.56 (s, 4H, Ar′); 2.75 (triplet-of-doublets) (1.85, triplet, partially obscured by tricyclohexyl resonances).

Dimerization of Methyl Acrylate with $[(C_3H_5)Pd(OEt_2)(P^nBu_3)]^+[BAr'_4]^-$ (7b). In a typical experiment, the sample was prepared in a drybox by charging $[(C_3H_5)Pd(OEt_2)(P^nBu_3)]^+[BAr'_4]^-$ (**7b**) (50 mg, 0.04 mmol) to a medium-walled glass Schlenk flask fitted with a Kontes high vacuum Teflon plug. The Schlenk flask was placed under an argon atmosphere, methyl acrylate (stabilized with 1 wt % 3,5-di-*tert*-butyl-4-hydroxyanisole) was introduced via syringe (0.96 g, 11 mmol, 284 equiv), and the reaction mixture was heated (60 °C, 24 h). Quantitative organic analyses were obtained with an Hewlett Packard 5890A gas chromatograph using a J & W Scientific DB-5 capillary column (30 M, 0.25-mm i.d., 0.25-mm film thickness), the following temperature program (50 °C for 4 min; 50−250 °C at 5 deg min^{-1}), and flame ionization detection. The assignment of products is based on comparison with an authentic sample of mixed diester products which was obtained from a reaction solution via distillation.

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Supporting Information Available: X-ray data for **18** including tables of fractional coordinates and isotropic thermal parameters, interatomic distances, intramolecular angles, intramolecular nonbonding distances, and intermolecular distances (12 pages). Ordering information is given on any current masthead page.

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