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Comparative Study on Catalytic Systems for the Alternating and Nonalternating CO/Ethene Copolymerization

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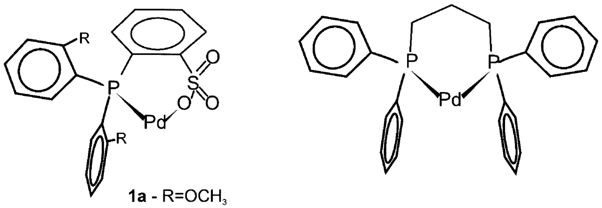
Drent et al. [*Chem. Commun.* **2002**, *9*, 964] have recently shown that a neutral (P−O)Pd(II) catalyst based on *o*-alkoxy derivatives of diphenylphosphinobenzene sulfonic acid (**1a**) can perform nonalternating CO/C_2H_4 copolymerization in which the resulting polyketone can have one or more subsequent ethylene units. We have analyzed this catalyst by comparing it to a cationic palladium catalyst, [(P−P)Pd(II)$^+$] (**1c**), (P−P) = dppp = $Ph_2P-(CH_2)_3-PPh_2$, that affords polyketones with strictly alternating CO and C_2H_4 units. We have also investigated a derivative (**1b**) of **1a** in which the *o*-methoxy substituents were replaced by a *o*-isopropyl group in order to investigate whether increasing the steric bulk enhances the degree of nonalternation.

Introduction

The coordination copolymerization of ethylene with polar monomers is currently a subject of considerable industrial and commercial interest.[1−11] To date the most successful polar coordination copolymerization process involves CO and ethylene.[2] The product is polyketone with strictly alternating CO and ethylene units. The catalysts developed for this process by Sen,[2] Drent,[11] and Brookhart[7] are all cationic and Pd(II) based. They have in addition for the most part two equivalent chelating nitrogen and phosphorus atoms attached to the Pd(II) center.

Drent has in a recent development shown that there exists a neutral Pd(II)-based complex with unsymmetrical chelating ligands that can copolymerize ethylene and CO in a nonalternating fashion where two or more ethylenes are inserted subsequently into the polyketone chain. Figure 1a depicts a neutral Pd(II)-based Drent catalyst[1] containing an anionic *o*-methoxy-substituted diphenylphosphino-based sulfonate (dppbs) co-ligand with an asymmetric (P−O) chelating ligand.

The new Drent catalyst has been the subject of considerable experimental[12] and theoretical[13] interest, as the new polyketones produced might exhibit improved thermal stability while retaining the excellent engineering properties of the strictly alternating polyketones. We have in a previous computational[13] study examined the influence of the steric bulk from the two *o*-methoxy-substituted phenyl groups on the ability of the Pd-(dppbs) system in Figure 1a to produce nonalternating polyketones.[13] It was shown that the steric bulk prevents the formation of chelate bonds between carbonyl oxygens of the polyketone chain and the metal center. The reduction in metal coordination makes it possible for decarbonylation of an acyl group to take place. If the subsequent insertion now is by ethylene rather than CO, a nonalternating chain has been formed.



1a - R=OCH_3
1b - R=C_3H_8

Pd(II) + dppbs ligand
(neutral)

1c

Pd(II) + dppp ligand
(cationic)

Figure 1. Schematic view of the nonalternating Drent system with *o*-methoxy (**1a**) and *o*-isopropyl (**1b**) groups and the strictly alternating palladium catalyst (**1c**).

We shall in the presented investigation extend our analysis by comparing the performance of the dppbs system by Drent given in Figure 1a with traditional symmetrical and cationic catalysts producing strictly alternating polyketones. The cationic catalyst will be exemplified by the bidentate diphosphine 1,3-bis(diphenylphosphino)propane (dppp) system given in Figure 1c, for which extensive experimental data are available.[14−17] In addition to our theoretical studies on the Pd(dppp)$^{2+}$ system, we will present results from an investigation of the Drent system with isopropyl groups instead of methoxy substituents (**1b**), for which, to the best of our knowledge, there are no experimental or theoretical data available in the literature. The emphasis will be on the role played by the overall charge of the catalyst and

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the symmetrical P—P versus asymmetrical P—O chelation. We shall finally comment on the role of the *o*-methoxy substituents.

Computational Details

Structures and energies of reactants, transition states, and intermediates for the investigated reaction pathways were obtained from density functional calculations using the Amsterdam Density Functional (ADF) program package.[18] To allow for a comparison with our published results on **1a**, the methodology adopted here is the same as the one employed in ref 13. Thus, all stationary points were optimized without any geometry constraints using the procedure developed by Versluis and Ziegler.[19,20] Use was made of the local density approximation augmented with the gradient corrections due to Becke (exchange) and Perdew (correlation)[21−23] for both energies and structures. A triple STO basis set with polarization function was employed for Pd, while all other atoms were described by a double-ζ plus polarization STO basis. The frozen core approximation was employed for the 1s electrons of the C and O atoms, up to and including the 2p of the P and S atoms and the 3d electrons of Pd. Finally, first-order scalar relativistic corrections were added to the total energy of the system.[24−26] For the cationic system **1c** use was made of a QM/MM method[27] in which the phenyl groups on phosphorus were replaced by hydrogen atoms in the QM region but represented by a Sybyl[28] force field in the MM region. This approach will be validated by extensive comparison to experiment.[14−17] The approximate reaction paths were evaluated by a linear transit method with the chosen reaction coordinate being the distance between the α-carbon of the growing polymer chain and a C of the coordinated monomer.

In QM/MM studies, the atoms in the MM region were approximated by the Sybyl force field.

Results and Discussion

Kinetic Scheme. The mechanism of CO/C_2H_4 copolymerization is presented in Scheme 1, and it involves two main competing cycles: the nonalternating (A → B → TS-3) and the strictly alternating (A → C → TS − 1 → D → E → TS-2) one.

