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Mechanistic Studies of Alkene/CO Polymerization with Palladium Complexes Promoted by $B(C_6F_5)_3$

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The reaction of $Pd(dppp)(OAc)_2$ [dppp = 1,3-bis(diphenylphosphino)propane] with $B(C_6F_5)_3$ in situ gives an efficient catalyst for alkene/CO polymerization in aprotic media. The borane is consumed during the polymerization, and its fluoroaryl groups are incorporated into the polymer chain ends. In the absence of the monomers the catalyst components react to give palladium(II)−pentafluoroaryl complexes formulated as $Pd(dppp)(C_6F_5)\{[B(C_6F_5)_3]_yOH\}$ (y = 1, **3a**; y = 2, **3b**). Complex **3a** can be isolated, albeit as an impure solid, and is itself a catalyst for the reaction. In light of these results a novel chain initiation process for the polymerization is proposed, involving insertion of monomers into a fluoroarylpalladium complex formed by aryl transfer from the borane to a palladium(II) complex. This facile initiation step, combined with the catalyst stability engendered by the presence of strong Brønsted acids, explains the effectiveness of this catalyst system in aprotic media.

Introduction

The synthesis of alternating copolymers of carbon monoxide and alkenes, particularly ethene, using palladium-based catalysts is of considerable industrial and academic interest.[1] Industrial involvement in this area stems fundamentally from the possibility of manufacturing high-performance polymers in one step from inexpensive raw materials, with recent impetus coming from the discovery by Drent of high-rate catalysts incorporating chelating phosphine ligands.[2] Since this discovery, a wide range of alkene/CO copolymers have been prepared, and the mechanism of the reaction has been probed extensively. Early mechanistic work by Sen et al.,[3] predating the discovery of high-rate catalysts, established that the active catalytic species are monocationic palladium complexes and that polymer chain growth proceeds by alternating migratory insertion reactions of acyl and alkyl complexes. Mechanistic detail regarding polymer chain initiation and termination reactions was added later.[4] Brookhart and co-workers[5] have further defined the mechanism, studying in detail the individual steps of the polymerization and establishing an accurate model of the alternating chain growth process, the conclusions of the latter work being supported by density functional calculations.[6] A generalized representation of the active species is shown in Figure 1.

We report here a study of palladium-based alkene/CO polymerization catalysts incorporating the Lewis acidic borane $B(C_6F_5)_3$,[7] where the presence of the borane results in novel catalytic behavior.[8] Our investigations of these catalysts have revealed that the aryl groups from the borane are incorporated into the end groups of the polymers produced and that the borane is consumed during the polymerization. We also report the results of mechanistic studies of this catalytic system, which reveal that the use of the borane promoter results in a novel chain initiation process involving aryl transfer from the borane to palladium. These results largely explain the wide utility of this borane in the catalysis of alkene/CO copolymerization. In addition, the well-defined aryl transfer step has broader relevance to the large body of polymerizations that use a fluoroaryl boron component.[9]

Results and Discussion

1. Catalytic Reactions with $B(C_6F_5)_3$. Initial studies showed that the in situ reaction of $Pd(dppp)(OAc)_2$ (**1**) and $B(C_6F_5)_3$ in dichloromethane gave a highly active catalyst for alkene/CO polymerization. A typical cumulative gas uptake profile for an alkene/CO polymeriza-

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† E-mail: cooleyna@bp.com.

[1] For some leading references see: (a) Sen, A. *CHEMTECH* **1986**, 48. (b) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663. (c) Gray, A. *Chem. Br.* **1998,** *March*, 44, and references therein.

[2] Drent, E. Eur. Pat. Appl. 121,965, 1984; *Chem Abstr.* **1985**, *102*, 46423.

[3] (a) Sen, A.; Lai, T.-W., *J. Am. Chem. Soc.* **1982**, *104*, 3520. (b) Lai, T.-W.; Sen, A., *Organometallics* **1984,** *3,* 866.

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[6] Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 7337.

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[8] For the first diclosure of alkene/CO copolymerization promoted by $B(C_6F_5)_3$ see: Cooley, N. A.; Kirk, A. P. Eur. Pat. Appl. 619335; *Chem. Abstr.* **1995**, *112*, 550920.

[9] Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345, and references therein.

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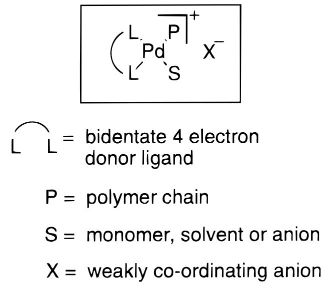

Figure 1. Generalized active species for alkene/CO copolymerization.

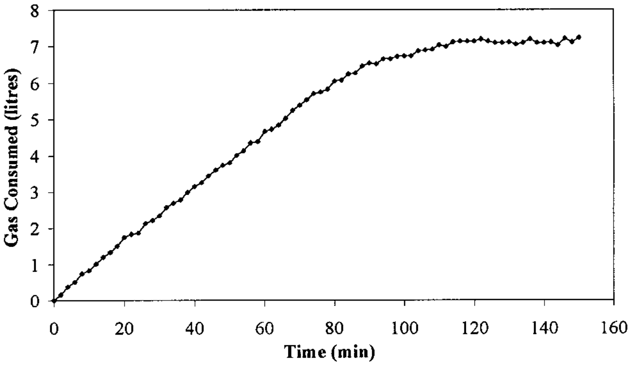

Figure 2. Cumulative gas uptake profile for a typical ethene/propene/CO terpolymerization reaction catalyzed by **1**/B(C_6F_5)$_3$.

tion with the catalyst formed from **1** and B(C_6F_5)$_3$, run under constant pressure conditions, shows a steady rate of reaction followed by a precipitous falloff in gas uptake later in the reaction (Figure 2).

