Polymerization of Acrylates by Neutral Palladium Complexes. Isolation of Complexes at the Initial Steps

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The polymerization of methyl acrylate by pentafluorophenyl complexes $[Pd_2(\mu\text{-}X)_2(C_6F_5)_2L_2]$ (L = tetrahydrothiophene (tht), X = Cl, **2**; L = tht, X = Br, **3**; L = $AsPh_3$, X = Br, **4**) gives atactic polymers in good yields. Mechanistic studies reveal that the polymerization of methyl acrylate starts by insertion of methyl acrylate in the Pd−aryl bond of the precatalyst to give the alkyl complexes *trans*-$[Pd_2(\mu\text{-}Cl)_2\{CH(CO_2Me)\text{-}CH_2C_6F_5\}_2(tht)_2]$ (**5**) and *trans*-$[Pd_2(\mu\text{-}Cl)_2\{CH(C_6F_5)CH_2CO_2Me\}_2(tht)_2]$ (**6**). These complexes can be isolated, and the X-ray crystal structure of **5** has been determined. Complexes **5** and **6** decompose mainly by β-H elimination but also by homolytic cleavage of the Pd−C bond in the light. In the presence of methyl acrylate, insertion of MA in hydrido−Pd species produces the alkyl complex *trans*-$[Pd_2(\mu\text{-}Cl)_2\{CH(CO_2Me)CH_3\}_2(tht)_2]$ (**9**). Then a radical polymerization is initiated by small amounts of the radicals generated from these complexes (**5**, **6**, or **9**). Formation of **9** is the regeneration pathway of radicals after a termination reaction has occurred by recombination of the growing radical with palladium and β-H elimination. The success of the polymerization requires a slow but steady supply of radicals by slow decomposition of alkyl complexes (**5** and **6**) or by slow generation of Pd−H species that provide new alkyl complexes (**9**), as well as an efficient recycling of the Pd−H generated in the termination step to **9**.

Introduction

There is a great deal of interest in the development of metal-based catalysts for the polymerization and copolymerization of polar monomers, which complement the commonly used radical or anionic processes, particularly for acrylate derivatives.[1,2] Efforts are aimed at finding systems tolerant to polar functionalities that perform the polymerization and especially the copolymerization of these monomers with nonpolar olefins at will. Metal complexes have been used to effect living and better-controlled radical homopolymerizations of acrylates.[3] Some lanthanocenes and group 4 metallocenes are active catalysts for the polymerization of acrylates. They follow mechanisms (enolate and group transfer) different from the insertion route operating in the same systems for nonpolar monomers.[4] Thus, they bring about block but not alternating copolymerization of acrylates and ethylene.[5] The hard Lewis acidic character of most early-transition-metal catalysts makes them incompatible with the presence of hard donor heteroatoms in the alkenes, because heteroatom coordination competes with double-bond coordination and prevents polymerization by an insertion route. In the search for less acidic centers, attention has turned toward late-transition-metal complexes. Following the discovery of the high activity of diimine cationic palladium complexes in the polymerization of ethylene by Brookhart et al.,[6] acrylates were also tried. These systems do not homopolymerize acrylates but incorporate them up to 12% in the ramifications of a polyethylene chain, at the expense of a significant lowering in the polymer yields.[7] Coordination of the carbonyl group to the metal after insertion of a methyl acrylate unit

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Chart 1

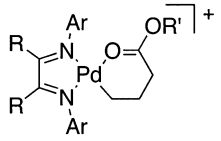


Table 1. Polymerization of Acrylates with Complexes 2−4[a]

entry	initiator (amt, mmol)	monomer (amt, mmol)	solvent	poly(MA) (% yield)	M_w[b]	M_w/M_n[b]
1	**2** (0.0014)[c]	MA (5.6)		89	3.2×10^6	6.2
2	**2** (0.0028)	MA (11.1)	CH_2Cl_2	82	1.9×10^5	2.2
3	**2** (0.0028)	MA (11.1)	$CHCl_3$	81	1.8×10^5	2.2
4	**2** (0.0028)	MA (11.1)	PhCl	93	2.5×10^5	2.4
5	**3** (0.0028)[d]	MA (5.6)	CH_2Cl_2	85	1.9×10^5	3.1
6	**4** (0.0028)[d]	MA (5.6)	CH_2Cl_2	73	3.0×10^5	2.1
7	**2** (0.0018)[d]	^{t}BuA (3.4)	CH_2Cl_2	66	5.1×10^5	4.8
8	**2** (0.0024)[d]	MMA (4.7)	CH_2Cl_2	6[e]	1.8×10^5	2.9

[a] Reaction conditions: solvent, 2 mL; 24 h; room temperature. [b] Determined by SEC in THF relative to polystyrene standards. [c] SEC in $CHCl_3$. [d] Solvent, 0.5 mL. [e] *mm*:*mr*:*rr* = 0.026:0.299:0.675, determined from the ^{1}H NMR spectrum in $CHCl_3$.

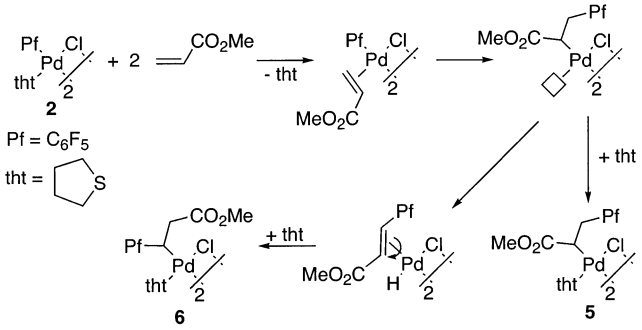
was observed, and the stability of the metallacycle formed (Chart 1) was deemed responsible for the inefficient polymerization.

Other less well-defined palladium systems show similar amounts of acrylate incorporation in the polyethylene chain.[8] Since the high electrophilicity of the metal in cationic complexes favors oxygen coordination, neutral derivatives have been tested. Grubbs et al. have developed very active neutral nickel catalysts, tolerant to polar groups, but they are ineffective for acrylates.[9] Novak et al.[10] and we and Sen[11] described neutral palladium complexes active in the polymerization of acrylates. We studied the activity of the system [PdBr(C_6F_5)(NCMe)$_2$] (**1**) in the presence of 1 equiv of PPh_3 and proved that polymer growth is a radical process, but insertion and β-H elimination reactions on the metal center are very influential on the polymerization process and activity of the system toward different monomers.[11] We describe here new neutral palladium catalysts for the polymerization of acrylates. They basically follow the same mechanism described for **1** + PPh_3, but the new catalytic system is easier to prepare and facilitates the control and monitoring of the reaction, which allows a better understanding of the mechanism.