Both cycles are initiated by the formation of CO and ethylene complexes with the Pd—alkyl species in a pre-equilibrium step (A → B and A → C, respectively). Next, the generated complexes undergo migratory insertion into the Pd—alkyl bond, leading to the formation of Pd—alkyl (B → TS-3 → A) or Pd—acyl (C → TS-1 → D) complexes. As depicted in Scheme 1, the ethylene insertion is assumed to be irreversible on the basis of earlier theoretical and experimental studies.[29,30] The CO insertion into the Pd—alkyl bond (C → TS-1 → D) was originally thought to be irreversible; however, our recent theoretical studies[13] have shown that decarbonylation also might be important. Accordingly, the decarbonylation process (D → TS-1 → C) is taken into account in Scheme 1. To complete the alternating cycle, the palladium center in the Pd—acyl complex interacts with either CO or ethylene to form the Pd—acyl/CO (D → F) or the Pd—acyl/C_2H_4 (D → E) complexes, which are in a dynamic equilibrium with each other. Contrary to the Pd—acyl/CO complex that forms a resting state, the Pd—acyl/C_2H_4 moiety is a precursor complex for the migratory insertion of the ethylene molecule into the Pd—acyl bond (E → TS-2 → A), yielding a strictly alternating polyketone. It must be emphasized that the possibility for CO insertion into the Pd—acyl bond that would lead to consecutive CO units within the formed copolymer chain is neglected on the basis of earlier theoretical studies.[29,30]

The presented mechanism has been analyzed with the use of our previously reported kinetic expression for the ratio of global rates for nonalternating, r_{na}, and alternating pathways, r_a:[13]

$$f_{na} = \frac{r_{na}}{r_a} = \left(\frac{k'_{C_2H_4}}{k_{CO}}\frac{[C_2H_4]}{[CO]}\frac{K_1}{K_2}\right)\left(\frac{K_4 k_{C_2H_4}[C_2H_4]}{K_4 k_{C_2H_4}[C_2H_4] + k_{CO}{}^{-1}}\right) \quad (1)$$

This equation consists of two main components, which have been discussed in detail elsewhere.[13] Briefly, the first one is the original expression by Brookhart[7]

$$\frac{r_{na}}{r'_a} = \frac{k'_{C_2H_4}}{k_{CO}}\frac{[C_2H_4]}{[CO]}\frac{K_1}{K_2} = F_B \quad (2)$$

developed by assuming that the degree of alternation can be explained in terms of the competition between CO and ethylene insertion into the Pd—alkyl bond without considering decarbonylation, where $r'_a = k_{CO}[C]$.

The second part of eq 1,

$$F_{cor} = \frac{K_4 k_{C_2H_4}[C_2H_4]}{K_4 k_{C_2H_4}[C_2H_4] + k_{CO}{}^{-1}} \quad (3)$$

is a function of the following rate and equilibrium coefficients:

- the rate of decarbonylation ($k_{CO}{}^{-1}$);
- the equilibrium constant for the formation of the ethylene complex E from D and free ethene (K_4);
- the rate of insertion of ethylene into the Pd—acyl bond of E ($k_{C_2H_4}$).

It indicates that nonalternation in eq 1 can be enhanced provided that F_{cor} is large enough. This can happen if the rate of decarbonylation ($k_{CO}{}^{-1}$) from D is larger than the effective propagation rate $K_4k_{C_2H_4}[C_2H_4]$ for ethylene insertion into the Pd—acyl bond of D. Finally, the percent nonalternation is given by

$$X_{na} = \frac{f_{na}}{1 + f_{na}} \times 100\% \quad (4)$$

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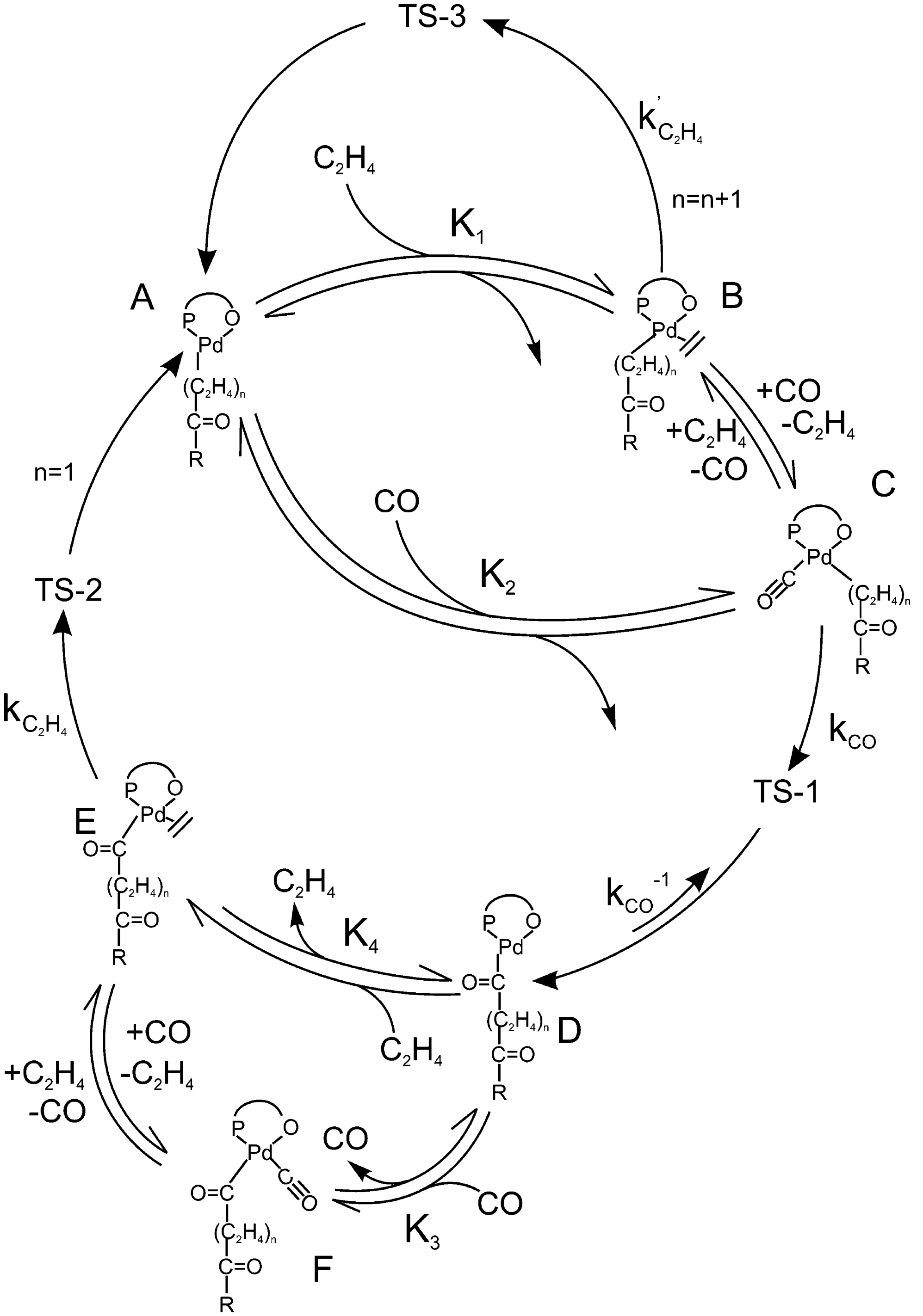
Scheme 1. Chain Propagation Mechanism for the CO/C_2H_4 Copolymerization Reaction



