Neutral Palladium Complexes as Catalysts for Olefin−Methyl Acrylate Copolymerization: A Cautionary Tale

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ABSTRACT: Neutral palladium complexes bearing pyrrole−imine ligands **(I−III)** have been synthesized, and their use as catalysts for olefin and vinyl monomer (co)polymerizations was investigated. Methyl acrylate (MA) has been homopolymerized in excellent yields (>95%) using these complexes. Copolymerizations of MA with norbornene or 1-hexene in the presence of these catalysts produce acrylate-enriched copolymers. Hypothesizing that metal enolates are potential intermediates in some of these polymerizations, palladium enolate complexes (**IV−VII**) containing ligand **1** were tested for their catalytic activity. Surprisingly, these complexes proved inactive toward acrylate and/or olefin polymerizations. Further mechanistic studies have shown that the homo- and copolymers obtained using these complexes arise from a radical mechanism rather than the anticipated metal-mediated process.

Introduction

The evolutionary trajectory of single-site catalyst discovery has again cycled and is refocused on late-transition-metal complexes. This resurgence of interest in late metal systems can be attributed, in large part, to the discovery by Brookhart et al. that cationic palladium(II) and nickel(II) complexes possessing bulky diimine ligands yield high molecular weight polymer.[1] The design of the supporting ligands is crucial—axial shielding of the metal center protects against the normally rapid chain transfer steps (β-hydride eliminations) that have long plagued late-metal catalyst systems. Most importantly, palladium complexes of these diimine ligands are also capable of producing copolymers with various functionalized vinyl comonomers (i.e., methyl acrylate (MA), methyl methacrylate, and functionalized cyclic olefins).[2,3]

Of the growing number of group VIII catalysts, palladium complexes are among the most versatile for both organic reactions and polymerizations.[4] Palladium-catalyzed reactions and their mechanisms have been the subject of extensive studies directed at discovering new and more efficient complexes that provide better control of product structures and properties. As far as olefin polymerizations are concerned, cationic palladium(II) complexes are the most commonly used and have been the main focus of such studies. The efficiency and versatility of palladium catalysts are evidenced by highly successful alternating copolymerization of olefins and carbon monoxide[5] and the polymerization of norbornene derivatives.[3,6]

Neutral transition-metal catalysts have also attracted considerable attention because of their special characteristics resulting from the reduced charge at the catalytic center.[7] Dramatic differences have been observed between neutral[8,9] and cationic[2,10] nickel catalysts. Although both species can display high activities in ethylene polymerizations, the neutral catalysts show considerably more tolerance toward polar groups. This has allowed the extension of their use to the copolymerization of ethylene with a wider range of α,ω-functionalized olefin monomers or polymerizations in polar solvents such as ketones, alcohols, and water.[9]

Being aware of the effect of overall charge of complexes on catalytic properties, we have initiated a systematic study of neutral transition-metal complexes. We report herein our polymerization results using palladium-based neutral complexes possessing 2-iminopyrrole ligands. Our investigations of these complexes have revealed that they are highly active initiators for MA homopolymerization and copolymerization with olefins. The copolymers produced are generally MA-enriched. Since there are a limited number of reports of MA polymerizations using transition-metal complexes and the polymerization mechanisms are not all well-established,[11,12] we have focused on mechanistic studies with the neutral palladium complexes as single-component initiators. Our results from these studies lead us to the conclusion that MA polymerizations, both homo- or copolymerizations with olefins, proceed via a free-radical mechanism in the presence of several neutral palladium complexes.

Results and Discussion

Syntheses of Neutral Palladium Complexes I−III. Achieving overall neutrality of the propagating palladium alkyl species requires replacing the neutral chelating ligands (e.g., α-diimine)[1−2,10] with their negatively charged counterparts. Our choice of anionic chelating ligand was a 2-iminopyrrole substituted at the 5-position with a methyl group (compound **1**). The methyl group was introduced into the 5-position of the pyrrole ring to prevent possible side reactions on the pyrrole and to provide partial shielding of the metal center. Ligand **1** was deprotonated using NaH and the anion allowed to react with (COD)PdMeCl in the presence of neutral, two-electron donor ligands to give palladium complexes **I−III** as air- and moisture-stable pale yellow solids (Scheme 1). The neutral donor ligands are necessary to stabilize the complexes and different ones were used in order to study their effect on catalytic activity. Attempts to prepare palladium complexes of **1** without added donor ligand produced an orange solid

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Scheme 1

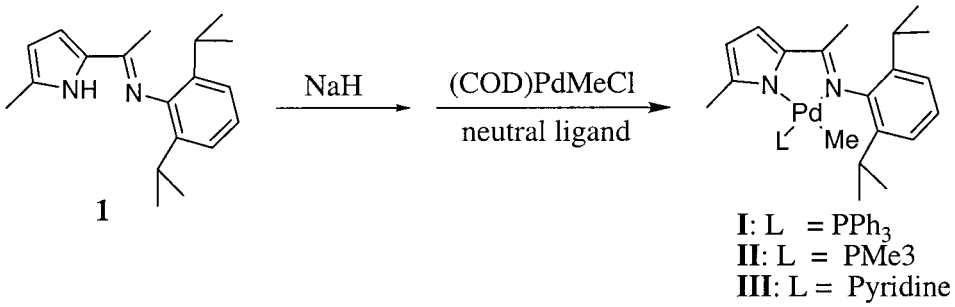


Table 1. Polymerization Results of Methyl Acrylate Using Complexes I−III[a]

entry	catalyst	rxn time (h)	polymer yield (%)	M_n (g/mol)	M_w/M_n
1	**I**	4	96.7	364 000	3.58
2	**II**	4	95.3	301 000	3.90
3	**III**	4	99.0	138 000	5.48
4	**I**	1 (quenched)	42.0	300 000	3.25
5	**II**	1 (quenched)	33.3	425 000	3.40
6	**III**	1 (quenched)	41.0	306 000	3.41
7	**I**[b]	1 (quenched)	35.0	312 000	3.34
8	**I**[c]	1 (quenched)	0		

[a] Polymerization conditions: 0.010 mmol of palladium complex, 2.0 mL of methyl acrylate, 5.0 mL of CH_2Cl_2, 50 °C. The molecular weight of polymers was determined by GPC in $CHCl_3$ vs polystyrene standards. [b] 0.050 mmol of 4-methoxyphenol (MEHQ) was used as inhibitor. [c] 0.050 mmol of gavinoxyl was used as inhibitor.

that displayed a very complicated ^{1}H NMR spectrum. Adding triphenylphosphine (PPh_3) to this orange solid afforded a small amount of $Pd(PPh_3)_4$ (4% yield) and an uncharacterized red oil instead of complex **I**. This red oil proved to be inactive in all polymerization attempts (vide infra).