Results and Discussion

Activity in the Polymerization of Acrylates. Dimeric palladium complexes [$Pd_2(\mu$-X$)_2(C_6F_5)_2L_2$] (L = tht (tht = tetrahydrothiophene), X = Cl (**2**); L = tht, X = Br, (**3**); L = $AsPh_3$, X = Br (**4**)) are active precursors for the polymerization of methyl acrylate (MA). Atactic high-molecular-weight polymers were obtained in good yields at room temperature in the light (Table 1). Interestingly, as reported before,[11] the analogous complex [$Pd_2(\mu$-Br$)_2(C_6F_5)_2(PPh_3)_2$] does not polymerize MA. Complex **2** also polymerizes other acrylates such as *tert*-butyl acrylate (^{t}BuA) but not methyl methacrylate (MMA), as shown in Table 1.

Scheme 1



Mechanistic Studies. The polymerizations of MA using **2** as initiator and the stoichiometric reactions of **2** with MA were followed by ^{19}F and ^{1}H NMR in $CDCl_3$. Initially the insertion of MA into the Pd−C_6F_5 bond gives the two alkyl palladium compounds **5** and **6** (Scheme 1),[12] which are clearly seen in the ^{19}F NMR spectrum, where typical signals for a C-bound pentafluorophenyl appeared (at about −140 ppm) at the expense of the starting material (ca. −120 ppm).[13] Coordination of MA to [$Pd_2(\mu$-Cl$)_2(C_6F_5)_2L_2$] (L = tht, **2**) must occur prior to this insertion, probably by substitution of tht in preference to bridge splitting. This is suggested by the following observations: (i) the polymerization activity of the dimeric complexes [Pd_2-(μ-X$)_2(C_6F_5)_2L_2$] decreases steeply (L = tht ≈ $AsPh_3$ ≫ L = PPh_3) with increasing coordination ability of L (in fact, the PPh_3 complex does not react with MA); (ii) a change in the halogen bridge does not produce a noticeable difference (cf. complexes **2** and **3**, Table 1, entries 2 and 5), as should be expected if bridge cleavage were involved (Scheme 1).

A yellow solid containing a mixture of **5** and **6** (**5**:**6** = 15:1) was isolated from the reaction of **2** with MA (Pd:MA = 1:5) in CH_2Cl_2 at room temperature for 55 min. The X-ray diffraction structure of a single crystal taken from this mixture corresponded to the major complex **5** and is shown in Figure 1. Selected distances and angles are given in Table 2. The compound is a dimeric σ-alkyl derivative resulting from insertion of MA into the Pd−C_6F_5 bond. The coordination plane is defined by a chiral carbon, the sulfur atom of a tht molecule, and two bridging Cl atoms, while the carboxylate group is not coordinated. Two diastereoisomers are produced, arising from the presence in the dimer of two chiral carbons formed unselectively. These are clearly seen in the ^{19}F NMR spectrum at low temperature, but the crystal studied contained only one of them. The alkyl and tht ligands are mutually trans across the bent bridges. The dihedral angle between both palladium coordination planes is 20.6°. The higher trans influence of the alkyl groups is reflected in the longer trans Pd−Cl bond

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(12) For simplicity the dimeric palladium complexes are represented in the scheme as homodimers, although mixed dimers are also expected. Heterodimers were not detected in this case, but they can be seen, for example, in the ^{19}F NMR spectrum of a mixture of **2** and **5** in $CDCl_3$.
(13) Albéniz, A. C.; Espinet, P.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1990**, *9*, 1079−1085.

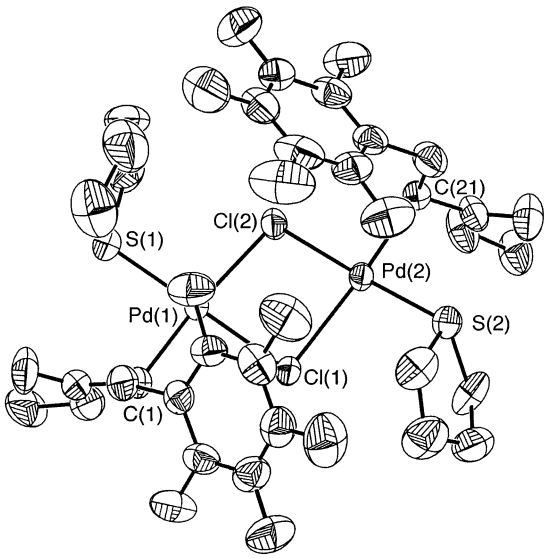


Figure 1. Molecular structure of the complex $[Pd_2(\mu\text{-}Cl)_2\{CH(CO_2Me)CH_2C_6F_5\}_2(tht)_2]$ (**5**). Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 5

Pd(1)−C(1)	2.063(7)	Pd(2)−C(21)	2.066(6)
Pd(1)−S(1)	2.299(2)	Pd(2)−S(2)	2.277(2)
Pd(1)−Cl(1)	2.3649(17)	Pd(2)−Cl(1)	2.4737(17)
Pd(1)−Cl(2)	2.4368(18)	Pd(2)−Cl(2)	2.3399(19)
C(1)−Pd(1)−Cl(1)	89.7(2)	C(21)−Pd(2)−Cl(2)	89.4(2)
S(1)−Pd(1)−Cl(2)	95.45(8)	S(2)−Pd(2)−Cl(1)	97.82(7)
Cl(1)−Pd(1)−Cl(2)	85.04(6)	Cl(1)−Pd(2)−Cl(2)	84.75(6)
C(1)−Pd(1)−S(1)	89.8(2)	C(21)−Pd(2)−S(2)	88.2(2)
Pd(1)−Cl(1)−Pd(2)	92.33(6)	Pd(1)−Cl(2)−Pd(2)	93.90(7)