Experimental and Calculated Heats of Reaction and Barriers of Activation. The reaction and activation energies for the CO/C_2H_4 copolymerization process starting from the Pd−alkyl complexes are summarized in Table 1. We compare here calculated activation energies for CO/C_2H_4 insertion into the Pd−alkyl bond and C_2H_4 insertion into the Pd−acyl bond with respect to the cationic (dppp)Pd^+ catalyst and two neutral (dppbs)Pd Drent-type catalysts. Included as well are experimental data due to Brookhart et al.[15] on (dppp)Pd^+. We shall in the following compare the (dppp)Pd^+ (**1c**) and (dppbs)Pd with R = *o*-methoxy (**1a**); see Figure 1. The (dppbs)Pd system (**1b**) with R = *o*-isopropyl will be discussed later.

As the paper is intended to compare a realistic model of the Drent system with the considered cationic (P−P)Pd(II)$^+$ model, we refer to our published mechanistic studies of the reaction with *o*-methoxy-substituted Drent catalyst[13] and the experimental findings of Brookhart et al.[15] presented in Table 1.

Before going into a detailed discussion of the results, we should point out that the cationic Pd(dppp)$^+$ system was divided into a QM and a MM part, while the Pd(dppbs) models were both treated with the full QM method. The choice of the QM/MM method in the former case is justified by the lack of electron-withdrawing or electron-donating substituents on the phenyl groups attached to the phosphorus centers in Pd(dppp)$^+$; therefore, their principal role is expected to be steric in origin. On the other hand, the substituents in the *ortho* position on the phenyls in the Pd(dppbs) model catalysts can also influence the electronic properties of the ligand.[31]

Table 1. Activation Parameters for Monomer Insertion with Respect to the Real Cationic dppp Complex, 1c, and the Neutral Drent Catalysts, 1a and 1b

catalyst	complex	$\Delta H^{\ddagger}$ [kJ/mol] (calc)	$\Delta H^{\ddagger}$ [kJ/mol] (exp)	$\Delta S^{\ddagger}$ [J/K·mol] (exp)	$\Delta G^{\ddagger}$ (63 °C) [kJ/mol] (exp)[a]
(dppp)Pd$^+$	(P−P)Pd(alkyl)(CH_2═CH_2)$^+$	70.5	66.5	−6.7	68.2
	(P−P)Pd(acyl)(CH_2═CH_2)$^+$	62.1			51.5
	(P−P)Pd(alkyl)(CO)$^+$	48.2			56.1
	decarbonylation	86.1			
(dppbs)Pd +*o*-methoxy	(P−O)Pd(alkyl)(CH_2═CH_2)	73.4[b]			
	(P−O)Pd(acyl)(CH_2═CH_2)	61.3[b]			
	(P−O)Pd(alkyl)(CO)	52.5[b]			
	decarbonylation	31.2[b]			
(dppbs)Pd +*o*-isopropyl	(P−O)Pd(alkyl)(CH_2═CH_2)	65.9			
	(P−O)Pd(acyl)(CH_2═CH_2)	62.4			
	(P−O)Pd(alkyl)(CO)	58.8			
	decarbonylation	26.1			

[a] Taken from ref 15. [b] Taken from ref 13.