Polymerization Studies. Our main interest in the study of these complexes was their possible application as catalysts in polymerization of vinyl monomers. Polymerizations of ethylene and α-olefins have been reported by using cationic Ni(II) and Pd(II) catalysts and neutral Ni(II) catalysts.[1,2,8−10] Abstraction of phosphine from the neutral complexes is crucial to produce high molecular weight polymer or to increase the catalytic activity. As would be expected, complexes **I**−**III** with the strongly binding donor ligands proved to be inactive for polymerization of both ethylene and 1-hexene. NMR scale experiments using ethylene and complex **I** showed no evidence of either ethylene oligomerization or any catalyst decomposition reactions. Surprisingly, these complexes still remained inactive when treated with phosphine sponges (i.e., $Ni(COD)_2$ or $B(C_6F_5)_3$) that are very effective at activating other neutral group VIII catalysts.[9,13]

The polymerization of functional olefins proved far more promising. Polymerizations of MA with complexes **I**−**III** were conducted in methylene chloride. Excellent yields (>95%) of poly(methyl acrylate) (PMA) were obtained using all three complexes when running the polymerization for 4 h in a water bath at 50 °C (Table 1, entries 1−3). The polymers produced have high molecular weights (M_n > 138 000) and show glass transition temperatures of 10.4 °C. According to the ^{1}H NMR and ^{13}C NMR spectra, atactic polymers were obtained in all cases (as were poly(methyl methacrylate) samples prepared in the same manner using complex **I**).[14] As a point of comparison, the cationic palladium catalysts of Brookhart showed no activity for MA homopolymerization, and they decompose in MA in the absence of other olefins.[10a]

The relative binding strength of neutral donor ligands to the palladium center was tested by ligand exchange reactions. Replacement of pyridine by (PPh_3) was performed by dissolving complex **III** and PPh_3 in C_6D_6 (**III**/Ph_3P = 1:1). The ^{31}P NMR spectra of the mixture recorded after 18 h showed the complete disappearance of free PPh_3 and only one peak at δ 41.6 ppm, which is identical to the resonance for the coordinated PPh_3 in complex **I**. These data are consistent with the complete replacement of pyridine by PPh_3. Consistent with this, the ^{1}H NMR spectrum exhibited signals for the Pd−CH_3 moiety in complex **I** and free pyridine. Similarly, addition of trimethylphosphine (PMe_3) into the C_6D_6 solution of complex **I** resulted into the complete replacement of PPh_3. These exchange reactions show that the binding strength of neutral donor ligand with palladium atom decreases in the following order: PMe_3 > PPh_3 > pyridine. On the basis of this series and the need to dissociate the donor ligands to free a coordination site for monomer, it is reasonable to expect the stability and activity of complexes bearing these ligands could reasonably reflect this trend. To directly compare the activity of our complexes with the different stabilizing ligands, competitive MA polymerizations were quenched after 1 h to limit monomer conversion and reduce viscosity problems. However, only slightly different activities were observed for these complexes and they followed the order **I** ≈ **III** > **II** (Table 1, entries 4−6): an ordering that does not parallel the binding strength of the donor ligands.

Complex **I** was also tested for its activity in copolymerizations of MA with olefins. For example, MA and norbornene were mixed at the mole ratio of 1:1 and polymerized at 50 °C. The polymer produced contained 87.7% of MA and 12.3% of norbornene. The glass transition temperature of copolymer increased from 10 to 31 °C due to the incorporation of the norbornene. MA and 1-hexene were also copolymerized successfully using complex **I** to produce MA enriched copolymer (Table 2). Interestingly, with the combination of ethylene and MA, only homo-PMA was obtained (vide infra).

Acrylate monomers can be polymerized through various mechanisms including anionic, radical, or group transfer polymerization (GTP). Brookhart and co-workers have reported that the copolymerization of MA and olefin catalyzed by cationic palladium(II) complexes proceeds through a coordination−insertion mechanism. These cationic palladium catalysts showed no activity for MA homopolymerization, and they were decomposed by MA in the absence of olefin comonomers.[10] However, MA homopolymerizations have been reported using neutral palladium catalysts by Sen[11] ((COD)PdMeCl/

Table 2. Copolymerizations of Methyl Acrylate and 1-Hexene[a]

		monomer (mmol)		monomer conversion (%)[b]		polymer composition (%)[c]	
initiator	time (h)	MA	hexene	MA	hexene	MA	hexene
complex **I**	1	22.2		38.2		100	
	2	22.2	20.0	8.3	0.56	94.3	5.7
	2	22.2	40.0	8.9	0.64	88.6	11.4
	4	11.1	40.0	16.7	0.87	84.2	15.8
benzoyl peroxide	2	22.2		45.2		100	
	2	22.2	20.0	2.1	0.15	94.0	6.0
	2	22.2	40.0	1.3	0.08	90.0	10.0
	2	11.1	40.0	5.4	0.23	86.6	13.4

[a] Polymerization conditions: 0.020 mmol of initiator, 2 mL of toluene, 50 °C. [b] Calculated by: polymer weight × % monomer in copolymer/monomer weight. [c] Calculated from the ratio of the methyl group of hexene and the methoxyl group of methyl acrylate in ^{1}H NMR spectra.