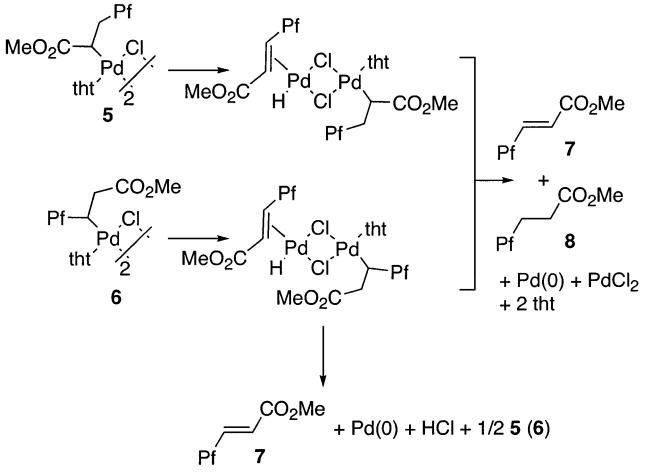
lengths (about 0.1 Å). The preference for coordination of the tht and bridge formation, rather than coordination of the carbonyl oxygen, can be attributed to the unfavorable four-membered metallacycle that should be formed and the reduced electrophilicity of the metal center in this neutral palladium complex compared to that of the cationic derivatives.[7]

The minor Pd-migration isomer **6** (Scheme 1) shows a low-field signal in the ^{1}H NMR spectrum (4.15 ppm) corresponding to the methine proton attached to the Pd-bound carbon. The rest of the signals are overlapped with the signals of the major complex **5** and the tht resonances but could be identified in a ^{1}H COSY experiment.

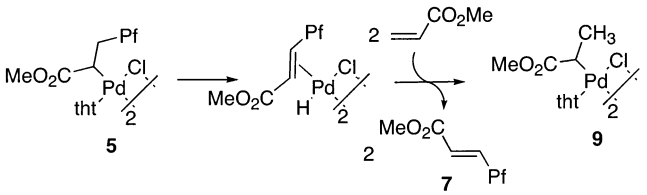
Both **5** and **6** decompose in solution to give the substituted olefin **7** and the alkane **8** (**7**:**8** = 3.9:1). The latter is formed by hydride transfer between palladium atoms in a dimer (Scheme 2).[11,14] Just a very small amount of **8** is formed when excess MA is present (this is the case for the polymerization reactions), since MA can act as a ligand and disfavors the formation of the dimeric complexes needed for H transfer.

Polymerization reactions inside the NMR probe (consequently in the dark) using **2** as precatalyst and a ratio of Pd to MA up to 1:220 in $CDCl_3$ were monitored by ^{19}F and ^{1}H NMR. The formation of **5** and **6** occurs

Scheme 2



Scheme 3



immediately, and at this point, no polymer is observed in the ^{1}H NMR spectrum. Complexes **5** and **6** decompose slowly to the substituted product **7**. An undetected palladium hydrido complex should be formed also, which reacts with MA to form the new palladium complex $[Pd_2(\mu\text{-}Cl)_2\{CH(CO_2Me)CH_3\}_2(tht)_2]$ (**9**) by insertion into the Pd−H bond (Scheme 3).[12] This is shown by the appearance of a doublet at 0.80 ppm, coupled to a signal at 3.40 ppm partially overlapped by other resonances in the spectrum but detected in ^{1}H COSY. When 40% of **5** + **6** had decomposed (13 h), the formation of a small amount of polymer (3%) was clear in the ^{1}H NMR spectrum (Figure 2).

Another organometallic complex is slowly formed during this process, with ^{19}F NMR chemical shifts very close to those of **5**. It could be a cis alkyl derivative across the bridge, an isomer of the trans complex **5** (the new putative cis complex is about 30% of the total amount of **5** after 14 h). Complexes **5** (cis and trans) and **6** continue decomposing to **7**, and no other fluorine-containing species are formed. Complete decomposition of **5** takes around 8 days (2 days for complex **6**) under these conditions (lower concentration of MA than in the polymerization reactions in Table 1).

The amount of polymer formed in this experiment is very low, suggesting that effective bulk polymerization of MA with **2** requires the presence of light, as typically happens in many radical processes. This was assessed experimentally. Two NMR tubes were charged with **2** and MA (Pd:MA = 1:220) in $CDCl_3$. Only one of the samples was protected from light. After the first 30 min both samples were a mixture of **5** (87%), **6** (5%), and **7** (8%), and no polymer had been formed. When the samples were checked again after 7 h more, the sample protected from light contained **5** (62%), **6** (3%), and **7** (35%) but no polymer, whereas the sample in the light showed 71% conversion of MA to poly(MA), in addition to **5** (50%) and **7** (30%), and new broad ^{19}F NMR signals

(14) The formation of the alkene **7** leaves a Pd−H moiety, and the H atom can transfer to another Pd by formation of a dimeric halo−hydrido species. Reductive elimination of alkyl and H leads to **8**. This has been studied in detail: Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *Organometallics* **1997**, *16*, 4030−4032.