Insertions of CO into an alkyl−palladium bond and ethylene into an acyl−palladium bond are the key steps in the alternating cycle, while the concurent nonalternating path involves insertion of ethylene into a palladium−alkyl species as the main elementary step. The catalytic cycles are initiated by the monomer coordination to the alkyl−palladium complex in a pre-equilibrium step; see Scheme 1. Looking at the energetics of the CO and C_2H_4 complex formations it is notable that the generation of the alkyl-Pd/C_2H_4 complex with (P−P)Pd is the only endothermic process (5.1 kJ/mol). The CO complex formation is exothermic in both cases (−33.2 and −77.4 kJ/mol for (P−P)Pd and (P−O)Pd, respectively). As for the ethylene complex with the (P−O)Pd system it is exothermic by 31.4 kJ/mol. Thus, both ethylene and CO are more strongly coordinated to the (P−O)Pd system. This is likely due to the lower electron density at the palladium center in the cationic (P−P)Pd complex, which will cause a lower binding energy to the monomers as a result of reduced back-donation from metal to the ligand. By looking at the ethylene complexes with the (P−P)Pd and (P−O)Pd complexes as presented in Figures 2f and 2d it is notable that in the former the monomer approach occurs from the axial position relative to the basal plane defined by the phosphorus atoms and the palladium. The orientation of the ethylene molecule relative to the basal plane is in turn important for the following migratory insertion step. The ethylene molecule in the axial position in Pd(dppp)$^+$ needs to be reoriented before insertion into the Pd−alkyl bond, as it needs to displace the oxygen atom from the polymer chain interacting with palladium prior to insertion. In the Pd(dppbs) system, the ethylene orientation is already appropriate for the following insertion, as it is situated nearly perpendicular to the basal plane and the interacting species (ethylene and polymer chain) are in close proximity to react. Likewise, the coordinated CO molecule is situated in the right fashion for the migratory insertion into the Pd−alkyl bond (see Figures 2g and 2i).

Once the monomer complexes with the alkyl species are formed, the monomer migratory insertion steps into the Pd−alkyl bond take place (see Figures 2j and 2l for the CO insertion into the Pd−alkyl bond or 2x and 2z for the C_2H_4 insertion into Pd−alkyl species, respectively). Looking at the computed activation barriers for the CO and ethylene insertions it is evident that the CO insertion is favored over the ethylene insertion in both cases, i.e., the cationic Pd(dppp)$^+$ and the neutral Pd(dppbs) catalysts. As expected, barrier heights for both processes are somewhat lower for the cationic system (by 4.3 and 2.9 kJ/mol for CO and ethylene, respectively). After passing TS-1, the Pd-(dppp)$^+$ system is stabilized significantly by the formation of a six-membered chelate (see Figure 2o) with the distance between the carbonyl oxygen from the polymer chain and the palladium center being 2.17 Å. The final acyl product is some 38 kJ/mol below the precursor Pd−alkyl/CO complex. On the other hand the polyketone coordinated to the Pd(dppbs) fragment does not form a chelate structure (see Figure 2m) as a result of the neutral charge of the system and the steric hindrance concentrated on one face of the asymmetric (P−O) ligand. In the same way, the acyl complex (Figure 2m) from the CO insertion lacks a chelate interaction for the neutral (P−O) system with a P−O distance of 4.55 Å, whereas such an interaction is clearly present in the cationic acyl complex with P−O = 2.17 Å (Figure 2o). The coordinatively unsaturated nature of the neutral Pd−acyl complex (Figure 2m) makes it possible for the species to decarbonylate, an option not available for the cationic counterpart (Figure 2o) that is coordinatively saturated. We shall expand on this point in the next section.

Factors of Importance for Rate of Alternating Copolymerization. By making use of the obtained reaction energies and activation barriers for the Pd(dppp)$^+$ system and analyzing the appropriate terms in the proposed kinetic expression (eq 1), one can understand the factors responsible for the perfectly alternating copolymerization of CO and C_2H_4. These data are compiled in Table 3. For monomer complexation energies, an entropy value of −27 eu was included. Entropy contributions to the activation energies were ignored, as they are known to be negligible in the case of intramolecular reactions.[7]

As expected, the factors that contribute to the Brookhart term (see eq 2 for definition), F_B, clearly exclude the possibility of ethylene misinsertion in the entire temperature range. The local concentration of Pd−alkyl/CO complexes is much higher than their ethylene analogues, as reflected in small values of the K_1/K_2 ratio. Likewise, the rate of ethylene insertion into the Pd−alkyl bond is much slower than for the CO insertion into the same species ($k'_{C_2H_4}/k_{CO} \ll 1$). As a consequence, the F_B term is very small (ca. 10^{-8}), pointing to a strictly alternating distribution of both comonomers within the growing copolymer chain with no detectable error. However, the correction term (see eq 2 for definition), F_{cor}, is quite high and increases with temperature (10^4 and 10^6 for 25 °C and 100−120 °C, respectively), as a result of the unfavorable thermodynamics of C_2H_4 complexation to the Pd−acyl fragment (K_4).

Thus, although the rate of decarbonylation, k_{CO}^{-1}, is slow due to the high barrier of 86 kJ/mol, the effective rate of ethylene insertion into the Pd−acyl bond given by $K_4 k'_{C_2H_4}[C_2H_4]$ is increasingly smaller, resulting in a F_{cor} term that grows with temperature, Table 3. The factor responsible for this term is