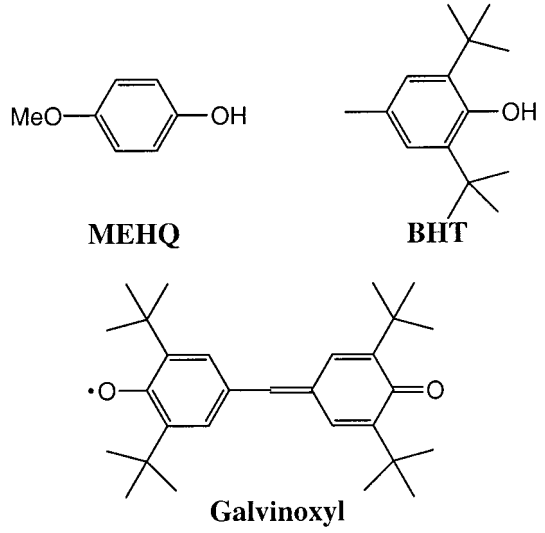
PR_3) and by Yamamoto[12] ($(PMePh_2)_2PdMe_2$). The copolymerization of MA and norbornene also reported by Sen afforded MA-enriched polymers.[11] A coordination mechanism has been proposed for these neutral catalysts based on the fact that polymers could be produced in the presence of a "radical inhibitor" (e.g., 4-methoxyphenol, MEHQ).[11]

As shown above, dramatic reactivity differences exist between our neutral palladium catalysts **I**−**III** and Brookhart's cationic complexes. The neutral catalysts **I**−**III** are active for MA homopolymerization but not active for olefin (e.g., ethylene and 1-hexene) homopolymerization, while the cationic complexes show the opposite behavior. Furthermore, the copolymers of MA and olefin obtained using these neutral complexes were inevitably MA-enriched, while the cationic complexes yield ethylene-rich copolymers. These dramatic differences encouraged us to perform mechanistic studies on the neutral palladium catalysts.

Mechanistic Studies. We evaluated the effect of radical inhibitors on our palladium catalysts, but the results suggest that using a nonspecific radical inhibitor in the presence of palladium complexes is an unreliable method of discounting a radical polymerization pathway. The use of MA inhibited with 200 ppm of MEHQ did not at all affect the activity of complex **I**. The ^{1}H NMR spectrum of complex **I** remained unchanged after heating for 1 h in the presence of MEHQ, indicating that no overt reaction takes place between the two reagents. Addition of excess MEHQ (MEHQ/complex **I** = 5:1) into the polymerization system caused only a slight decrease in monomer conversion from 42% to 35% after a 1 h quench (Table 1, entries 4 and 7). It is obvious that MA polymerizations using complex **I** are not inhibited by MEHQ. Identical results were obtained by another phenolic radical scavenger, 2,6-di-*tert*-butyl-4-methylphenol, BHT: MA polymerization proceeded without hindrance in the presence of BHT.

When a different free radical scavenger, galvinoxyl, was added to the polymerization system, the polymerization was completely inhibited, and no polymer was obtained. ^{1}H NMR spectroscopy revealed that complex **I** was very stable in the presence of 5 equiv of galvinoxyl. Furthermore, we found that gavinoxyl did not affect the activity of Brookhart's cationic palladium catalyst toward ethylene polymerizations, thus supporting the supposition that galvinoxyl will not inhibit or retard a polymerization proceeding through a coordination mechanism.

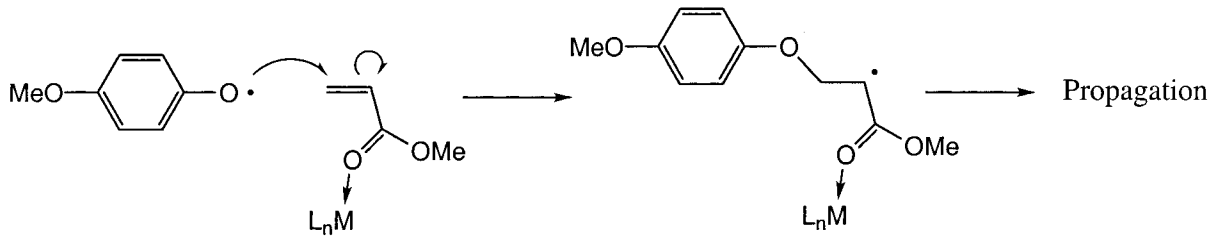
Control polymerizations of MA were performed using (COD)PdClMe/PPh_3 as the initiator and either MEHQ and galvinoxyl as inhibitors. The results of these experiments were essentially identical to the results obtained from complexes **I**−**III**. That is, MEHQ showed little effect on the MA polymerization while galvinoxyl completely quenched the reaction.



All of these results suggest that the phenolic inhibitors MEHQ and BHT are inefficient radical inhibitors for polymerizations run in the presence of neutral palladium complexes. The exact reason for the failure of phenols to inhibit polymerizations under these conditions remains unknown; however, it has been reported that hydroquinones can actually act as accelerators of radical polymerizations in the presence of Lewis acids, e.g., alkylboranes.[15] It is proposed that this unusual behavior results from coordination of the Lewis acid to the carbonyl of the monomer and activating it to a sufficiently high enough level that the normally inactive phenoxy radical (formed via usual inhibition steps) now adds to the double bond and initiates polymerization. Our working hypothesis is that a similar process occurs in these palladium systems—monomer activation by coordination of the MA carbonyl metal followed by addition of a phenoxy radical (Scheme 2). Galvinoxyl, with its extended conjugation, is far more stable and unable to add across the activated acrylate double bond and therefore functions as a standard radical trap. On the basis of these studies, we conclude that using radical inhibitors alone is not a reliable method for ruling out possible mechanisms.

The relative reactivities of MA and ethylene (or other α-olefins) are quite different in coordination and radical polymerization reactions. In coordination polymerizations catalyzed by cationic palladium catalysts, the ethylene out competes the electron-deficient MA so that the MA incorporation in copolymers remains low even

Scheme 2



if an excess amount of MA is used in the reaction.[10] However, the reactivity of MA is considerably higher in radical polymerization (MA/ethylene, r_1/r_2 = 19.4/0.020).[16] Severe reaction conditions, high ethylene pressures, and high polymerization temperatures are required in order to produce ethylene-enriched copolymers.