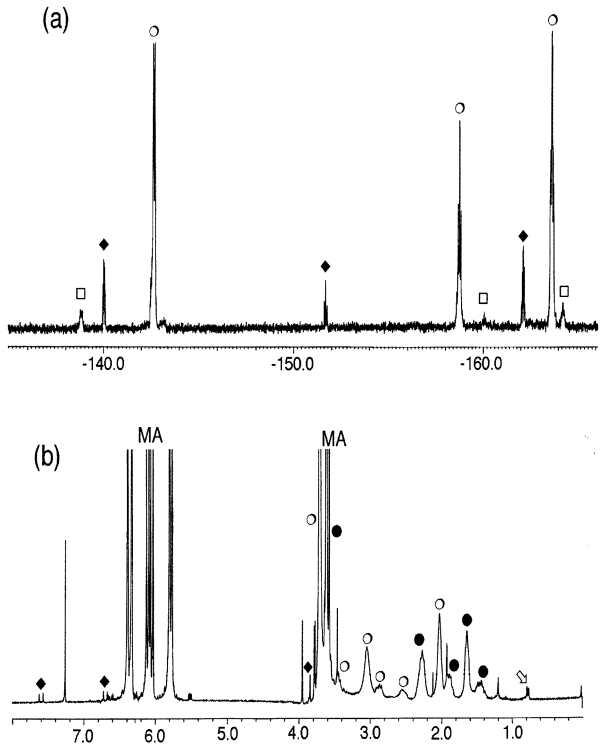
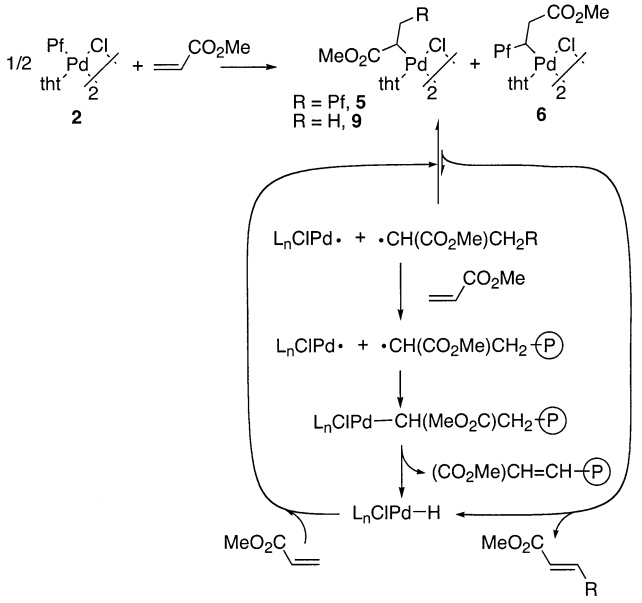


Figure 2. ^{19}F (a) and ^{1}H (b) NMR spectra of a mixture of **2** and MA (MA:Pd = 25:1) after 4 h: (○) **5**; (□) **6**; (◆) **7**; (⇒) **9**; (●) poly(MA).

(F_{ortho}: −140.5, −142, −143.2 ppm) accounting for the remaining 20% of fluorine-containing species. The polymer obtained in this reaction was isolated, recrystallized, and characterized by ^{19}F and ^{1}H NMR. The same broad fluorine signals detected in the reaction mixture were present in the polymer, supporting that at least part of the reaction involves the incorporation of a Pf-containing fragment (Pf = pentafluorophenyl; it was estimated by ^{19}F NMR that about 20% average polymer chains contained Pf; see the Experimental Section). The ^{1}H NMR spectrum showed signals at δ 6.8 (dd, J = 17.6, 8.8 Hz) and 5.9 (d, J = 17.6 Hz) typical of a (CO_2Me)-CH=CH− terminal group in the polymer. Additional experiments showed that, as observed before for the catalytic system **1** + PPh_3,[11] oxygen and radical traps such as galvinoxyl and DPPH inhibit the reaction, whereas 2,6-di-*tert*-butylphenol (TBP) does not. All these features, along with the polymer characteristics, support a radical mechanism for polymer growth (Scheme 4).

The initiating radical species have to be formed from complexes **5** and **6**, since these are formed from **2** before any polymer appears. The radical species may be formed by homolytic splitting of the Pd−C bond in **5** and **6** (and eventually **9**, once this complex has been formed). In other words, the alkyl complexes should be in a dynamic equilibrium with minute amounts of the radicals produced in this homolytic cleavage. In fact, mixtures of **5** and **6** in $CDCl_3$ decompose under UV irradiation (365 nm) to **7** (and small amounts of its cis isomer), **8**, and other Pf-containing products (about 8%), which increased their ratio (to 15%) if the decomposition was carried out in the air. These were identified as the hydroxy esters $PfCH_2CH(OH)CO_2Me$ (**10**) and $PfCH(OH)CH_2CO_2Me$ (**11**) and their corresponding keto esters $PfCH_2C(O)CO_2Me$ (**12**) and $PfC(O)CH_2(CO_2Me)$ (**13**) in a 1.2:1.2:1.5:1 molar ratio. Derivatives **10**−**12** were separated by TLC and identified spectroscopically and by MS, whereas **13** could only be identified in the reaction mixture. Compounds **7** and **8** are the expected products of decomposition by β-H elimination and are formed also in the dark, but **10**−**13** reveal the formation of radicals generated by cleavage of the Pd−C bond in **5** or **6**, which are trapped by their very fast reaction with O_2.[15] The peroxide radicals formed can either couple or react with Pd−H species to give hydroperoxides. In both cases their eventual decomposition gives compounds **10**−**13**.[15] Thus, complexes **5** and **6** behave simultaneously as a slow source of Pd−H (via β-H elimination) and as a reservoir of minute concentrations of radicals. In the presence of MA, the radicals initiate the polymerization. However, it is worth noting that galvinoxyl does not give detectable amounts of radical coupling Pf-containing species when it reacts with **5** or **6**. The only observed products are **7** and a small amount of **8**.[16] This means that, for the Pf radicals in that small a concentration, the coupling with galvinoxyl is not sufficiently fast to trap them. Probably when galvinoxyl stops this polymerization (see below), its action as a hydride trap is crucial.

Scheme 4



These data support the polymerization mechanism shown in Scheme 4. It starts with the detected insertion of MA into the Pd−C_6F_5 bond. The resulting complexes **5** and **6**, plus **9** formed by β-H elimination and MA insertion, can provide the radicals that add to MA and bring about polymer growth. Since **5** and **6** are fairly stable, they act as a kind of reservoir of radical species and of Pd−H (hence of **9**), providing a slow but steady supply of catalytically active species. Eventually the growing radical will recombine with [Pd] and the resulting alkyl will undergo β-H elimination and liberate an olefin that accounts for the terminal olefin group

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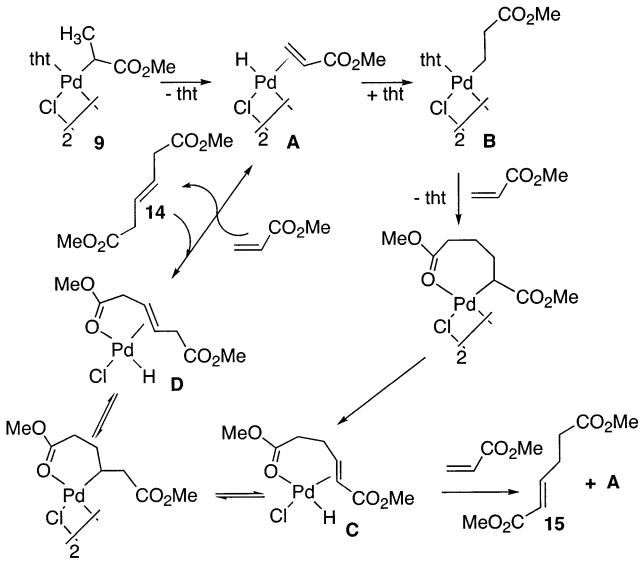
(16) The presence of galvinoxyl dramatically reduces the amount of **8**, since it reacts with the palladium hydride species formed and halts the H transfer process.[18]