Reaction rates for **1**/B(C_6F_5)$_3$ are typically 10 kg g Pd^{-1} h^{-1} for the production of ethene/propene/CO terpolymers with approximately 6 propene monomers per 100 monomers and number average molecular weights (M_n) of approximately 20 000 (ref 10). Catalyst longevity varies, but in general a high borane concentration leads to longer catalyst lifetime. The catalyst can be reactivated by addition of more B(C_6F_5)$_3$, although the catalyst does not usually reattain the rates seen initially. Addition of solutions of **1** to deactivated catalyst solutions does not result in further polymerization. Therefore, the observed decrease in activity is attributable primarily to borane depletion. However, some catalyst degradation is also evidently occurring, as adding another charge of borane does not give the same high rate obtained initially.

The polymers produced using this catalyst have molecular weight distributions in the expected region for single-site catalysts with polydispersities (M_w/M_n) generally between 2 and 3. Propene incorporation is random as far as can be determined by NMR spectroscopy and is predominantly 1,2-, although some 1,3-incorporation is observed, as is the case for other catalysts.[4a] The end groups of the polymers however differ significantly from those seen previously. ^{19}F and ^{13}C NMR spectra of a representative polymerization show the presence of alkyl, **a**, alkenyl, **b**, and pentafluorophenyl end groups. The pentafluorophenyl end groups can be differentiated into the substructures **c**, **d**, and **e** (Figure 3).

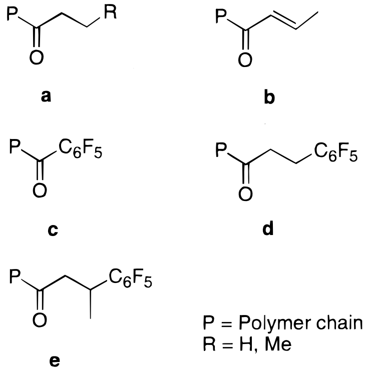

Figure 3. Polymer end groups observed in a typical ethene/propene/CO terpolymerization reaction catalyzed by **1**/B(C_6F_5)$_3$.

Under typical reaction conditions alkyl end groups predominate, and from ^{1}H and ^{13}C NMR spectra it was determined that these outnumber alkenyl groups in the ratio 4:1. A combination of polymer analyses (M_n from GPC and fluorine microanalysis) leads to the estimate that, under typical reaction conditions, pentafluorophenyl end groups constitute about 15−25% of the total end groups. The relative ratio of these pentafluorophenyl end groups can be more accurately determined by ^{19}F NMR (see Experimental Section), and under representative conditions substructures **c**, **d**, and **e** were found to constitute 5, 76, and 19%, respectively, of the total pentafluorophenyl end groups. Fluorine microanalysis and ^{19}F NMR spectroscopy of a complete reaction mixture showed that at the end of the reaction 47% of the pentafluorophenyl groups were present as polymer end groups; the remainder had formed pentafluorobenzene. The consumption of the borane accords with the experimental observation that addition of B(C_6F_5)$_3$ will reactivate the catalyst (see above).

The above end group characterization shows that incorporation of pentafluorophenyl groups is a significant pathway in alkene/CO polymerization catalysis by **1**/B(C_6F_5)$_3$. Furthermore, the observation that these catalysts can be *reinitiated* by the addition of further B(C_6F_5)$_3$ indicates strongly that this reagent is involved in catalyst initiation.

2. Reaction of 1 with B(C_6F_5)$_3$. This reaction was studied by NMR spectroscopy in order to gain insight into the formation of the active species. After initial experiments gave complex mixtures of products, a series of experiments was conducted in which water and borane concentrations were varied systematically. These experiments comprised two parallel sets of reactions, one set in essentially dry CD_2Cl_2, used as received, and one in CD_2Cl_2, to which water had been added. In each set 0.5, 1, 2, and 5 molar equiv of B(C_6F_5)$_3$ relative to **1** were added. NMR spectra across a range of nuclei were then recorded; the ^{31}P{^{1}H} NMR spectra are shown in Figure 4.

The product formed on adding 0.5 molar equiv of B(C_6F_5)$_3$ to **1** is the same both in the absence and presence of added water. On the basis of its NMR spectra this complex is formulated as Pd(dppp)(C_6F_5)(OAc), **2** (see Experimental Section). Addition of 1 molar

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(10) Based on the assumption that Mn as determined by gel permeation chromatography of a polymer solution in hexafluoro-2-propanol relative to a poly(methyl methacrylate) standard is approximately 3 times the absolute value.

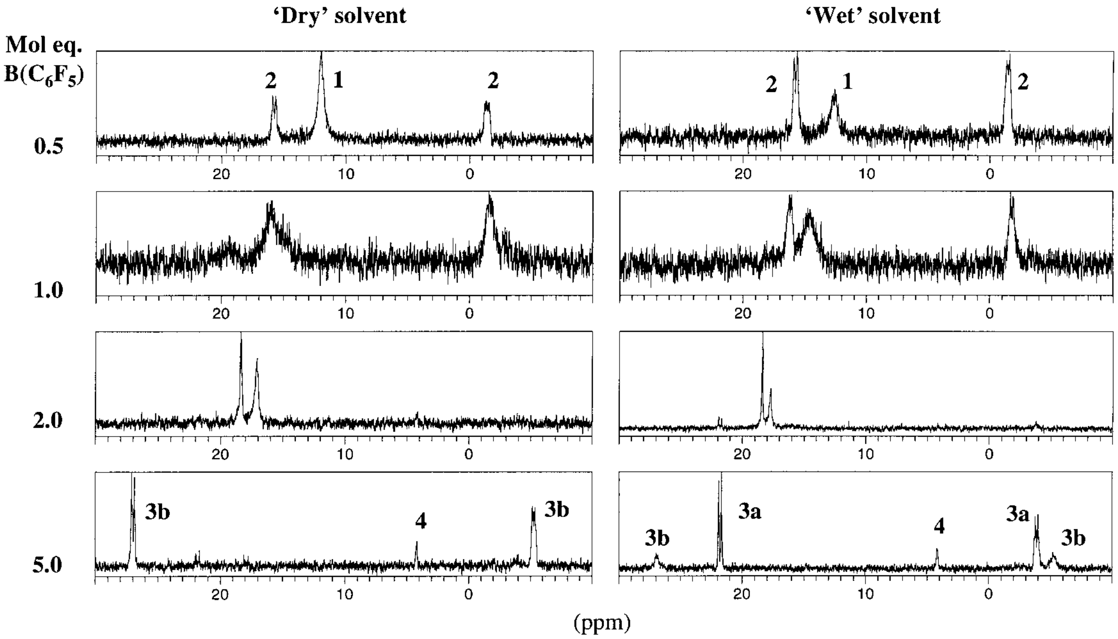

Figure 4. $^{31}P\{^1H\}$ NMR spectra from reaction of **1** with 0.5, 1, 2, and 5 equiv of $B(C_6F_5)_3$ in both wet and dry CD_2Cl_2.