Therefore, the monomer content and distribution sequence in copolymers provide useful insights into the polymerization mechanism. As described above, MA−norbornene copolymers were produced by using complexes **I**−**III** as catalysts. Unfortunately, the monomer distribution of MA−norbornene copolymers cannot be clearly delineated using ^{13}C NMR spectroscopy due to multiple peak overlap. However, early workers reported the copolymerization of MA with 1-hexene using a radical initiator, although the microstructure of copolymer was not determined.[17] We examined the MA/hexene copolymerization using complex **I** as a catalyst to provide a point of comparison. Another series of control experiments were performed under the same conditions (monomer feeds, temperatures (50 °C), times, etc.) using the radical initiators benzoyl peroxide and di(4-*tert*-butylcyclohexyl)peroxydicarbonate. The conversion of monomers was kept low so that compositional drift of the feed would not be a factor in this analysis. As summarized in Table 2, copolymerizations initiated by palladium complex produced copolymers with essentially the same 1-hexene content as the control copolymerizations run using the radical initiators. The copolymers were all found to be MA-enriched, even in the cases where 1-hexene was used in excess. For both systems (radical initiators and metal complexes), the presence of 1-hexene dramatically decreased the polymer productivity compared with MA homopolymerization. Furthermore, as evidenced by NMR spectroscopy, atactic hompolymer and copolymers were obtained from both systems. These findings again support a radical mechanism for these palladium-initiated polymerizations. The fact that the tacticity of the polymers is independent of the ligands on the metal supports a true free radical process.

NMR spectral analysis of the polymer microstructure revealed the polymers produced in the copolymerization of MA and 1-hexene is a copolymer with long runs of MA and isolated hexenes in the backbone. The ^{1}H NMR spectrum of a MA/hexene copolymer prepared using **I** is shown in Figure 1. The methoxyl peak at δ 3.6, the MA methine proton at δ 2.3, and the hexene methyl triplet at δ 0.8 are easily distinguished and can be used to calculate copolymer composition. The region from δ 1.0−2.0 includes the poorly resolved peaks attributed to methine and methylene hydrogens on the polymer backbone and methylene hydrogens on the hexene side chain.

The ^{13}C NMR spectrum of the same polymer is much more definitive, as shown in Figure 2. Two signals were observed for the carbonyl carbon (δ 175.0 and 175.9

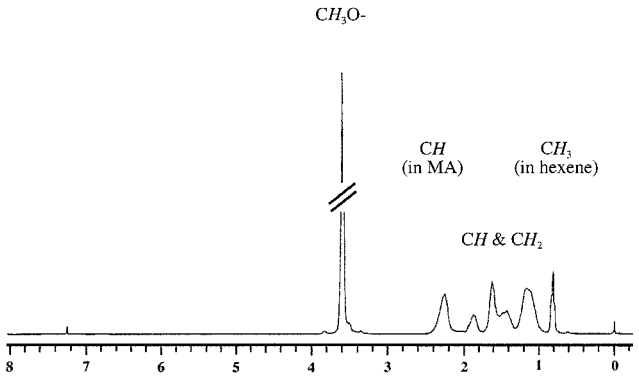


Figure 1. ^{1}H NMR spectrum of MA−hexene copolymer produced by complex **I** (15.8% hexene incorporation).

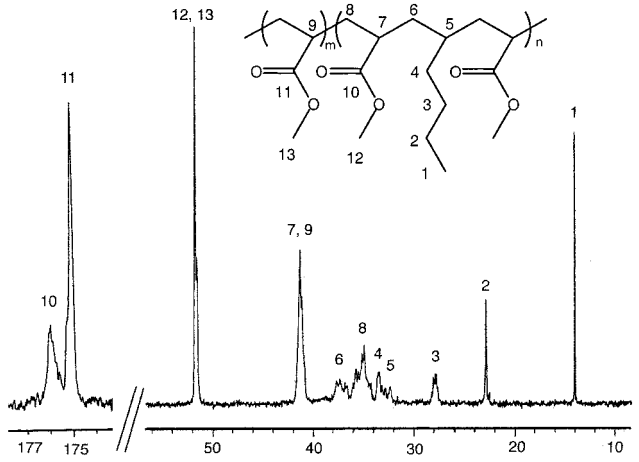


Figure 2. ^{13}C NMR spectrum of MA−hexene copolymer produced by complex **I** (15.8% hexene incorporation).

ppm). The peak at δ 175.0 ppm, which is the same as in homo-PMA, is assigned to the carbonyl carbon in long MA runs. The peak at δ 175.9 ppm is assigned to a MA carbonyl adjacent to a hexene. This assignment is based on the ^{13}C NMR spectra of alternating copolymers of MA and α-olefin, which display a carbonyl carbon signal at δ 176 ppm.[18] The presence of this peak also provides evidence that the hexene is incorporated into the same chains as MA. The peaks for the methoxyl carbon, methylene carbon, and methine carbon in MA unit are assigned on the basis of the ^{13}C NMR spectrum of MA homopolymer.[14] The remaining peaks are attributed to the carbons in hexene unit and the assignments of these peaks are based on the ^{13}C NMR spectrum of poly(1-hexene).[19] The peaks at δ 37 and 33 ppm are attributed to the methylene and methine carbons of hexene on the polymer backbone. The other four peaks (δ 14.1, 22.9, 28.0, and 33.6 ppm) are assigned to the carbon atoms in the side chain (butyl group of hexene). The absence of peaks between 38 and 41 ppm is evidence that hexene−hexene diads are not present in the copolymer

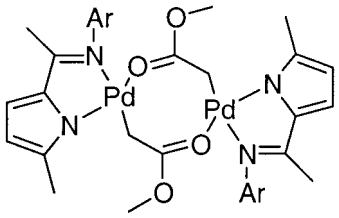
and that the 1-hexene is nearly randomly distributed in the copolymer chains.

Attempts to copolymerize MA with ethylene only produced MA homopolymer. The polymerization reaction was carried out in a glass pressure reactor. The reactor was charged with 12 mL of toluene, 1.0 mL of MA (11.1 mmol), and 2.0 mL of catalyst solution (0.010 M in toluene) via gastight syringe. The ethylene pressure was raised to 100 psig (6.9×10^5 Pa), and the polymerization mixture was stirred in while heated to 50 °C. After 4 h, 0.94 g of polymer was obtained. The ^{1}H and ^{13}C NMR spectra of this material were identical to the spectra of MA homopolymer and indicated that no (or only a negligible amount) ethylene was incorporated in the PMA.