Scheme 5

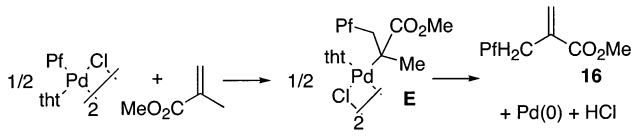


observed in the polymer by ^{1}H NMR. In this termination process Pd−H is formed, which reenters the cycle by reaction with MA to give **9**. Radical disproportionation could also be a termination pathway forming the terminal olefin group observed in the ^{1}H NMR, but the stability of acrylate radicals makes this pathway less favorable than for other radical species.[17]

The effect of the radical traps used in the polymerization (galvinoxyl, DPPH, TBP) parallels the observed reactivity of these compounds with palladium hydrides.[18] TBP does not react with Pd−H species and does not affect the polymerization process. Galvinoxyl and DPPH halt the polymerization of MA by a 2-fold mechanism. First, they can destroy the palladium hydrido complexes formed in the reaction medium either from **5** or in the termination step at the bottom of Scheme 4, avoiding in the latter case the regeneration of **9** and reducing seriously the TON. This detrimental effect is important whether the radical traps are added at the beginning or at any stage of the reaction. In addition, but probably with less incidence in the halting of the reaction, these additives can trap the growing polymeric radical species, disfavoring the propagation step (Scheme 4).

After the formation of poly(MA) has been going on for several hours, the formation of the MA dimer (MeO_2C)-CH_2CH=$CHCH_2(CO_2Me)$ (**14**), as a mixture of *E* and *Z* isomers (*E*:*Z* = 4:1), is observed by ^{1}H NMR. Only later, partial isomerization of **14** to the 2-alkene (MeO_2C)CH=$CHCH_2CH_2(CO_2Me)$ (**15**) is observed. The selective dimerization of MA to **14** (and not to a mixture of regioisomers) indicates that it is produced from a palladium linear alkyl complex (**B**, Scheme 5). Somewhat surprisingly, the first product observed is **14**, although the formation of **14** implies a pathway through the precursor of **15**: namely, **C**.[19] This means that the reversible Pd migration connecting **C** and **D** is very fast, and which olefin is formed first depends on the decoordination rate, which, from the results observed, is

Scheme 6



faster for **14**. Eventually the equilibria afford the most stable olefin, **15**, which appears slowly because it needs to be formed by decoordination from a particularly stable 6.5-membered palladacycle.[20] Brookhart and Hauptman have found a very similar effect in the dimerization of MA catalyzed by rhodium complexes.[21] The processes described are favored when less free MA is present. Otherwise MA can associatively substitute either the coordinated MA in **A**, producing a fast exchange before rotation and readdition, or the coordinated oxygen in the chelating metallacycles, thus halting the whole process.

Methyl methacrylate (MMA) is not polymerized by **2**. The reaction of MMA and **2** using the ratio Pd:MMA = 1:220 was monitored by ^{19}F and ^{1}H NMR. No intermediate palladium alkyl species was observed, and only the substituted olefin **16** was formed (Scheme 6). After 40 min complex **2** had disappeared, and **16** was the only fluorine-containing product present in solution. This indicates that β-H elimination from the methyl group in MMA is much faster than the β-H elimination from the methylene group (the only β-H source existing for MA). The fast formation of palladium hydride from **E** produces a high concentration of hydride species and leads to its immediate decomposition. Thus, **E** cannot play the role of a slow but sustained source of radicals and hydrides that **5**, **6**, and **9** play in the reaction with MA, and the initiator is consumed irreversibly in the early stages of the reaction.

It is worth noting that the addition of MMA to a running MA polymerization reaction will also halt the process. A three-experiment batch was set up under the same conditions. After 30 min batch 1 was quenched, yielding 0.1 g of polymer; MMA was added to batch 2 to reach a ratio MA:MMA = 1:1; a volume of inert solvent, identical to the volume of MMA used for batch 2, was added to batch 3. After 11 days batches 2 and 3 were quenched, recovering 0.12 g of polymer in batch 2 and 0.5 g of polymer in batch 3. The recovered polymer in batch 2 had incorporated some MMA, as determined by ^{1}H NMR. Since radical polymerization of MMA is a favorable process, this result indicates that MMA incorporation in the growing radical results in termination of the polymerization as soon as the equilibrium of recombination of the new radical with palladium allows fast β-H elimination (Scheme 4). In addition, MMA will avoid the formation of new radicals (Scheme 6).

In conclusion, the polymerization of methyl acrylate by these systems is initiated by insertion of methyl

(17) Kochi, J. K. *Free Radicals*; Wiley: New York, 1973; Vol. I, p 50.

(18) Albéniz, A. C.; Espinet, P.; López-Fernández, R.; Sen, A. *J. Am. Chem. Soc.* **2002**, *124*, 11278−11279.

(19) For economy the alkene complexes are represented uniformly as monomeric chelated with terminal Cl, although probably equilibria exist with their Cl-bridged dimeric isomers with monodentate alkenes (bonded either by the ketone or by the double bond). The dominant species will vary with the size of the cycle.

(20) For closely related palladium migration processes see: (a) Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *Organometallics* **1996**, *15*, 5010−5017. (b) Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *Organometallics* **1997**, *16*, 4138−4144. (c) Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *Organometallics* **1997**, *16*, 5964−5973.

(21) Brookhart, M.; Hauptman, E. *J. Am. Chem. Soc.* **1992**, *114*, 4437−4439.

acrylate in the Pd−aryl bond of the precatalyst. A radical polymerization can be initiated by the radicals generated from these alkyl complexes (**5**, **6**) but also from the alkyl complex **9** generated by insertion of MA in hydrido−Pd species. The latter is the regeneration pathway of radicals after a termination reaction has occurred. For this reason, the main pathway by which the radical traps halt this polymerization seems to be the annihilation of H−Pd species (hydride trapping), more than radical trapping itself.