equiv of $B(C_6F_5)_3$ to **1** also results in the formation of **2**, and additionally, some precipitation from solution occurs. The concurrent formation of pentafluorobenzene in our experiments at this borane concentration both with and without added water indicates that adventitious water was present in all cases. All of our reactions therefore contain strong Brønsted acids of the form $B(C_6F_5)_3{\cdot}xH_2O$, formed from the reaction of $B(C_6F_5)_3$ with adventitious H_2O in the dichloromethane solvent.[11] Addition of 2 molar equiv of $B(C_6F_5)_3$ to **1** again gives pentafluorobenzene in significant quantities. Only small amounts of species with $Pd{-}C_6F_5$ groups were detected however, and on the basis of the NMR spectra, it is likely that dicationic species of the general formula $[Pd(dppp)L_2]^{2+}2A^-$ are the major products. The likely path for the formation of such species is the protonolysis of the initially formed $Pd{-}C_6F_5$ complexes by strong Brønsted acids, formed in the presence of water, to give pentafluorobenzene. It should be noted that the borane does not react significantly with water to give pentafluorobenzene in the absence of the palladium complex under these conditions.

Addition of 5 molar equiv of $B(C_6F_5)_3$ to **1** results in the immediate formation of two similar complexes, **3a** and **3b**. In our experiments complex **3a** predominates in the presence of added water, and only **3b** is formed when only adventitious water was present. In addition to **3a** and **3b**, a small amount of $Pd(dppp)(C_6F_5)_2$ (**4**) was also obtained. Complex **3a** was readily converted to **3b** in solution by the addition of a further 5 equiv of $B(C_6F_5)_3$. By contrast, our attempts to convert **3b** to **3a** by water addition resulted in a mixture of products. It is clear from the $^{31}P\{^1H\}$ and ^{19}F NMR spectra (see Experimental Section) that both **3a** and **3b** contain the diphosphine and a coordinated C_6F_5 group, leaving the ligand at the fourth coordination site as the major point of difference. Examination of the ^{19}F NMR spectra of a number of solutions of **3a** shows that the complex contains a single $B(C_6F_5)_3$ moiety with resonances at −135.1, −161.5, and −166.8 ppm. Similarly **3b** contains two equivalent $B(C_6F_5)_3$ moieties with ^{19}F NMR signals at −135.1, −160.6, and −166.6 ppm. On the basis of these NMR chemical shifts and the precedent of the ligation of a $B(C_6F_5)_3OH$ moiety in platinum chemistry,[12] we have formulated **3a** as $Pd(dppp)(C_6F_5)[B(C_6F_5)_3\text{-}OH]$. It is therefore likely that the conversion of **3a** to **3b** upon addition of $B(C_6F_5)_3$ is analogous to the recently reported reaction[13] of $B(C_6F_5)_3OH^-$ with $B(C_6F_5)_3$ to give $B(C_6F_5)_3(\mu\text{-}OH)B(C_6F_5)_3^-$, and on this basis we have formulated **3b** as $Pd(dppp)(C_6F_5)[B(C_6F_5)_3(\mu\text{-}OH)B\text{-}(C_6F_5)_3]$. This structure is fully consistent with the NMR data. Complex **3a** can be obtained as an impure solid by precipitation from solution with hexanes (see Experimental Section). Redissolution of this solid in CD_2Cl_2 and treatment with $B(C_6F_5)_3$ again gives **3b**, confirming that **3b** is best formulated as an adduct of **3a**. The above results and structural proposals are summarized in Scheme 1.

3. Relevance of Aryl Transfer Reactions to Catalysis of Alkene/CO Polymerization. The facile transfer of a pentafluorophenyl group from boron to palladium is surprising; compounds such as $B(C_6F_5)_3$ and anions such as $B(C_6F_5)_4^-$ are generally employed in catalysis precisely because of their inertness to reaction with electrophilic metal centers.[9] Aryl transfer from $B(C_6F_5)_3$ has been observed previously, but the reactions were slow.[14] This reaction also has precedent in the transfer of aryl groups from arylboranes to platinum(II), where aryl transfer is believed to be facilitated by bridged intermediates, formed by coordinated water for example.[15] It is also relevant that aryl

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[11] Siedle, A. K.; Lamanna, W. M.; Newmark, R. A., Stevens, J., Richardson, D. E., Ryan, M. *Makromol. Chem., Makromol. Symp.* **1993**, *66*, 215.