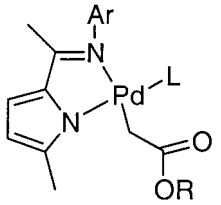
NMR polymerization experiments were performed to gain a clear insight into the MA polymerizations. Measured amounts of MA were combined with complex **I** in C_6D_6, and the reaction mixtures were kept at room temperature. ^{1}H NMR spectra were recorded after specified times. For three different experiments with MA/Pd ratios of 50:1, 5:1, and 1.5:1 ([**I**] ca. 0.014 M), the conversions of MA over a period of 20 h were 78%, 52%, and 23%, respectively. The conversions after an additional 24 h were increased to 91%, 62%, and 35%, respectively. Three major points can be derived from these studies. First, all of the initiator is not activated. Second, the conversion of monomer was higher at relatively higher MA/Pd ratios. This is consistent with a radical mechanism in which less bimolecular termination occurs at high monomer concentration. Finally, although insertion of olefins into Pd−C bonds has been observed in many systems,[20] no evidence from ^{1}H NMR spectroscopy was uncovered that supports the insertion of MA into the Pd−Me bond in these studies. In fact, as evidenced by ^{1}H NMR spectroscopy, there was no significant change observed for complex **I**. The Pd−C is not, however, inert toward all insertion chemistry—it readily inserts carbon monoxide to form the metal acyl derivative.[21]

Our attempts to directly observe radicals using ESR spectroscopy were unfortunately less than definitive. A weak radical signal could be detected when complex **I** was heated at 50 °C in the presence of MA, demonstrating the presence of radicals, but it lacked the resolution necessary for full structural characterization. This somewhat ambiguous result is not unexpected for systems producing transient rather than persistent radicals, and time-resolved ESR techniques (unavailable to the authors at this time) would probably prove more fruitful.

Possible mechanisms of polymerization of acrylates include pseudo-anionic routes that propagate through a metal enolate intermediate.[22] This possibility was also examined. Brookhart and co-workers have demonstrated that a palladium enolate is an intermediate in the coordination−insertion copolymerization of MA and ethylene.[10] The reaction of the cationic palladium alkyl complex with MA at −80 °C produces a palladium enolate, which isomerizes to a five- or six-membered ring chelate upon increasing the temperature. Four palladium enolates **IV**−**VII** have been successfully prepared using ligand **1**. In contrast to the instability of cationic palladium enolates, we have found the neutral palladium enolates to be very stable at temperatures up to 50 °C. Attempts at MA polymerizations have been performed using these neutral palladium enolates as initiators, but surprisingly, none of them showed activity. The insertion of MA into the Pd−CH_2COOR moiety was not observed in NMR experiments. It thus appears that enolate complexes are not intermediates in these polymerizations, making the possibility of a true coordination mechanism even more remote.



IV
Ar = 2,6-i$Pr_2C_6H_3$



V: R = Me, L = Ph_3P
VI: R = t-Bu, L = Ph_3P
VIII: R = t-Bu, L = THF

The combination of the above results supports a free-radical mechanism rather than the anticipated metal-mediated process for polymerization of MA initiated by complexes **I**−**III**. Like complexes **I**−**III**, $(PMePh_2)_2$-$PdMe_2$ and (COD)PdMeCl/R_3P also are neutral palladium complexes containing a Pd−Me bond that can initiate MA homopolymerizations, although the coordination mechanism have been assumed for the two latter systems. The fact that essentially identical atactic PMA is produced from all of these complexes demonstrates a lack of sensitivity to the ligands on the metal and suggests that a true free radical is the intermediate. Radical polymerizations initiated by transition-metal complexes are not rare. Late-metal complexes, especially iron and cobalt complexes, have already been used to initiate the radical polymerization through the homolysis of a metal−alkyl bond, which can be attributed to the weak metal−alkyl bond in late-metal complexes.[23] In addition, numerous metal-mediated redox systems have also been reported, and extensive studies have been carried out on systems that undergo homolytic cleavage of metal−ligand bonds.[24] With the supportive evidence presented above, we conclude that MA polymerization initiated by neutral palladium complexes proceeds through a radical propagation mechanism.

Conclusions

We have prepared several neutral palladium alkyl derivatives and investigated their use as initiators for both MA homo- and copolymerizations. MA can be polymerized in excellent yield using these complexes (>95%). Likewise, MA and olefins have been successfully copolymerized, and the copolymers produced are generally acrylate-rich. Collectively, all of our mechanistic studies support a radical mechanism for MA

polymerization using neutral palladium complexes. The fact that polymer is also produced in the presence of the phenoxy radical inhibitors, MEHQ and BHT, is attributed to the inefficiency of these inhibitor under these conditions, and therefore, this result cannot be used to exclude the possibility of a radical mechanism. The origin of the initiating radicals from these neutral palladium complexes has yet to be elucidated; however, a possible source is through homolytic cleavage of the Pd−Me bond. Thus, a cautionary note is presented here: neutral palladium(II) complexes appear prone to trace radical reactions that can effectively initiate the polymerization of reactive monomers (acrylates, α-olefins, etc.), and extraordinary measures must be gone to in order to eliminate this possibility.

Experimental Section

General Consideration. All manipulations of air- and/or water-sensitive compounds were performed using standard Schlenk techniques. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a GE-300 or Varian Gemini-300 spectrometer (300 MHz for ^{1}H). Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane. The ^{31}P NMR spectra were referenced to external H_3PO_4. Infrared spectra were recorded on a Jasco FT/IR-410 series Fourier transform infrared spectrometer. Elemental analysis was performed by Atlantic Microlab, Inc. GPC analysis of the molecular weight of polymers was performed on a Jasco system comprised a PU-1580 intelligent HPLC pump, a RI-1530 intelligent refractive index detector, and a Borwin-GPC control system. Two PL-Gel mixed columns were used for analysis with HPLC grade chloroform at a flow rate of 1.0 mL/min. The molecular weight was calibrated with polystyrene standards. DSC scans were ran on a TA Instruments DSC2920 modulated differential scanning calorimeter at a rate of 10 °C /min.