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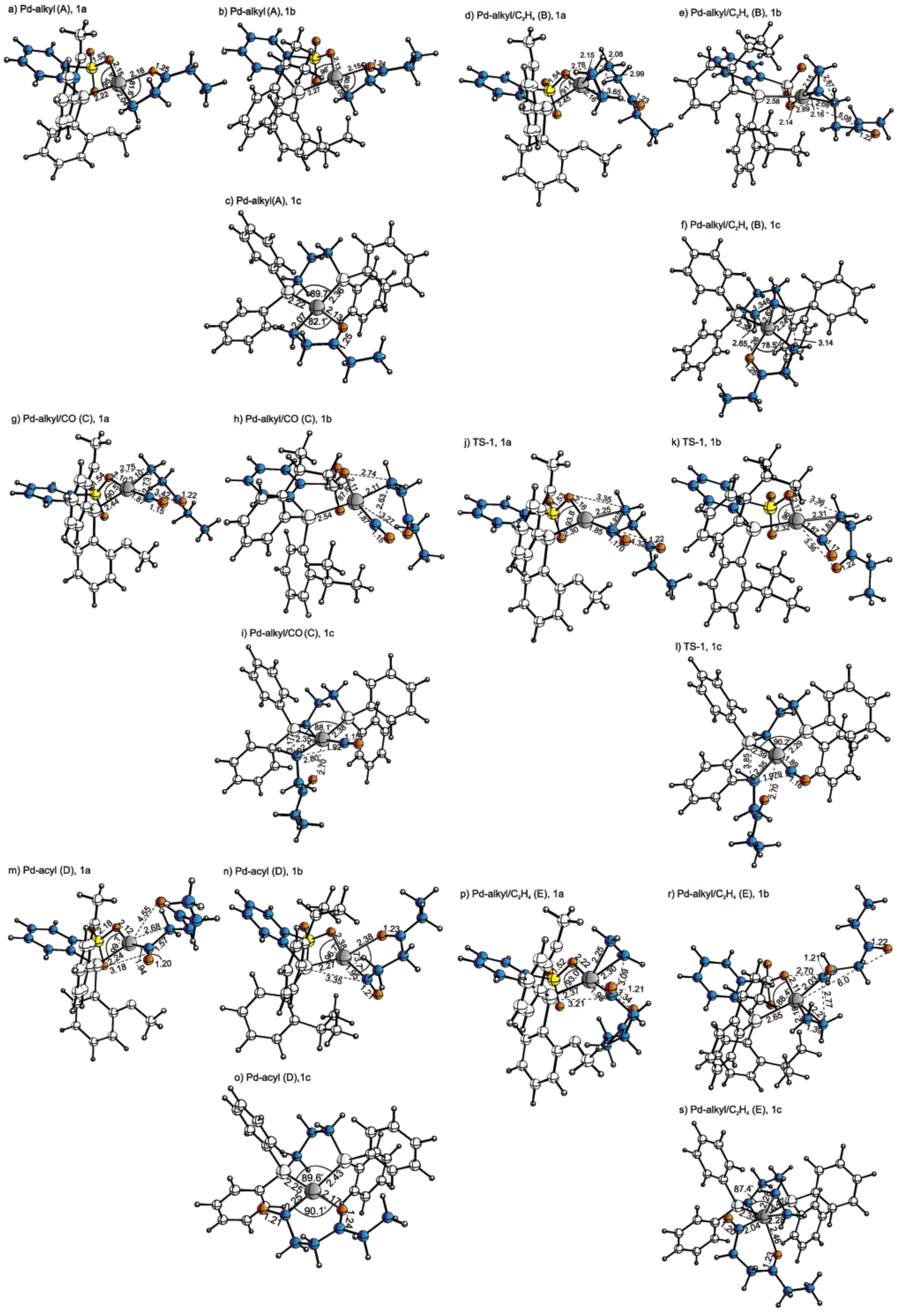