Experimental Section

General Considerations. ^{19}F and ^{1}H NMR spectra were recorded on Bruker AC-300 and ARX-300 instruments. Chemical shifts are reported in δ (ppm) and referenced to Me_4Si (^{1}H) or $CFCl_3$ (^{19}F). The spectra were recorded at 293 K unless otherwise noted. Size exclusion chromatography (SEC) was carried out on a Waters SEC system using a two-column bed (Styragel 7.8 × 300 mm columns: 50−100 000 D and 2000−4 000 000 D) and Waters 410 differential refractometer. SEC samples were run in THF at room temperature and calibrated to polystyrene standards. Solvents were dried over CaH_2, distilled, and deoxygenated before use. Methyl acrylate, *tert*-butyl acrylate, and methyl methacrylate (Aldrich) were distilled and deoxygenated prior to use. Galvinoxyl, 2,2-bis(4-*tert*-octylphenyl)-1-picrylhydrazyl (DPPH), 2,6-di-*tert*-buylphenol (TBP), and $AsPh_3$ were purchased from Aldrich. 1,3,5-$C_6F_3Cl_3$ was purchased from Fluorochem Ltd. $[PdBr(C_6F_5)(NCMe)_2]$ (**1**),[13] $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2]$ (**2**),[22] and $[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(tht)_2]$ (**3**)[22] were synthesized by literature procedures. All the reactions described were carried out under an inert atmosphere. Polymer tacticity was determined by integration of the methine and the methylene signals in the ^{1}H NMR spectrum.

***trans*-$[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(AsPh_3)_2]$ (4).**[23] A solution of $AsPh_3$ (0.054 g, 0.175 mmol) in CH_2Cl_2 (20 mL) was added dropwise at room temperature to a stirred solution of $[PdBr(C_6F_5)(NCMe)_2]$ (**1**; 0.076 g, 0.175 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 10 min, and the solvent was evaporated to dryness. The residue was triturated in EtOH (10 mL) to yield a yellow solid which was filtered, washed with EtOH, and air-dried. Yield: 0.103 g (90%). Anal. Calcd for $C_{48}H_{30}As_2Br_2F_{10}Pd_2$: C, 43.70; H, 2.29. Found: C, 43.78; H, 2.56. ^{19}F NMR (282 MHz, δ, $CDCl_3$): −162.9 (m, $2F_{meta}$), −160.4 (t, $1F_{para}$), −118.2 (m, $2F_{ortho}$). ^{1}H NMR (300 MHz, δ, $CDCl_3$): 7.52 (m, 2H; Ph), 7.35 (m, 3H; Ph).

***trans*-$[Pd_2(\mu\text{-}Cl)_2\{CH(CO_2Me)CH_2C_6F_5\}_2(tht)_2]$ (5) and *trans*-$[Pd_2(\mu\text{-}Cl)_2\{CH(C_6F_5)CH_2CO_2Me\}_2(tht)_2]$ (6).** To a solution of $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2]$ (**2**; 0.200 g, 0.252 mmol) in CH_2Cl_2 (8 mL) was added methyl acrylate (0.217 g, 2.521 mmol). The mixture was stirred for 55 min at room temperature and evaporated to dryness. The residue was washed with *n*-hexane (3 × 1.5 mL) and then triturated in Et_2O (5 mL). The yellow solid was filtered, washed with Et_2O, and air-dried. Yield: 0.087 g (36%). Anal. Calcd for $C_{28}H_{28}Cl_2F_{10}O_4S_2Pd_2$: C, 34.80; H, 2.92. Found: C, 34.84; H, 3.02.

Data for **5** are as follows. ^{19}F NMR (282 MHz, δ, $CDCl_3$): −163.5 (m, $2F_{meta}$), −158.5 (t, $1F_{para}$), −142.6 (m, $2F_{ortho}$). ^{1}H NMR (300 MHz, δ, $CDCl_3$): 3.65 (s, 3H; OCH_3), 3.48 (m, 1H; C*H*CO_2CH_3), 3.10 (br, 4H; SCH_2), 2.90 (m, 1H; C*H*HC_6F_5), 2.58 (m, 1H; CH*H*C_6F_5), 2.08 (br, 4H; SCH_2CH_2).

Data for **6** are as follows. ^{19}F NMR (282 MHz, δ, $CDCl_3$): −164.1 (m, $2F_{meta}$), −159.8 (t, $1F_{para}$), −138.7 (m, $2F_{ortho}$). ^{1}H NMR (300 MHz, δ, $CDCl_3$, 273 K): 4.15 (t, J = 7.80 Hz, 1H; CHC_6F_5), 3.65 (s, 3H; OCH_3), 3.10 (br, 4H; SCH_2), 3.04 (m, 1H; C*H*HCO_2CH_3), 2.62 (m, 1H; C*H*HCO_2CH_3), 2.08 (br, 4H; SCH_2CH_2).

(22) Usón, R.; Forniés, J.; Navarro, R.; García, M. P. *Inorg. Chim. Acta* **1979**, *33*, 69−75.

(23) Usón, R.; Forniés, J.; Nalda, J. A.; Lozano, M. J.; Espinet, P.; Albéniz, A. C. *Inorg. Chim. Acta* **1989**, *156*, 251−256.

Table 3. Crystal Data for Complex 5

empirical formula	$C_{28}H_{28}Cl_2F_{10}O_4Pd_2S_2$
fw	966.32
temo	293(2) K
wavelength (Mo Kα)	0.710 69 Å
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	
a	15.114(5) Å
b	12.028(5) Å
c	19.611(5) Å
α	90.000(5)°
β	102.628(5)°
γ	90.000(5)°
V, *Z*	3479(2) Å^3, 4
density (calcd)	1.845 g/cm^3
abs coeff	1.394 mm^{-1}
F(000)	1904
abs cor method; transmissn factor max, min	SADABS; 1.000 000, 0.804 450
cryst size	0.05 × 0.13 × 0.15 mm^3
scan range, deg	1.38 ≤ θ ≤ 23.27
no. of rflns collected, indep	16 355, 5004
completeness to $\theta = \theta_{max}$	99.9%
no. of data/restraints/params	5004/0/435
goodness of fit on F^2	1.042
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0424, wR2 = 0.0974
R indices (all data)	R1 = 0.0617, wR2 = 0.1083
largest diff peak and hole	1.335 (close to Pd) and −0.603 e Å^3

X-ray Crystal Structure Determination of 5. Crystals of **5** suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a solution of **5** in CH_2Cl_2. The crystal selected was mounted on the tip of a glass fiber. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with graphite-monochromated Mo Kα radiation. Reflections were collected, intensities were integrated, and the structure was solved by the direct methods procedure.[24] Non-hydrogen atoms were refined anisotropically, and hydrogens were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Relevant crystallographic data are gathered in Table 3.