Materials. Anhydrous benzene, toluene, tetrahydrofuran, and methylene chloride were passed through columns packed with Q5 catalysts and molecular sieves prior to use. Benzene-d_6 was dried over CaH_2, vacuum-transferred, degassed by repeated freeze−pump−thaw cycles, and stored over 4 Å molecular sieves. Chloroform-*d* was dried over 4 Å molecular sieves. Methyl acrylate, 1-hexene, and norbornene were dried over CaH_2, vacuum-transferred, and degassed by repeated freeze−pump−thaw cycles. Polymer grade ethylene was purchased form National Welders Supply Co. and used for both polymerizations and NMR experiments without further purification. (COD)PdMeCl[25] and 2-acetyl-5-methyl-pyrrole[26] were prepared according to published procedures. Complexes **IV**−**VII** were synthesized through the reaction of ligand **1**, Na_2PdCl_4, and lithium enolates. A paper describing the preparation and crystal structures of these complexes will be published elsewhere.[27] Unless otherwise noted, all other compounds were purchased from Aldrich Chemical Co. and used as received.

Synthesis of Ligand 1. $TiCl_4$ (1.47 mL, 13.3 mmol) in 20 mL of toluene was added dropwise to a solution of 2,6-diisopropylaniline (10 mL, 54 mmol) in 50 mL of toluene. The resulting mixture was stirred at 90 °C for 30 min followed by the addition of 1.65 g (13.3 mmol) of 2-acetyl-5-methylpyrrole. The reaction mixture was stirred overnight, poured into dilute Na_2CO_3 solution, and extracted with methylene chloride. The organic phase was dried over Na_2SO_4 and evaporated in vacuo. The residue was dissolved in ether and treated with concentrated hydrochloride to at 0 °C. Subsequently, the white precipitate was removed by filtration. The filtrate was washed with dilute Na_2CO_3 solution, dried over anhydrous Na_2SO_4, and evaporated. The crude product was recrystallized from pentane to yield **1** as bright yellow crystals. Yield, 2.42 g (75%). ^{1}H NMR ($CDCl_3$): δ 9.5−8.5 (br 1 H, N-*H*), 7.14−7.06 (m, 3 H, ph-*H*), 6.54 (d, 1 H, pyrrole-*H*), 5.98 (d, 1 H, pyrrole-*H*), 2.81 (m, 2 H, *i*Pr−C*H*), 2.36 (s, 3 H, pyrrole-CH_3), 1.93 (s, 3 H, imine-CH_3), 1.12 (dd, 12 H, *i*Pr−CH_3). ^{13}C NMR ($CDCl_3$): δ 157.1 (imine C), 146.0, 137.4, 132.2, 131.4, 123.5, 123.0, 112.5, 108.2 (pyrrole, ph-C), 28.1 (*i*Pr-*C*H), 23.6, 23.3 (*i*Pr-*C*H_3), 16.9, 13.2 (pyrrole- and imine-*C*H_3). IR (KBr): 3427.1 (s, N−H), 2960.0 (s), 2864.7 (m), 1605.5 (vs, imine C=N), 1495.5 (s), 1436.7 (m), 1364,4 (m), 1319.8 (m), 1221.2 (s), 1189.1 (m), 1044.5 (s), and 772.3 (vs) cm^{-1}. mp 107−9 °C. Anal. Calcd for $C_{19}H_{26}N_2$: C, 80.80; H, 9.28; N, 9.92. Found: C, 80.52; H, 9.28; N, 9.95.

Synthesis of Complex I. A solution of ligand **1** (0.282 g, 1.0 mmol) in THF (20 mL) was added to sodium hydride (50 mg, 2.0 mmol). The resulting mixture was stirred at room temperature for 30 min, filtered, and evaporated. The solid residue was dissolved in 20 mL of benzene to form a clear yellow solution. The solution was transferred by cannula to a Schlenk tube containing 0.265 g of (COD)PdMeCl (1.0 mmol) and 0.262 g of PPh_3 (1.0 mmol). The resulting mixture was stirred at room temperature overnight and filtered. Removal of all volatiles in vacuo gave the crude product as a yellow solid. Recrystallization from benzene/pentane afforded 0.550 g (83% yield) of **I**. ^{1}H NMR (C_6D_6): δ 7.90−7.15 (m, 9 H, ph-*H*), 7.11 (d, 1 H, J_{HH} = 3.7, pyrrole-*H*), 7.00−6.90 (m, 9 H, ph-*H*), 6.33 (d, 1 H, J_{HH} = 3.7, pyrrole-*H*), 3.65 (m, 2 H, *i*Pr−C*H*), 2.02 (s, 3 H, pyrrole-CH_3), 1.49 (s, 3 H, imine-CH_3), 1.38 (d, 6 H, J_{HH} = 6.6, *i*Pr−CH_3), 1.18 (d, 6 H, J_{HH} = 7.3, *i*Pr−CH_3), 0.09 (d, 3 H, J_{PH} = 4.4, Pd−CH_3). ^{13}C NMR (C_6D_6): δ 169.5 (imine C), 147.9, 144.0, 142.7, 142.0, 135.8 (d, J_{CP} = 12.9), 134.1, 133.8, 130.8, 126.4, 124.0, 119.5, 112.8 (pyrrole- and ph-C), 28.7 (*i*Pr-*C*H). 24.5, 24.1 (*i*Pr-*C*H_3), 18.4, 18.2 (d, J_{CP} = 3.7, pyrrole- and imine-*C*H_3), 10.8 (d, J_{CP} = 9.7, Pd-*C*H_3). ^{31}P NMR (C_6D_6): δ 41.6 (s). IR (KBr): 2960.9 (s), 1555.1 (vs, imine C=N), 1476.0 (s), 1435.5 (s), 1297.1 (s), 1095.1 (s), 1044.8 (s), 744.4 (s), and 695.0 (s) cm^{-1}. mp 207−8 °C. Anal. Calcd for $C_{38}H_{43}N_2PPd$: C, 68.62; H, 6.52; N, 4.21. Found: C, 68.67; H, 6.36; N, 4.00.

The product is air stable in solid state but decomposes in solution upon longer standing, resulting in Pd(0).