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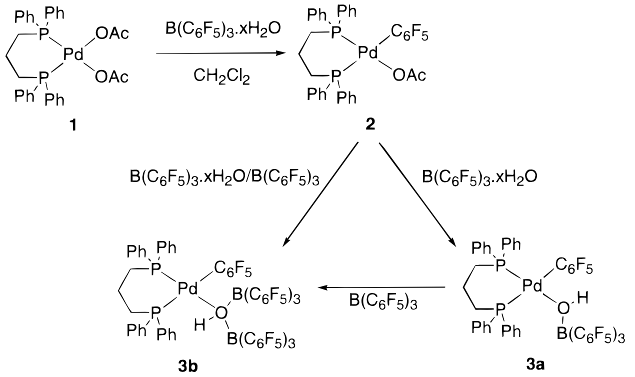
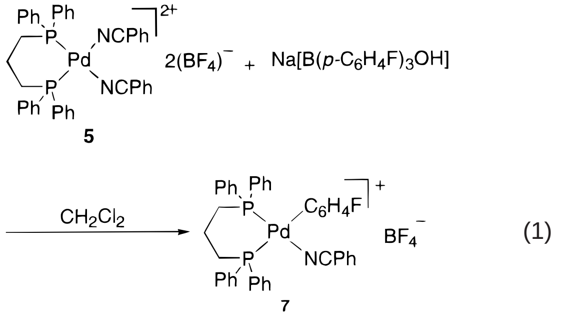
Scheme 1. Proposed Reactions of 1 with $B(C_6F_5)_3$



and alkyl transfer reactions from organoboron reagents are part of the catalytic cycles for many palladium complex-catalyzed cross-coupling reactions.[16] Here again bridged species, particularly those formed via alkoxide complexes, are thought to be important in aiding transfer from boron.[17] To test whether similar intermediates are involved in aryl transfer in this case, the reactions of $[Pd(dppp)(PhCN)_2][BF_4]_2$, **5**, with a variety of organoboron compounds have been studied. The reaction of **5** with $B(C_6F_5)_3$ is facile, even under essentially anhydrous conditions, giving $[Pd(dppp)(PhCN)(C_6F_5)]BF_4$, **6**, identified from its NMR spectra. In contrast a solution of **5** and $B(p\text{-}C_6H_4F)_3$ in dichloromethane, under analogous conditions, is stable with respect to aryl transfer (approximately 4% formation of aryl transfer product after 1 h). However, when a dichloromethane solution of **5** is treated with $Na[B(p\text{-}C_6H_4F)_3OH]$, a rapid reaction occurs to give a mixture comprising mainly (64%) a monocationic arylated product **7** (eq 1).

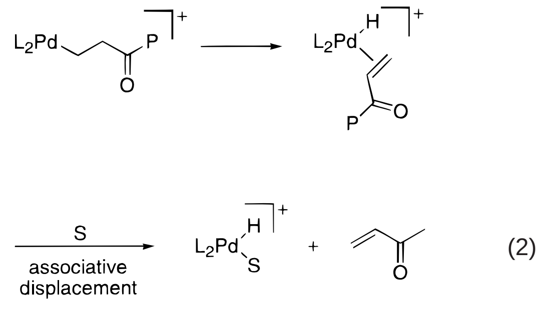


The contrasting reactivity of $B(p\text{-}C_6H_4F)_3$ and $Na[B(p\text{-}C_6H_4F)_3OH]$ with **5** confirms that aryl transfer is facilitated by the presence of groups capable of bridging boron and palladium (eq 1). In addition, it is notable that transfer from $B(C_6F_5)_3$ is more facile than transfer from $B(p\text{-}C_6H_4F)_3$, and this observation lends weight to the idea that the aryl transfer is not a conventional electrophilic aromatic substitution.[18]

The above observations firmly establish the possibility that aryl transfer to a palladium(II) precursor is a step in the catalytic cycle. Furthermore, the presence of water sets up the well-precedented protonolysis of the initially formed arylpalladium(II) complex, and this provides a potential route to pentafluorobenzene,[19] the major byproduct of the alkene/CO polymerization reaction using catalysts containing $B(C_6F_5)_3$.

To further probe the possible intermediacy of the above palladium(II) arylation reaction in alkene/CO copolymerization, further polymerizations were conducted using **3a** as the procatalyst. In the absence of additional $B(C_6F_5)_3$ the reaction gave an initial rate of 4 kg g Pd^{-1} h^{-1} but quickly deactivated. With added $B(C_6F_5)_3$ the polymerization gives an activity similar to the **1**/$B(C_6F_5)_3$ catalyst, cf. 8.5 kg g Pd^{-1} h^{-1} and 10 kg g Pd^{-1} h^{-1}, respectively, and a longer catalytic lifetime. In the absence of additional $B(C_6F_5)_3$ the end group distribution obtained with **3a** is very similar to that obtained with **1**/$B(C_6F_5)_3$, with substructures **c**, **d**, and **e** constituting 9, 77, and 14%, respectively, of the total pentafluorophenyl end groups. These reactions are fully consistent with the proposal that aryl transfer to a palladium(II) complex is the route by which the polymerization is initiated.

4. Formation of Alkyl and Alkenyl End Groups. In the closely related palladium- and nickel-based alkene polymerization catalysts reported by Brookhart and co-workers[20] chain termination results from β-hydride elimination followed by associative ligand substitution of the alkene coordinated polymer chain by the substrate, giving unsaturated polymer end groups. It is likely that a similar chain termination operates in the present case to give an intermediate palladium hydride (eq 2).



S = solvent, anion or monomer, P = polymer chain

As well as producing alkenyl end groups, insertion of ethene into the intermediate hydride species results in a alkyl chain end. Therefore, a β-elimination chain transfer mechanism, operating alone, would produce equal numbers of alkenyl and alkyl polymer end groups. Given that alkyl end groups substantially outnumber

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(15) Siegmann, K.; Pregosin, P. S.; Venanzi, L. M. *Organometallics* **1989**, *8*, 2659.

(16) (a) Littke, A. F.; Gregory, C. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 3387. (b) Old, D. W.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 9722. For selected reviews and monographs, see: (c) Suzuki, A. Acc. *Chem. Res.* **1982**, *15*, 178. (d) Miyaura, N., Yamada, K., Suginome, H. Suzuki, A., *J. Am. Chem. Soc.* **1985**, *107*, 972. (e) Suzuki, A. *Pure Appl. Chem.* **1985**, *57*, 1749. (f) Suzuki, A. *Pure Appl. Chem.* **1991**, *63*, 419. (g) Suzuki, A. *Pure Appl. Chem.* **1994**, *66*, 213. (h) Miyyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(17) Suzuki, A. In *Metal-Catalysed Cross Coupling Reactions*; Diedrich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Chapter 2.