a) Pd-alkyl (A), 1a

b) Pd-alkyl (A), 1b

c) Pd-alkyl (A), 1c

d) Pd-alkyl/C_2H_4 (B), 1a

e) Pd-alkyl/C_2H_4 (B), 1b

f) Pd-alkyl/C_2H_4 (B), 1c

g) Pd-alkyl/CO (C), 1a

h) Pd-alkyl/CO (C), 1b

i) Pd-alkyl/CO (C), 1c

j) TS-1, 1a

k) TS-1, 1b

l) TS-1, 1c

m) Pd-acyl (D), 1a

n) Pd-acyl (D), 1b

o) Pd-acyl (D),1c

p) Pd-alkyl/C_2H_4 (E), 1a

r) Pd-alkyl/C_2H_4 (E), 1b

s) Pd-alkyl/C_2H_4 (E), 1c

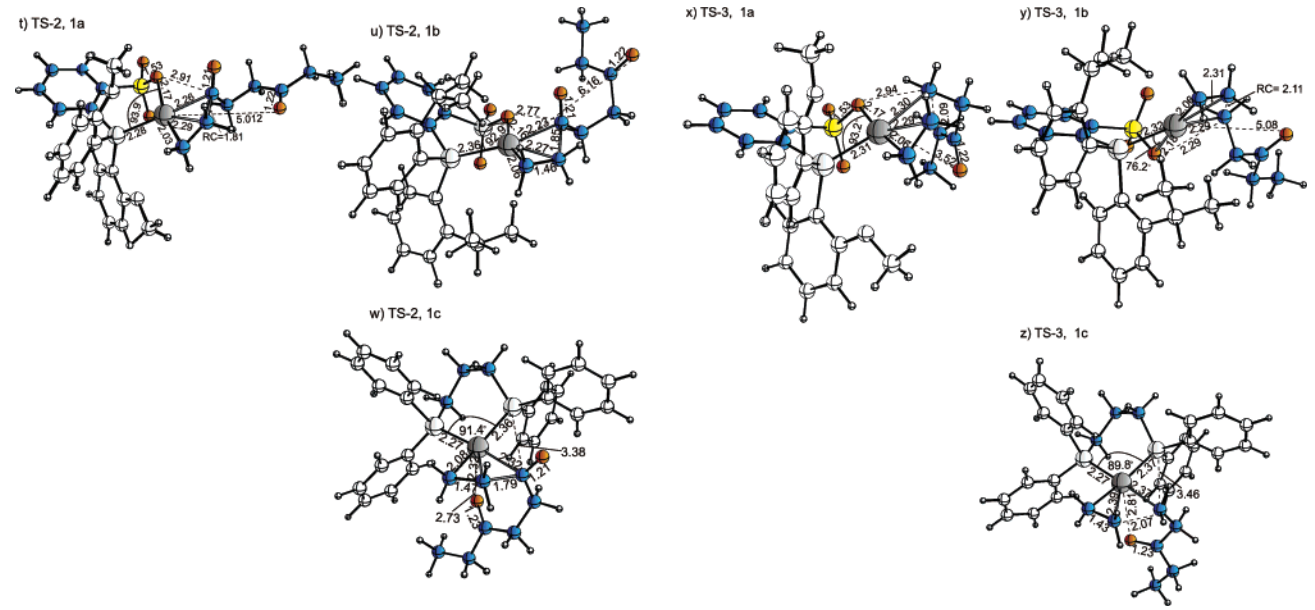

Figure 2. Optimized geometries of all the stationary points on the potential energy surface for the CO/C_2H_4 copolymerization process with **1a** (Pd(dppbs)+methoxy), **1b** (Pd(dppbs)+isopropyl), and **1c** (Pd(dppp)$^+$) complexes. Appropriate atoms are differentiated by the color and size of the spheres: palladium (large, dark gray); phosphorus (medium size, light gray); sulfur (medium size, yellow); oxygen (medium size, red); carbon (medium size, blue), and hydrogen (small, white). For clarity, all atoms within the bulky groups at phosphorus centers are white.

Table 2. Monomer Binding Energies for the Real Pd(dppp)$^+$ Complex, 1b, and the Neutral Drent Catalyst, 1a

catalyst	complex	$\Delta H°$ [kJ/mol] (calc)	$\Delta G°$ [kJ/mol] (exp)^{a,b}	$\Delta H°$ [kJ/mol] (exp)
(dppp)Pd$^+$	(P−P)Pd(alkyl)/(CH_2═CH_2)$^+$	5.1	22.0^a	−19.0^a
	(P−P)Pd(acyl)/(CH_2═CH_2)$^+$	−25.2	16.3^b	−24.9^d
	(P−P)Pd(alkyl)/(CO)$^+$	−33.2	16.2^b	−25.0^d
	(P−P)Pd(acyl)/(CO)$^+$	−35.6	−4.9^b	−45.9^d
(dppbs)Pd +*o*-methoxy	(P−O)Pd(alkyl)/(CH_2═CH_2)	−31.4^c		
	(P−O)Pd(acyl)/(CH_2═CH_2)	−73.0^c		
	(P−O)Pd(alkyl)/(CO)	−77.4^c		
	(P−O)Pd(acyl)/(CO	−99.7^c		
(dppbs)Pd +*o*-isopropyl	(P−O)Pd(alkyl)/(CH_2═CH_2)	−18.2		
	(P−O)Pd(acyl)/(CH_2═CH_2)	−77.5		
	(P−O)Pd(alkyl)/(CO)	−74.8		
	(P−O)Pd(acyl)/(CO	−134.6		

[a] Taken from ref 15. [b] Taken from ref 17. [c] Taken from ref 13. [d] Estimated by assuming $\Delta S° = -27$ cal/(mol·K)$^{-1}$.

Table 3. Analysis^b of Nonalternation in CO/C_2H_4 Copolymerization Catalyzed by the Real Cationic Pd(dppp)$^+$ System,^{c} 1c

T [°C]	K_1/K_2^{d} × 10^6	$k'_{C_2H_4}$/k_{CO}^{d} × 10^4	K_4^{e} × 10^8	F_B^{d} × 10^8	F_{cor}^{e} × 10^{-6}	X_{na}^{f} calcd	X_{na}^{f} exptl^g
25	0.195	1.239	4.07	0.019	0.026	5.01 × 10^{-4}	10^{-5}
100	4.35	7.559	0.53	2.598	1.415	3.5	
110	6.01	9.119	0.43	4.325	2.140	8.5	
120	8.16	10.9	0.35	7.016	3.170	18.2	

[a] Reaction conditions according to Drent et al.:[1] 20 bar of CO; 30 bar of C_2H_4; 0.04 mmol (9 mg) of Pd; solvent MeOH (100 mL). Solubilities of ethene and CO in methanol from Henry's law constants of the comonomers in methanol at 90 °C reported by Vavasori et al.[16] [b] For definition of different components see eqs 1−3. [c] See **1c** of Figure 1. [d] See eq 2. [e] See eq 3. [f] See eq 4. [g] Experimental value from ref 15.

the complexation constant K_4 from coordination of ethylene to the cationic complex **1c**. It is small, as ethylene must displace the chelate bond between the ketone oxygen and Pd (Figure 2m), and further diminishes with steric bulk and the positive charge on the **1b** model, which reduces back-donation. It is thus not surprising that the Pd−ethylene bond is some 48 kJ/mol stronger in the neutral complex **1b** (Figure 2p), where the back-donation is more dominant and an internal Pd−O chelate bond absent. In addition with rising temperatures K_4 will diminish due to the dissociation entropy, $\Delta S°$. The rate by which K_4 diminishes with temperature will depend on the value adopted for $\Delta S°$. We note on the other hand that $k_{C_2H_4}$ is nearly the same for **1a** and **1c**, as they have similar insertion barriers of 62.1 kJ/mol (**1c**) and 61.3 kJ/mol (**1a**), respectively.

Utilizing the calculated kinetic and thermodynamic data for **1c**, Tables 1 and 2, in conjunction with the kinetic expressions of eqs 1−4 makes it now possible to get the degree of nonalternation X_{na} as a function of temperature for the cationic system **1c**. We predict for 25 °C an X_{na} value of 5 × 10^{-4}, in excellent agreement with the experimental value of 10^{-5}. However, with increasing temperature the degree of nonalternation is predicted to rise to 18% at 120 °C. Although no experimental values are available, the estimate might be exaggerated due to difficulties with estimating $\Delta S°$. However, qualitatively X_{na} should rise with T. We shall return to the point shortly.