Synthesis of Complex II. The reaction was carried out according to the same procedure as for **I**, except that trimethylphosphine was used instead of triphenylphosphine. Yield 78%. ^{1}H NMR (C_6D_6): δ 7.10−6.96 (m, 4 H, pyrrole- and ph-*H*), 6.40 (m, 1 H, pyrrole-*H*), 3.26 (m, 2 H, *i*Pr−C*H*), 2.66 (s, 3 H, pyrrole-CH_3), 1.81 (s, 3 H, imine-CH_3), 1.10 (d, 6 H, J_{HH} = 6.6, *i*Pr−CH_3), 1.06 (d, 3 H, Pd−CH_3), 0.96 (d, 6 H, J_{HH} = 6.6, *i*Pr−CH_3), 0.55 (d, 9 H, J_{PH} = 9.6, P−CH_3). ^{13}C NMR (C_6D_6): δ 167.7 (imine C), 148.7, 148.1, 142.7, 141.7, 126.0, 124.3, 117.8, 113.3 (pyrrole- and ph-C), 28.4 (*i*Pr-*C*H). 24.0, 23.8 (*i*Pr-*C*H_3), 18.0, 17.3 (pyrrole- and imine-*C*H_3), 14.5 (d, J_{CP} = 31.8, P-*C*H_3), −4.4 (d, J_{CP} = 13.2, Pd-*C*H_3). ^{31}P NMR (C_6D_6): δ −10.7 (s). IR (KBr): 2959.2 (s), 2904.8 (m), 2867.6 (m), 1556.8 (vs, imine C=N), 1472.4 (s), 1435.5 (m), 1379.8 (m), 1360.8 (m), 1297.9 (vs), 1199.3 (m), 1180.5 (m), 1051.0 (vs), 963.5 (s), 942.1 (s), 775.7 (s), 742.2 (s), and 736.9 (s) cm^{-1}. mp 172−4 °C Anal. Calcd for $C_{23}H_{37}N_2PPd$: C, 57.68; H, 7.79; N, 5.85. Found: C, 57.74; H, 7.80; N, 5.77.

Synthesis of Complex III. The reaction was carried out according to the same procedure as for **I**, except that pyridine (5 equiv) was used instead of triphenylphosphine. Yield 77%. ^{1}H NMR (C_6D_6): δ 8.33 (dd, 2 H, pyridine-H^1), 7.15−7.12 (m, 3 H, ph-*H*), 7.00 (d, 1 H, J_{HH} = 3.7, pyrrole-*H*), 6.50 (t, 1H, pyridine-H^3), 6.36 (d, 1 H, J_{HH} = 3.7, pyrrole-*H*), 6.11 (m, 2 H, pyridine-H^2), 3.69 (m, 2 H, *i*Pr−C*H*), 1.88 (s, 3 H, pyrrole-CH_3), 1.55 (s, 3 H imine-CH_3), 1.48 (d, 6 H, J_{HH} = 7.3, *i*Pr−CH_3), 1.11 (d, 6 H, J_{HH} = 6.6, *i*Pr−CH_3), 0.12 (s, 3 H, Pd−CH_3). ^{13}C NMR (C_6D_6): δ 169.9 (imine C), 153.4, 145.7, 144.5, 142.7, 140.4, 136.7, 126.7, 125.1, 124.0, 118.3, 111.8 (aromatic-C), 28.5 (*i*Pr-*C*H). 24.5, 24.2 (*i*Pr-*C*H_3), 17.6, 15.7 (pyrrole- and imine-*C*H_3), 3.2 (Pd-*C*H_3). IR (KBr): 2964.2 (s), 2924.3 (m), 2870.7 (m), 1545.7 (vs, imine C=N), 1472.6 (s), 1448.3 (s), 1437.2 (s), 1382.0 (m), 1361.7 (m), 1306.8 (s), 1046.0 (vs), 777.2 (m), 758.6 (m), and 740.5 (m) cm^{-1}. mp 169 °C (dec). Anal. Calcd for $C_{25}H_{33}N_3Pd$: C, 62.30; H, 6.90; N, 8.72. Found: C, 61.99; H, 6.84; N, 8.61.

Reaction of Complex I with Trimethylphosphine. 13.3 mg of complex **I** (0.020 mmol) was dissolved in 0.70 mL of C_6D_6 in an NMR tube. PMe_3 (0.020 mL, 1.0 M in toluene) was added

to the NMR tube via gastight syringe. The tube was capped with a septum, wrapped with Parafilm, and kept at ambient temperature for 2 h. Then ^{1}H and ^{31}P NMR spectra were acquired. ^{31}P NMR spectrum consists of two peaks (δ −4.3 and −10.7), which are assigned to the free PPh_3 and coordinated PMe_3. ^{1}H NMR spectrum revealed that the doublet for Pd−CH_3 in complex **I** completely disappeared.

Reaction of Complex III with Triphenylphosphine. Complex **III** (9.6 mg, 0.020 mmol) and PPh_3 (5.2 mg, 0.020 mmol) were dissolved in 0.70 mL of C_6D_6 in an NMR tube. The tube was shaken briefly to dissolve the solid and kept at ambient temperature for 18 h. Then ^{1}H and ^{31}P NMR spectra were acquired. ^{31}P NMR spectrum displays only one peak at δ 41.6, which is the same as the phosphine signal of complex **I**. ^{1}H NMR spectrum exhibits signals of free pyridine and the Pd−CH_3 in complex **I**.

Unsuccessful Ethylene Homopolymerization Using Complexes I−III. The ethylene polymerizations were carried out in a 3 oz. glass pressure reactor equipped with a magnetic stirring bar. The reactor was repeatedly evacuated and refilled with nitrogen and finally filled with ethylene gas (ambient pressure). Toluene (13 mL) and the palladium complex (2.0 mL, 0.010 M in toluene) were added to the reactor via a gastight syringe. The ethylene pressure was increased to 100 psig, and constant pressure was applied by continuously feeding the ethylene gas. The reactor was vigorously stirred for 4 h in a 25.0 °C water bath. After the gas was vented, the reaction mixture was poured into 50 mL of methanol to precipitate polymer. Unfortunately, no polymer was obtained.

The polymerization reactions have also been tried in CH_2Cl_2 or at elevated temperature (50 °C), but no polymer was produced, either.

Unsuccessful Ethylene Homopolymerization Using Complex I/Ni(COD)$_2$. A 3 oz. glass pressure reactor was charged with toluene (11 mL), complex **I** (2.0 mL, 0.010 M in toluene), and $Ni(COD)_2$ (2.0 mL, 0.020 M in toluene) via a gastight syringe. The polymerization reaction was carried out according to the same procedure as above. But no polymer was obtained. Similarly, no polymer was obtained using $B(C_6F_5)_3$ instead of $Ni(COD)_2$ as phosphine scavenger.