(18) Electron-withdrawing substutents on the aryl groups of the borane would be expected to slow the rate of aryl transfer for a reaction pathway analogous to, for example, the proton-induced cleavage of aryl borates (see ref 15). The opposite substituent dependency is observed in the present case.

(19) Kurosawa, H.; Urabe, A.; Miki, K.; Kasai, N. *Organometallics* **1986**, *5*, 2002.

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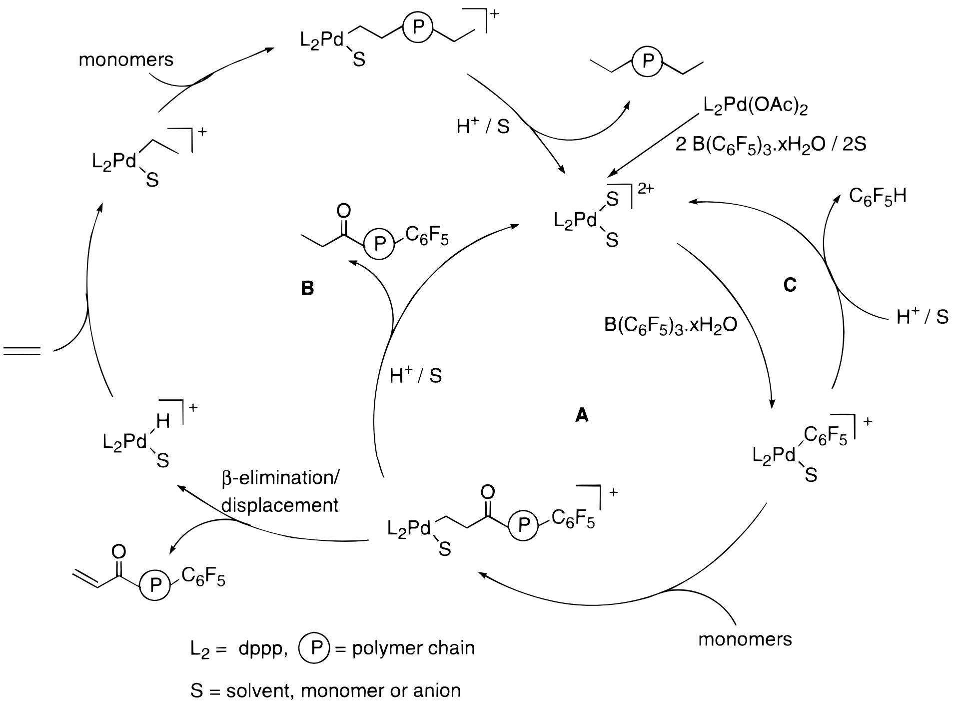
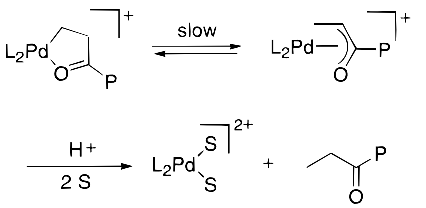
Scheme 2. Proposed Mechanism for Alkene/CO Polymerization with Palladium Complexes Promoted by $B(C_6F_5)_3$



alkenyl end groups, there must be another route to saturate chain ends. It is likely therefore that alkyl end groups are also formed by protonolysis: a well-precedented termination mechanism in alkene/CO polymerization.[21] This seems especially likely given the availability of hydrated $B(C_6F_5)_3$ during catalysis, providing the necessary Brønsted acid. The molecular weight of the polymer is however largely insensitive to the concentration,[22] or even the type, of triarylborane used. This is best explained by protonolysis taking place after a relatively slow isomerization of an alkyl palladium complex into an enolate species (eq 3).[21]



(3)

S = solvent, anion or monomer

P = polymer chain

5. Proposed Mechanism. The above evidence has led to a working hypothesis in which polymerization is initiated by aryl transfer from boron to palladium; this gives a Pd−aryl complex which undergoes migratory insertion of a monomer. Analysis of pentafluorophenyl polymer end groups indicates that an ethene molecule is usually inserted first. Following chain propagation, some termination occurs via *β*-hydrogen elimination/displacement. However, protonolysis is the main termination route, leaving the catalyst ready for reinitiation by aryl transfer. The pentafluorobenzene byproduct results from protonolysis of the palladium aryl intermediates. Thus we have two polymer-producing catalytic cycles (A and B) and a catalytic cycle (C) producing pentafluorobenzene (Scheme 2).

6. Catalysis in the Absence of Boranes. The minor polymer-producing catalytic cycle (B) does not result in the consumption of the promoter, and it would be desirable if the reaction could proceed through this cycle alone in an aprotic diluent. This has been achieved previously with low-activity catalysts under mild conditions.[23] We have employed a number of catalysts in order to achieve this goal, but have not matched the catalytic performance of **1**/ $B(C_6F_5)_3$; the use of **3a** without added $B(C_6F_5)_3$ as a procatalyst, for example, falls into this category. Our best results have come from using **1** in combination with $[B(C_6F_5)_4][(CH_3)_2NH(C_6H_5)]$ in dichloromethane,[23] which forms a mildly active catalyst, prone to deactivation.[24] It is noteworthy that products formed with this system show no evidence for aryl transfer.

Conclusions

In summary, the combination of a facile and efficient means of catalyst initiation combined with increased catalyst stability with respect to reduction[25] afforded by

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[21] Zuideveld, M. A.; Kramer, P. C. J.; Van Leewen, P. W. N. M.; Klusener, P. A. A.; Stil, H. A.; Roobek, C. F. *J Am. Chem. Soc.* **1998**, *120*, 7977.

[22] Initial polymerization rates and intrinsic viscosities (a measure of molecular weight) of the products from ethene/propene/CO polymerizations with **1**/$B(C_6F_5)_3$ and **1**/$B(p\text{-}C_6H_4Cl)_3$ under standard conditions (see Experimental Section) were found to be identical, within experimental error.

[23] See ref 3 for example.