Factors of Importance for Rate of Nonalternating Copolymerization. Utilizing the activation and reaction data for the *o*-methoxy-substituted Drent system, **1a**, we are provided with factors of importance for the rate of nonalternation, listed in Table 4. These data were already published elsewhere[13] for **1a**

Table 4. Analysis[b] of Nonalternation in CO/C_2H_4 Copolymerization Catalyzed by the Real Pd(dppbs)[c] (with *o*-methoxy groups), 1a

T [°C]	$K_1/K_2{}^d \times 10^7$	$k'_{C_2H_4}/k_{CO}{}^d \times 10^3$	$K_4{}^e$	$F_B{}^d \times 10^9$	$F_{cor}{}^e \times 10^{-7}$	$X_{na}{}^f$ calc[d]	$X_{na}{}^f$ exptl[g]
25	0.09	0.218	6.4	0.01	0.05	7.5×10^{-4}	
100	3.66	1.187	0.02	3.43	1.49	4.9	4.7
110	5.39	1.415	0.01	6.02	2.12	11.3	7.3
120	7.78	1.672	0.006	10.0	3.0	23.3	11.0

[a] Reaction conditions according to Drent et al.:[1] 20 bar of CO; 30 bar of C_2H_4; 0.04 mmol (9 mg) of Pd; solvent MeOH (100 mL). Solubilities of ethene and CO in methanol from Henry's law constants of the comonomers in methanol at 90 °C reported by Vavasori et al.[16] [b] For definition of different components see eqs 1−3. [c] See **1a** of Figure 1. [d] See eq 2. [e] See eq 3. [f] See eq 4. [g] Experimental value from ref 1.

but are repeated here for comparison with the catalyst (dppp)-Pd^+, discussed in the previous section.

Similar to the $Pd(dppp)^+$ catalyst, the *o*-methoxy-substituted Drent system (**1a**) appears to be a strictly alternating one at low temperature, but its chances for ethylene misinsertion rise to ca. 20% with temperature. Surprisingly, the amount of double ethylene units is only slightly improved compared to **1c**. Analyzing the individual factors of eq 1, F_{cor} is an order of magnitude smaller than for **1c** due to a strong preference for the formation of the Pd−alkyl/CO complexes. Again, the term is effectively balanced by F_{cor} (see eq 3), which depends on the competitions between decarbonylation of the Pd−acyl complex and the ethylene migratory insertion into the Pd−alkyl bond. Contrary to $Pd(dppp)^+$, this behavior is caused by the strong destabilization of the Pd−acyl complex shown in Figure 2m. Now, the Pd−acyl moiety lies 21.3 kJ/mol above the precursor Pd−alkyl/CO complex, and its characteristic feature is lack of any chelating interaction; the copolymer chain is oriented in the same way as the polymer chain attached to the precursor Pd−alkyl/CO complex with the distance between its carbonyl oxygen and palladium 4.55 Å. The destabilized Pd−acyl complex is shown to easily decarbonylate, as the barrier for the process is very low, ca. 31 kJ/mol, compared to **1c**, ca. 86 kJ/mol (see Table 1).

It would appear that the high rate of decarbonylation (k_{CO}) for **1a** compared to **1c** qualitatively is the explanation for the high degree of nonalternation observed for the Drent catalyst. However, quantitatively F_{cor} is only 1 order of magnitude larger for **1a** (Table 3) than for **1c** (Table 4). The reason for this is that the lack of chelating Pd−O bond in the neutral acyl complex (Figure 2m) not only accelerates the rate of decarbonylation but also increases the degree of ethylene complexation (K_4) and thus the rate ($K_4 k_{C_2H_4}[C_2H_4]$) of ethylene insertion into the Pd−acyl bond. The increase in X_{na} and F_{cor}, one would expect due to $k_{CO}{}^{-1}$, is thus reduced by a corresponding increase in K_4. It should be noted that the olefin complexation to the Pd−acyl complex is stronger (48 kJ/mol) in **1a** compared to **1c** not only due to the lack of a competing Pd−O bond but also due to a larger metal-to-ethylene back-donation in the neutral complex.

The Isopropyl System. In this section we shall briefly assess the influence of increasing steric bulk of the *o*-substituent in the Drent system from R = OMe (**1a**) to R = ^iPr (**1b**). Such a comparison should also reveal whether oxygen is an essential part of the *o*-substituted **1a**.[31]

Table 1 provides a set of theoretically determined activation parameters for **1b**. In comparing **1a** and **1b**, a systematic improvement is observed in many of the parameters that point to **1b** as the better catalyst for nonalternation. The migratory insertion of ethylene into the palladium−alkyl bond is the rate-controlling step for nonalternation. However, the activation barrier for the process is markedly reduced for **1b** compared to **1a** (by 7.5 kJ/mol) and **1c** (by 4.6 kJ/mol), thus increasing the chances for ethylene misinsertion in **1b**. Moreover, the barrier height for the competing CO insertion is increased (by 6.3 and 10.6 kJ/mol for **1a** and **1c**, respectively) and the barrier of decarbonylation is enhanced compared to **1a** (by 5.1 kJ/mol). On the other hand neither $k_{C_2H_4}$ nor K_4 differ much between **1a** and **1b**.

Table 5. Analysis[b] of Nonalternation within CO/C_2H_4 Copolymer Obtained with Use of the Real Drent's Catalyst[c] (with *o*-isopropyl groups), 1b

T [°C]	$K_1/K_2{}^d \times 10^8$	$k'_{C_2H_4}/k_{CO}{}^d$	$K_4{}^e$	$F_B{}^d \times 10^9$	$F_{cor}{}^e \times 10^{-7}$	$X_{na}{}^f$ calcd	$X_{na}{}^f$ exptl[g]
25	0.012	0.054	59.2	0.003	0.066	3.41×10^{-3}	
100	1.19	0.097	0.111	9.14	1.865	14.6	
110	1.92	0.103	0.058	15.64	2.637	29.2	18.3
120	3.02	0.109	0.031	26.04	3.664	48.8	

[a] Reaction conditions according to Drent et al.:[1] 20 bar of CO; 30 bar of C_2H_4; 0.04 mmol (9 mg) of Pd; solvent MeOH (100 mL). Solubilities of ethene and CO in methanol from Henry's law constants of the comonomers in methanol at 90 °C reported by Vavasori et al.[16] [b] For definition of different components see eqs 1−3. [c] See 1b of Figure 1. [d] See eq 2. [e] See eq 3. [f] See eq 4. [g] Since there are no experimental data for **1b**, experimental values from ref 1 for the *o*-isopropyloxy-substituted Drent system are quoted.