NMR Study of Ethylene Polymerization with Complex I. 6.7 mg of complex **I** (0.010 mmol) was dissolved in 0.70 mL of C_6D_6 in an NMR tube. The tube was cooled in liquid nitrogen, evacuated, and refilled with ethylene gas. After warming to ambient temperature, the tube was kept under the ethylene atmosphere (20 psig) for 24 h. Then ^{1}H NMR spectrum was acquired. The ^{1}H NMR spectrum exhibited no any new peak except of the signals of ethylene monomer and complex **I**.

Unsuccessful 1-Hexene Homopolymerization Using Complex I. A 50 mL Schlenk tube was charged with 13.3 mg of complex **I** (0.020 mmol), 5.0 mL of CH_2Cl_2, and 5.0 mL of 1-hexene. The mixture was stirred at ambient temperature for 18 h. A fraction of the reaction mixture (ca. 10 μL) was removed and analyzed by ^{1}H NMR spectroscopy. The rest of the reaction mixture was poured into 50 mL of methanol to precipitate polymer. Unfortunately, no polymer was obtained. The ^{1}H NMR spectrum revealed that 1-hexene was not dimerized or isomerized.

General Procedure for Polymerization of MA by Complexes I −III. A 50 mL Schlenk tube was charged with the appropriate amount of palladium complex, 5.0 mL of CH_2Cl_2, and 2.0 mL of MA (22.2 mmol). The Schlenk tube was sealed and placed in a 50 °C water bath. After the reaction mixture was stirred for the specified reaction time, methanol was then added to precipitate the polymer. The polymer was recovered by filtration and dried under vacuum at 60 °C for 24 h. The results are summarized in Table 1.

General Procedure for MA Polymerization in the Presence of Free-Radical Inhibitor. A 50 mL Schlenk tube was charged with the appropriate amount of palladium complex and free-radical inhibitor. To this mixture, 5.0 mL of CH_2Cl_2 and MA (2.0 mL, 22 mmol) were added, and the Schlenk tube was sealed and placed in a 50 °C heating bath. After the reaction mixture was stirred for the specified reaction time, methanol was then added to precipitate the polymer. The polymer was recovered by filtration and dried under vacuum at 60 °C for 24 h.

MA Polymerization Using Complex I as Initiator and MEHQ as Inhibitor. The reaction was conducted according to the above general procedure for 1 h using complex **I** (0.010 mmol) and MEHQ (0.050 mmol). 0.670 g of polymer was obtained.

MA Polymerization Using Complex I as Initiator and Galvinoxyl as Inhibitor. The reaction was conducted according to the above general procedure for 1 h using complex **I** (0.010 mmol) and galvinoxyl (0.050 mmol). No polymer was obtained.

MA Polymerization Using (COD)PdClMe/PPh$_3$ as Initiator and MEHQ as Inhibitor. The reaction was conducted according to the above general procedure for 18 h using (COD)-$PdClMe/PPh_3$ (0.020 mmol, Pd/PPh_3 = 1:1) and MEHQ (0.100 mmol). 1.53 g of polymer was obtained.

MA Polymerization Using Complex I as Initiator and Galvinoxyl as Inhibitor. The reaction was conducted according to the above general procedure for 18 h using (COD)-$PdClMe/PPh_3$ (0.020 mmol, Pd/PPh_3 = 1:1) and galvinoxyl (0.100 mmol). No polymer was obtained.

General Procedure for Copolymerization of MA and 1-Hexene by Complex I. A 50 mL Schlenk tube was charged with complex **I** (2.0 mL, 0.010 M in toluene), MA, and 1-hexene. The Schlenk tube was sealed and placed in a 50 °C water bath. After the reaction mixture was stirred for the specified reaction time, methanol was then added to precipitate the polymer. The polymer was recovered by filtration and dried under vacuum at 60 °C for 24 h. The results are summarized in Table 2.

General Procedure for Copolymerization of MA and 1-Hexene with Benzyl Peroxide as Free-Radical Initiator. A 50 mL Schlenk tube was charged with benzyl peroxide (2.0 mL, 0.010 M in toluene), MA, and 1-hexene. The Schlenk tube was sealed and placed in a 50 °C water bath. After the reaction mixture was stirred for the specified reaction time, methanol was then added to precipitate the polymer. The polymer was recovered by filtration and dried under vacuum at 60 °C for 24 h. The results are summarized in Table 2.

Copolymerization of MA and Norbornene by Complex I. A 50 mL Schlenk tube was charged with complex **I** (2.0 mL, 0.010 M in toluene), 1.0 mL of MA (11.1 mmol), and 1.0 g of norbornene (10.6 mmol, wt % = 50% in toluene). The Schlenk tube was sealed and placed in a 50 °C water bath. The reaction mixture was stirred for 2 h. Methanol was then added to precipitate the polymer. 0.075 g of polymer was obtained. This material shows a glass transition temperature of 31 °C.

Copolymerization of MA and Ethylene Using Complex I. The polymerization reaction was carried out in a 3 oz. glass pressure reactor equipped with a magnetic stirring bar. The reactor was repeatedly evacuated and refilled with nitrogen and finally filled with ethylene of ambient pressure. Toluene (12 mL), MA (1.0 mL, 11.1 mmol), and the solution of complex **I** (2.0 mL, 0.010 M in toluene) were added to the reactor via a gastight syringe. The ethylene pressure was increased to 100 psig, and constant pressure was applied by continuously feeding the ethylene gas. The reactor was vigorously stirred for 4 h in a 50 °C water bath. After the gas was vented, methanol was then added to precipitate the polymer. 0.94 g of polymer was obtained. This material shows the same glass transition temperature (T_g = 10 °C) and ^{1}H NMR spectrum as PMA.

General Procedure for NMR Experiments. A NMR tube was charged with 0.010 mmol of palladium complex under argon atmosphere and capped with a septum. C_6D_6 (0.7 mL) and the appropriate amount of monomer were then added to the NMR tube via a gastight syringe. The tube was shaken briefly to make a homogeneous solution and kept at room temperature. Then ^{1}H NMR spectra were acquired after the specified time. The conversion of methyl acrylate was estimated by the ratio of methoxyl groups of monomer and polymer in ^{1}H NMR spectra.

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