[24] The highest rate reaction we have seen with the system gave an initial polymerization rate of approximately 4000 g g Pd^{-1} h^{-1}, with steady deactivation to a rate of approximately 300 g g Pd^{-1} h^{-1} over a period of 30 min. The conditions were similar to those detailed in the Experimental Section except that $[B(C_6F_5)_4][(CH_3)_2NH(C_6H_5)]$ was used in place of $B(C_6F_5)_3$ and higher concentrations of both catalyst components were employed.

the presence of $B(C_6F_5)_3$ and its hydrates provides a convenient means of generating high-activity alkene/CO polymerization catalysts in aprotic diluents. This adds flexibility to the conditions under which such polymerizations can be conducted, but at the cost of the consumption of the borane promoter.

Integral to this catalysis is the facile initiation by aryl transfer from boron to palladium(II). This is surprising given the strong electron-withdrawing substituents on $B(C_6F_5)_3$ and may be aided by the formation of bridged intermediates which lower the activation barrier to electrophilic aromatic substitution. This result is also more generally important as arylboranes and borates are widely used as cocatalysts, particularly for polymerization catalysis. A wide variety of polymerization-active systems have been reported, many of which are based on late transition metals,[26] and it would be prudent to be aware of possible aryl transfer processes taking place when these catalysts are used in combination with aryl boranes or borates.

Experimental Section

General Considerations. All operations were performed in a dinitrogen-filled Vacuum Atmospheres glovebox or using Schlenk line techniques. Solvents were purified by distillation from an appropriate drying agent: dichloromethane (CaH_2) and *n*-hexane (Na/Ph_2CO). $B(C_6F_5)_3$ was purchased from Boulder Scientific and used without further purification for polymerization experiments and preparative scale reactions. For NMR scale reactions this reagent was sublimed prior to use. Ethene, carbon monoxide, and propene were purchased from Air Products. The starting materials $[Pd(dppp)(OAc)_2]$, **1**, and $[Pd(dppp)(PhCN)_2](BF_4)_2$, **5**, were synthesized by slight modifications of literature procedures for close analogues.[27] Other reagents were obtained from commercial suppliers. ^1H (400 MHz), ^{19}F (376 MHz), and ^{31}P (162 MHz) NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer. NMR spectra of polymer samples were obtained from solutions in hexafluoro-2-propanol/CD_2Cl_2. Polymer molecular weights were determined using a Waters 150CV GPC system with hexafluoro-2-propanol diluent.

Procedure for Ethene/Propene/CO Polymerization Catalyzed by 1/$B(C_6F_5)_3$. Propene (25.7 g, 0.61 mol) and a solution of $B(C_6F_5)_3$ (0.086 g, 0.17 mmol) in CH_2Cl_2 (100 mL) were charged to a 300 mL autoclave. The stirred contents of the autoclave were heated to 70 °C and pressurized to 48 bar G with a 1:1 mixture of carbon monoxide and ethene. A solution of $[Pd(dppp)(OAc)_2]$ (6.0 mg, 0.009 mmol) in dichloromethane (10 mL) was injected into the autoclave, and the pressure was adjusted to 50 bar G. The reaction pressure was maintained during the polymerization by the addition of a 1:1 mixture of carbon monoxide and ethene on demand from ballast vessels of known volume. After 3 h the polymerization was terminated by releasing the pressure and cooling the reaction mixture. The polymer was collected by filtration, washed with acetone, and dried under reduced pressure. The polymer was obtained as a white powder. Yield = 9.30 g. The rate of polymerization was determined by fitting of a first-order curve to the cumulative gas uptake profile (for example, Figure 2). NMR analysis showed the polymer to contain alternating units originating in CO and alkene, with 6.2 per 100 monomers originating in propene. Fluorine microanalysis: 1600 ppm. Palladium microanalysis: 36 ppm. Alkyl and alkenyl chain ends were quantified using ^1H NMR spectroscopy: ethyl ends $\delta = 1.10$ (t, $J_{HH} = 7.6$ Hz, $C\mathit{H}_3CH_2C(O)-$); propyl ends $\delta = 1.58$ (m, $J_{HH} = 7.2$ Hz, $CH_3C\mathit{H}_2CH_2C(O)-$); propenyl ends $\delta = 7.03$ (dq, $J_{HH} = 15.3, 6.8$ Hz, $CH_3C\mathit{H}{=}CHC(O)-$), 1.94 (dd, $J_{HH} = 6.8, 1.5$ Hz, $C\mathit{H}_3CH{=}CHC(O)-$); other signals are obscured by overlap with main-chain resonances. Fluorinated chain ends were quantified using ^{19}F NMR spectroscopy: $C_6F_5C(O)-$ $\delta = -140.4$ (ortho-F), -148.7 (para-F), -160.6 (meta-F); $C_6F_5CH_2CH_2C(O)-$ $\delta = -144.2$ (ortho-F), -157.8 (para-F), -163.2 (meta-F); $C_6F_5CH_2CH(CH_3)C(O)-$ $\delta = -143.6$ (ortho-F), -157.8 (para-F), -163.2 (meta-F).

NMR Scale Reactions of 1 with $B(C_6F_5)_3$ (in Situ Preparation of 2, 3a, and 3b): General Considerations. All manipulations were carried out in a drybox, the NMR tubes used having a Youngs' tap fitting. Experiments in "dry" CD_2Cl_2 used this solvent as received in 10 mL ampules from Aldrich; experiments in "wet" CD_2Cl_2 used a stock solution of the same solvent to which deionized water had been added (1.8 μL of H_2O in 10 mL of CD_2Cl_2). Spectra were initially recorded within 30 min, although later experiments showed that in all cases reactions were essentially complete by the time spectra could be recorded, and no changes were observed in the reaction products even after extended periods (up to 1 week). The mole percent (mol %) of reaction products are given as percentages of the total soluble palladium species as determined by $^{31}P\{^1H\}$ NMR spectroscopy.