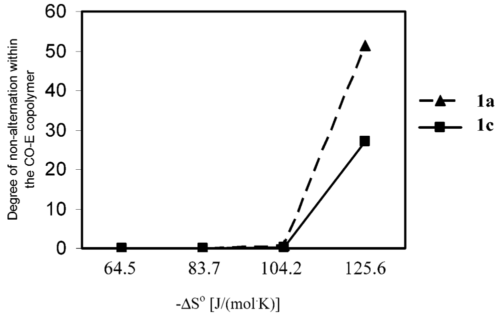

Figure 3. Degree of nonalternation within the CO/C_2H_4 copolymer chain vs entropy at 100 °C for the **1a** and **1c** systems.

As before, we use the calculated activation and reaction energies to obtain the rate and equilibrium constants that ultimately determine the degree of nonalternation. The data over the entire range of temperature from 25 to 120 °C are summarized in Table 5.

The increase in both $k_{C_2H_4}/k_{CO}$ and $k_{CO}{}^{-1}$ for **1b** compared to **1a** leads to a higher degree of nonalternation for **1b** throughout the temperature range. It would further appear that oxygen as an internal part of the substituent R is not a requirement for nonalternation. This observation is in line with recent experimental results due to Rieger et al.,[12] who demonstrated that replacing R = OMe by R = Me results in a comparable degree of nonalternation.

Analysis of Entropy Effects. We shall here briefly discuss how sensitive our calculated degree of nonalternation (X_{na}) is to the adopted value for the entropy ($\Delta S°$) of ethylene association for the neutral Drent system **1a** and the cationic copolymerization catalyst **1c**. The Brookhart term F_B is not so sensitive to changes in entropy, as it depends on ratios of rate and equilibrium constants, where entropy contributions to a large degree are factored out. On the other hand F_{cor} is strongly dependent on $\Delta S°$ through the equilibrium constant K_4. We display in Figure 3 the percent nonalternation at 100 °C for **1a** (dotted line) and **1c** (solid line) at different values of $\Delta S°$. It is clear from Figure 3 that X_{na} strongly depends on the adopted value of $\Delta S°$ and as expected increases with $|\Delta S°|$. Thus small differences in $\Delta S°$ between **1a** and **1c** can strongly influence the relative degree of nonalternation.

Concluding Remarks

We have compared two different catalytic systems with respect to copolymerization of ethylene. They include the (P−P)Pd$^+$ complex, (P−P) = dppp = $Ph_2P-(CH_2)_3-PPh_2$, proven to yield a purely alternating distribution of CO and C_2H_4 monomers within the formed polyketone chain, and the (P−O)Pd complex, (P−O) = dppbs = $Ph_2P-Ph-SO_3$, leading to a copolymer involving some consecutive ethylene units. Such a comparison has provided us with some insight into factors of importance for the design of efficient catalyst for the nonalternating CO/C_2H_4 copolymerization. In addition to the comparison of cationic and neutral complexes, we have made comparative calculations on the neutral Pd(dppbs) complex **1b**, where the more bulky ^{i}Pr group has replaced OMe (**1a**) as the substituent R.

We have shown that the neutral Drent system **1a** in contrast to the cationic alternating CO/ethylene copolymerization catalyst **1c** can undergo decarbonylation, which will help nonalternation. The decarbonylation is possible because the Pd−acyl complex of **1a** in contrast to **1c** does not form a Pd−O chelate bond between the metal and a carbonyl group on the polyketone chain. The lack of the chelate bond makes decarbonylation easier, as there is no requirement for an internal breakup of the Pd−O bond. The absence of a Pd−O bond is due to the complex being neutral and especially the asymmetric steric bulk around palladium. Thus the replacement of the aryl groups in **1a** with hydrogens introduces a weak Pd−O chelate bond.[13] The lack of a Pd−O chelate bond will also enhance the constant K_4 for complexation of ethylene to the Pd−acyl complex. This enhancement that reduces nonalternation is strongly temperature-dependent. However, the temperature dependence is difficult to determine, as it depends on the entropy of ethylene complexation to the Pd−acyl complex, a parameter that is hard to determine computationally.

Attention was also given to the substituent R in the *o*-position on the aryl groups in the Drent system by making the change from R = OMe (**1a**) to R = ^{i}Pr (**1b**). It was shown that the increased steric bulk in **1b** will enhance the degree of nonalternation by influencing the rate of decarbonylation ($k_{CO}{}^{-1}$) as well as the ratio $k_{C_2H_4}/k_{CO}$ from the monomer insertion into the Pd−alkyl bond. With increasing steric hindrance the ethylene migratory insertion is facilitated as steric bulk aids the isomerization process that is required prior to monomer insertion. In the case of CO, this steric effect is not important for the isopropyl-substituted system due to the modest size of the CO molecule. On the other hand, when methoxy substituents are placed on the aryl groups in the Drent system, repulsion occurs between the negatively charged oxygens on CO and methoxy. This repulsion aids the required isomerization, thus lowering the insertion barrier. The comparison between **1a** and **1b** would also indicate that one can increase nonalternation without oxygen in the R-substituent.

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