General Procedure for the Polymerization of Acrylates. Methyl acrylate (0.956 g, 11.1 mmol) was added to a solution of $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2]$ (**2**; 0.0022 g, 0.0028 mmol) in CH_2Cl_2 (2 mL). The reaction proceeded in daylight at room temperature for 24 h, although the high viscosity that was generated halted the stirring after 5 h. The polymer was precipitated on pouring the mixture onto MeOH (30 mL). The MeOH was decanted off, and the polymer was dried under vacuum to yield 0.786 g of poly(methyl acrylate) (82%): M_w = 1.9 × 10^5, M_w/M_n = 2.2. ^{1}H NMR (300 MHz, δ, $CDCl_3$): 3.68 (s, 6H; OCH_3), 2.34 (br, 2H; C*H*$(CO_2CH_3)^s$, C*H*$(CO_2CH_3)^i$), 1.95 (br, 1H; CH*H*^{i}), 1.68 (br, 2H; CH_2^s), 1.51 (br, 1H; CH*H*^{i}). In this and all following data lists, i = isotactic and s = syndiotactic.

The same procedure was used for other monomers and/or solvents (see Table 1) and also for the tests of the influence of additives (molar ratio Pd:additive = 1:1).

Poly(*tert*-butyl acrylate): 66% yield; atactic polymer; M_w = 5.1 × 10^5, M_w/M_n = 4.8. ^{1}H NMR (300 MHz, δ, $CDCl_3$): 2.23 (br, 2H; C*H*$(CO_2t\text{Bu})^s$, C*H*$(CO_2t\text{Bu})^i$), 1.81 (br, 1H; CH*H*^{i}), 1.60 (br, 1H; CH*H*^{i}), 1.51 (br, 2H; CH_2^s), 1.43 (s, 18H; *t*Bu).

Poly(methyl methacrylate): 6% yield; *mm*:*mr*:*rr* = 0.026:0.299:0.675. M_w = 1.8 × 10^5, M_w/M_n = 2.9. ^{1}H NMR (300 MHz, δ, $CDCl_3$): 3.6 (s, 6H; OCH_3), 2−1.7 (br, 4H; CH_2), 1.2 (s, 3H; CH_3^{mm}), 1.0 (s, 3H; CH_3^{mr}), 0.8 (s, 3H; CH_3^{rr}).

Polymerization of Methyl Acrylate in the Presence of Methyl Methacrylate. To a solution of $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2$-

(24) The data analysis and drawings were performed with the following programs: SMART V5.051, 1998. SAINT V6.02, 1999. Sheldrick, G. M. SHELXTL V5.1; Bruker AXS, Inc. Madison, WI, 1998.

$(tht)_2$] (**2**; 0.005 g, 0.007 mmol) in CH_2Cl_2 (3 mL) was added methyl acrylate (2.390 g, 27.8 mmol). The resulting solution was divided into three equal samples. After 30 min the samples were treated as follows: sample 1 was quenched by adding it to a large excess of MeOH, resulting in the precipitation of 0.098 g (12%) of polymer ($M_w = 2.6 \times 10^5$, $M_w/M_n = 4.3$). Methyl methacrylate (1.0 mL, 9.3 mmol) was added to sample 2, and the reaction was allowed to continue for 11 days, after which time quenching with MeOH afforded 0.116 g of copolymer ($M_w = 2.9 \times 10^5$, $M_w/M_n = 5.0$; MA:MMA ratio in polymer, 1:1.9). CH_2Cl_2 (1 mL) was added to sample 3, to keep the same concentration of sample 2, and quenching after 11 days yielded 0.503 g (66%) of polymer ($M_w = 2.6 \times 10^5$, $M_w/M_n = 2.7$).

The extent of monomer incorporation in the copolymer was determined by integration of the methoxy signals (methyl acrylate/methyl methacrylate copolymer) in the ^{1}H NMR spectra.

Monitoring of the Polymerization of Methyl Acrylate by NMR. $[Pd_2(\mu\text{-Cl})_2(C_6F_5)_2(tht)_2]$ (**2**; 0.004 g, 0.005 mmol) was dissolved in $CDCl_3$ (0.6 mL) in an NMR tube. Methyl acrylate (0.191 g, 2.221 mmol) was added to the solution. The polymerization was monitored by ^{19}F and ^{1}H NMR, and the formation of **5**, **6**, **7**,[11] **8**,[11] **9**, **14**, and **15** was observed as described in the text. The identities of **14** and **15** were checked by comparison with independently synthesized samples.

Data for **7** are as follows.[25] ^{19}F NMR (282 MHz, δ, $CDCl_3$): -162.0 (m, $2F_{meta}$), -151.5 (t, $1F_{para}$), -139.9 (m, $2F_{ortho}$).

Data for **8** are as follows.[25] ^{19}F NMR (282 MHz, δ, $CDCl_3$): -162.9 (m, $2F_{meta}$), -157.2 (t, $1F_{para}$), -144.1 (m, $2F_{ortho}$).

Data for **9** are as follows. ^{1}H NMR (300 MHz, δ, $CDCl_3$): 3.60 (s, 3H; OCH_3), 3.40 (1H; C*H*CO_2CH_3), 0.80 (d, $J = 8.90$ Hz, 3H; CH_3).