Reactions in "Dry" CD_2Cl_2: (i) Reaction of 1 with 0.5 equiv of $B(C_6F_5)_3$. CD_2Cl_2 (1 mL) was added to **1** (6.4 mg, 0.01 mmol) and $B(C_6F_5)_3$ (2.6 mg, 0.005 mmol) in an NMR tube to give a colorless solution. A mixture of unreacted **1** (60 mol %) and **2** (40 mol %) was obtained. **1**: ^1H NMR $\delta = 7.70$ (m, 8H, ArH), 7.43 (m, 4H, ArH), 7.36 (m, 8H, ArH), 2.48 (m, 4H, $-C\mathit{H}_2CH_2C\mathit{H}_2-$), 2.05 (m, 2H, $-CH_2C\mathit{H}_2CH_2-$), 1.26 (s, 6H, $-O(O)CC\mathit{H}_3$); $^{31}P\{^1H\}$ NMR $\delta = 10.7$ (s). **2**: ^1H NMR $\delta = 1.47$ (br, $O(O)CC\mathit{H}_3$); ^{19}F NMR $\delta = -117.1$ (m, 2F, ortho-C_6F_5), -162.8 (br t, 1F, para-C_6F_5), -164.1 (t, 2F, meta-C_6F_5); $^{31}P\{^1H\}$ NMR $\delta = 15.8$ (br d), -1.5 (m, $^2J_{PP} = 43.5$ Hz).[28]

(ii) Reaction of 1 with 1 equiv of $B(C_6F_5)_3$. CD_2Cl_2 (1 mL) was added to **1** (6.4 mg, 0.01 mmol) and $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol) in an NMR tube to give a colorless solution. The formation of a small amount of white precipitate was observed in this case. A mixture of unreacted **1** (24 mol %) and **2** (76 mol %) was obtained, as well as pentafluorobenzene.

(iii) Reaction of 1 with 2 equiv of $B(C_6F_5)_3$. CD_2Cl_2 (1 mL) was added to **1** (6.4 mg, 0.01 mmol) and $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol) in an NMR tube to give a yellow solution. The formation of a small amount of gray precipitate was observed. ^1H and ^{19}F NMR data were complex and could not be fully assigned in this case; however ^{31}P NMR data are consistent with a symmetric dicationic palladium species (42 mol %); $^{31}P\{^1H\}$ NMR $\delta = 18.3$ (s). In addition pentafluorobenzene, complex **1**, and small amounts (5 mol %) of **3b** were observed.

(iv) Reaction of 1 with 5 equiv of $B(C_6F_5)_3$. CD_2Cl_2 (1 mL) was added to **1** (6.4 mg, 0.01 mmol) and $B(C_6F_5)_3$ (25.6 mg, 0.05 mmol) in an NMR tube to give a pale yellow solution. A mixture of **3b** (92 mol %) and **4** (8 mol %) was obtained. **3b**: ^{19}F NMR $\delta = -117.2$ (br m, 2F, ortho-$Pd-C_6F_5$), -135.1 (m, 12F, ortho-$[B(C_6F_5)_3]_2OH$), -159.7 (br t, 2F, meta-$Pd-C_6F_5$), -161.5 (m, 12F, meta-$[B(C_6F_5)_3]_2OH$), -165.8 (br t, 1F, para-$Pd-C_6F_5$), -165.8 (m, 6F, para-$[B(C_6F_5)_3]_2OH$); $^{31}P\{^1H\}$ NMR $\delta = 27.0$ (br d), -5.2 (m, $^2J_{PP} = 34.8$ Hz).[28] **4**: ^{19}F NMR $\delta = -114.8$ (br d, 4F, ortho-$Pd-C_6F_5$), -158.3 (br m, 2F, meta-$Pd-C_6F_5$), -164.5 (br t, 1F, para-$Pd-C_6F_5$); $^{31}P\{^1H\}$ NMR $\delta = 4.2$ (s).

(v) Reaction of Products from (iv) with Additional Water. Water (0.9 μL, 0.05 mmol) was added to reaction (iv).

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[25] Catalyst reduction is the principal means of deactivation of most polyketone catalysts.[1b]

[26] For a leading reference see: Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

[27] (a) For **1**: Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632. (b) For **5**: Davies, J. A.; Hartley, F. R.; Murray, S. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2246.

[28] P−F coupling was highly complex in this case, and J_{PF} coupling constants could not be determined.

A complex mixture of products was obtained, consisting of **2** (46 mol %), **4** (24 mol %), and a characteristic signal for a dicationic palladium species (30 mol %), $^{31}P\{^1H\}$ NMR $\delta = 18.3$.

Reactions in "Wet" CD_2Cl_2: (i) Reaction of 1 with 0.5 equiv of $B(C_6F_5)_3$. CD_2Cl_2 (1 mL) was added to **1** (6.4 mg, 0.01 mmol) and $B(C_6F_5)_3$ (2.6 mg, 0.005 mmol) in an NMR tube to give a colorless solution. A mixture of unreacted **1** (31 mol %) and **2** (69 mol %) was obtained.

(ii) Reaction of 1 with 1 equiv of $B(C_6F_5)_3$. CD_2Cl_2 (1 mL) was added to **1** (6.4 mg, 0.01 mmol) and $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol) in an NMR tube to give a colorless solution. The formation of a small amount of white precipitate was observed in this case. Again, a mixture of unreacted **1** (50 mol %) and **2** (50 mol %) was obtained, as well as pentafluorobenzene.

(iii) Reaction of 1 with 2 equiv of $B(C_6F_5)_3$. CD_2Cl_2 (1 mL) was added to **1** (6.4 mg, 0.01 mmol) and $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol) in an NMR tube to give a yellow solution. The formation of a small amount of gray precipitate was observed. As in the dry case, a complex mixture was obtained; however ^{31}P NMR data are consistent with a symmetric dicationic palladium species being the majority species (52 mol %). In addition, pentafluorobenzene was observed.

(**iv) Reaction of 1 with 5 equiv of $B(C_6F_5)_3$.** CD_2Cl_2 (1 mL) was added to **1** (6.4 mg, 0.01 mmol) and $B(C_6F_5)_3$ (25.6 mg, 0.05 mmol) in an NMR tube to give a colorless solution. A mixture of **3a** (65 mol %), **3b** (27 mol %), and **4** (7 mol %) was obtained. **3a**: ^{19}F NMR $\delta = -118.4$ (m, 2F, ortho-Pd$-C_6F_5$),), -135.1 (m, 6F, ortho-$B(C_6F_5)_3OH$), -160.2 (br t, 1F, para-Pd$-C_6F_5$), -160.6 (m, 6F, meta-$B(C_6F_5)_3OH$), -162.8 (br t, 2F, meta-Pd$-C_6F_5$), -166.6 (m, 3F, para-$B(C_6F_5)_3OH$); $^{31}P\{^1H\}$ NMR $\delta = 21.8$ (dt, $^3J_{PF} = 7.8$ Hz), -3.8 (m, $^2J_{PP} = 41.0$ Hz).

(v) Reaction of Products from (iv) with an Additional 5 equiv of $B(C_6F_5)_3$. $B(C_6F_5)_3$ (25.6 mg, 0.05 mmol) was added to reaction (iv). Clean conversion of **3a** to **3b** was observed (91 mol %) as well as small remaining amounts of **4** (9 mol %).

Larger Scale Preparation of Pd(dppp)(C_6F_5)-[$B(C_6F_5)_3OH$] (3a). [Pd(dppp)$(OAc)_2$] (0.2 g, 0.32 mmol) was added to a solution of $B(C_6F_5)_3$ (1.0 g, 2.0 mmol) in CH_2Cl_2 (20 mL). The reaction was stirred vigorously at room temperature for 45 min and then concentrated under reduced pressure to 10 mL. Addition of hexane gave a yellow/orange oil, which was decanted, washed with further portions of hexane (3 × 10 mL), and dried in vacuo to give an orange solid residue. NMR spectroscopy data of this sample were consistent with the mixture of reaction products of the analogous NMR scale reaction described above. The impure nature of this compound precluded elemental analysis.

Reaction of [Pd(dppp)$(NCPh)_2$]$(BF_4)_2$ with $B(C_6F_5)_3$. A solution of [Pd(dppp)$(NCPh)_2$]$(BF_4)_2$ (50 mg, 0.06 mmol) and $B(C_6F_5)_3$ (35 mg, 0.07 mmol) in anhydrous CH_2Cl_2 (1 mL) was stirred for 10 min. The $^{31}P\{^1H\}$ NMR spectrum of the resulting pale yellow solution shows characteristic peaks for a monoarylated complex, which accounts for over 95 mol % conversion to this product; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) $\delta = 19.0$ (dd), -2.0 (m, P trans to $-C_6F_5$), $J^2_{PP} = 40.0$ Hz.

Reaction of [Pd(dppp)$(NCPh)_2$]$(BF_4)_2$ with B(*p*-$C_6H_4F)_3$. A solution of [Pd(dppp)$(NCPh)_2$]$(BF_4)_2$ (50 mg, 0.06 mmol) and B(*p*-$C_6H_4F)_3$ (20 mg, 0.07 mmol) in anhydrous CH_2Cl_2 (1 mL) was stirred for 10 min. The $^{31}P\{^1H\}$ NMR spectrum of the resulting pale yellow solution shows characteristic peaks for a monoarylated complex, which account for 4 mol % conversion to this product after 1 h; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) $\delta = 23$ (dd), -2 (m, P trans to $-C_6F_5$), $J^2_{PP} = 50.4$ Hz

Reaction of [Pd(dppp)$(NCPh)_2$]$(BF_4)_2$ with Na[B(*p*-$C_6H_4F)_3OH$]. A suspension of Na[B(*p*-$C_6H_4F)_3OH$] (22 mg, 0.066 mmol) in anhydrous CH_2Cl_2 (1 mL) was treated with [Pd(dppp)$(NCPh)_2$]$(BF_4)_2$ (50 mg, 0.060 mmol) and stirred for 10 min. The $^{31}P\{^1H\}$ spectrum of the resulting pale orange solution shows characteristic peaks for a monoarylated complex, which accounts for 64 mol % conversion to this product; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) $\delta = 20.6$ (dd), -4.3 (m, P trans to $-C_6F_5$), $J^2_{PP} = 50.4$ Hz. ^1H and ^{19}F NMR spectra of this reaction contained a large number of overlapping peaks, which could not be unequivocally assigned.

Ethene/Propene/CO Polymerization Catalyzed by 3a/$B(C_6F_5)_3$. This was performed as detailed for **1**/$B(C_6F_5)_3$ using propene (23.4 g, 0.61 mol), CO/C_2H_4 (1:1, 50 bar G), $B(C_6F_5)_3$ (0.102 g, 0.20 mmol), and **3a** (0.017 g, 0.01 mmol, prepared according to a larger scale procedure described above) at 70 °C for 3 h. The polymer was obtained as a white powder. Yield = 9.8 g. NMR analysis showed the polymer to contain alternating units originating in CO and alkene, with 5.0 per 100 monomers originating in propene. GPC analysis (hexafluoro-2-propanol, relative to a poly(methyl methacrylate) standard): $M_n = 60\,000$; $M_w = 116\,000$; $M_w/M_n = 1.9$; $M_{pk} = 91\,000$.

Ethene/Propene/CO Polymerization Catalyzed by 3a. This reaction was carried out in the absence of additional $B(C_6F_5)_3$; otherwise the same procedure was performed as detailed for **1**/$B(C_6F_5)_3$ using propene (25.7 g, 0.61 mol), CO/C_2H_4 (1:1, 50 bar G), and **3a** (0.006 g, 0.009 mmol, prepared according to a larger scale procedure described above) at 70 °C for 3 h. The polymer was obtained as a white powder. Yield = 0.8 g. NMR analysis showed the polymer to contain alternating units originating in CO and alkene, with 4.3 per 100 monomers originating in propene. GPC analysis (hexafluoro-2-propanol, relative to polystyrene): $M_n = 63\,000$; $M_w = 144\,000$; $M_w/M_n = 2.3$.

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