The polymerization experiments controlling the light source were carried out similarly. New broad signals (that are present in the final polymer) were observed in the ^{19}F NMR spectra when the polymerization was carried out in the presence of light. After 5 days, this sample was added to a large excess of MeOH. The polymer obtained was filtered, dissolved in CH_2Cl_2, and precipitated in MeOH. ^{19}F and ^{1}H NMR spectra of the polymer were taken to analyze the end groups. ^{1}H NMR (300 MHz, δ, $CDCl_3$): 6.8 (dd, $J = 17.6$, 8.8 Hz, 1H; (CO_2Me)-CH=C*H*P), 5.9 (d, $J = 17.6$ Hz, 1H; (CO_2Me)C*H*=CHP). ^{19}F NMR (282 MHz, δ, $CDCl_3$): -162.6 (b, $2F_{meta}$), -156.3 (b, $1F_{para}$), -143.2 (b, $2F_{ortho}$). The rest of the signals cannot be assigned to distinct Pf groups. Broad signals in the characteristic ^{19}F regions indicated in parentheses are observed as follows: -161.5 (b, F_{meta}), -162.35 (b, F_{meta}), -155 (b, F_{para}), -140.5 (b, F_{ortho}), -142 (b, F_{ortho}).

Estimation of the C_6F_5 Contents of Poly(methyl acrylate). A sample of poly(methyl acrylate) was repeatedly dissolved and precipitated to remove any traces of nonpolymeric materials. A 16.5 mg amount of of polymer was completely dissolved in 0.5 mL of acetone, and 0.1 mL of a solution of 1,3,5-$C_6F_3Cl_3$ (8.5×10^{-4} M, used as internal standard) was added. A ^{19}F NMR spectrum of the solution was recorded, using a d_6-acetone capillary for the lock. The number of equivalents of C_6F_5, estimated by integration, was 3.8×10^{-5}. For $M_n = 8.6 \times 10^4$ this corresponds to 20% of C_6F_5-containing chains. However, this result has to be considered just as an estimate, because at the low level of F-concentration achieved at the solubility limit of the polymer the Teflon contained in the NMR probe distorts the baseline and makes the adjustment of the baseline extremely difficult.

Photochemical Decomposition of Mixtures of 5 and 6. A mixture of *trans*-$[Pd_2(\mu\text{-Cl})_2\{CH(CO_2Me)CH_2C_6F_5\}_2(tht)_2]$ (**5**) and *trans*-$[Pd_2(\mu\text{-Cl})_2\{CH(C_6F_5)CH_2CO_2Me\}_2(tht)_2]$ (**6**; 0.021 g, 0.021 mmol) (**5**:**6** = 15:1) was dissolved in $CDCl_3$ in the presence of air. The NMR tube was irradiated for 9 h using a 365 nm (6 W) lamp. A mixture of **7** (and its corresponding cis isomer) and **8** as major products, in addition to **10**−**13**, was observed in the ^{19}F NMR spectra. The sample was evaporated to dryness and the residue chromatographed by preparative TLC (silica plate) using a mixture of ethyl acetate and *n*-hexane (1:3) as eluent. Compounds **10**−**12** were separated and characterized by NMR and GC-MS.

Data for **10** are as follows. ^{19}F NMR (282 MHz, δ, $CDCl_3$): -162.9 (m, $2F_{meta}$), -156.2 (t, $1F_{para}$), -143.0 (m, $2F_{ortho}$). ^{1}H NMR (300 MHz, δ, $CDCl_3$): 4.41 (m, 1H; C*H*CO_2Me), 3.85 (s, 3H; $CHCO_2CH_3$), 3.20 (m, $J = 14.3$, 5.2 Hz, 1H; CH*H*C_6F_5), 3.05 (m, $J = 14.3$, 8.1 Hz, 1H; C*H*HC_6F_5), 2.85 (d, $J = 6.1$ Hz, 1H; CH(O*H*)). MS (EI, *m*/*z* (relative intensity)): 271 ($M - H^+$, 1), 252 (55) 250 (50), 211 (90), 181 (97), 163 (100), 89 (34), 59 (6).

Data for **11** are as follows. ^{19}F NMR (282 MHz, δ, $CDCl_3$): -161.8 (m, $2F_{meta}$), -154.4 (t, $1F_{para}$), -143.0 (m, $2F_{ortho}$). ^{1}H NMR (300 MHz, δ, $CDCl_3$): 5.53 (m, 1H; C*H*C_6F_5), 3.75 (s, 3H; $CHCO_2CH_3$), 3.22 (d, $J = 5.7$ Hz, 1H; CH(O*H*)), 3.15 (dd, $J = 16.7$, 9.7 Hz, 1H; CH*H*CO_2CH_3), 2.75 (dd, $J = 16.7$, 4.1 Hz, 1H; C*H*HCO_2CH_3). MS (EI, *m*/*z* (relative intensity)): 270 (M^+, 1), 197 (100), 177 (65), 167 (6), 74 (21), 59 (3).

Data for **12** are as follows. ^{19}F NMR (282 MHz, δ, $CDCl_3$): -162.2 (m, $2F_{meta}$), -154.4 (t, $1F_{para}$), -142.2 (m, $2F_{ortho}$). ^{1}H NMR (300 MHz, δ, $CDCl_3$): 4.28 (s, 2H; $CH_2C_6F_5$), 3.93 (s, 3H; CO_2CH_3). MS (EI, *m*/*z* (relative intensity)): 268 (M^+, 9), 209 (7), 181 (100), 59 (10).

Data for **13** are as follows. ^{19}F NMR (282 MHz, δ, $CDCl_3$): -160.1 (m, $2F_{meta}$), -147.7 (t, $1F_{para}$; chemical shift characteristic of the C_6F_5CO group), -140.7 (m, $2F_{ortho}$).

The decomposition of mixtures of **5** and **6** under nitrogen, in the presence of galvinoxyl and with the light source controlled (365 nm and in the dark), were carried out in the same way.

Monitoring of the Reaction with Methyl Methacrylate by NMR. $[Pd_2(\mu\text{-Cl})_2(C_6F_5)_2(tht)_2]$ (**2**; 0.003 g, 0.004 mmol) was disolved in $CDCl_3$ (0.6 mL) in an NMR tube, and methyl methacrylate (0.187 g, 1.870 mmol) was added to the solution. The reaction was monitored by ^{19}F and ^{1}H NMR. The formation of **16** was observed.[11]

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Supporting Information Available: Tables giving crystallographic data for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) ^{19}F NMR spectral data for **7** and **8** were mistaken in ref 11. The corrected chemical shifts are given here.