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Pd^{2+}-Catalyzed Cyclocopolymerization of 1,5-Hexadiene and CO: Regioselectivity of Olefin Insertion

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ABSTRACT: The cyclocopolymerization of 1,5-hexadiene and CO with Shell-type catalyst systems comprising palladium(II) complexes in the presence of chelating phosphines yields soluble cyclocopolymers containing 5- and 6-membered cyclic ketones. Cyclocopolymerization of 1,5-hexadiene and CO in the presence of $Pd(OAc)_2$, 1,3-bis(diphenylphosphino)propane (Dppp), 1,4-naphthaquinone, and $Ni(ClO_4)_2\cdot 6H_2O$ in chloroform/methanol (100−20/1) afforded a soluble cyclocopolymer **2** containing both 5- and 6-membered ring ketones in the polymer backbone. Cyclocopolymerization under similar conditions in the presence of 1,3-bis(diisopropylphosphino)propane (Dipp) gave a soluble cyclocopolymer **3** containing only 6-membered rings. Epimerization of the 6-membered ring cyclocopolymer **3** with 4-(dimethylamino)-pyridine provided evidence for an initial prevailingly *cis* microstructure (ca. 3/1 *cis/trans*) for the 2,5-disubstituted cyclohexanone repeating units of the cyclocopolymer. The regioselectivity for insertion of 1,5-hexadiene into the Pd−acyl bonds was inferred from the nature of the ring formed in the cyclocopolymerization. The formation of 5-membered cyclopentanone repeating units was interpreted as a signature for an initial 2,1-insertion of 1,5-hexadiene; the formation of 6-membered cyclohexananone rings was interpreted in terms of an initial 1,2-insertion of the 1,5-hexadiene.

Introduction

The synthesis of olefin/CO copolymers has been an area of considerable interest for many years.[1−3] Initial methods employing either free radical or transition metal-containing initiators under extremely high pressures and temperatures yielded copolymers whose CO content varied markedly with the partial pressure of CO.[1,4] It was later discovered[5] that several neutral Pd−phosphine complexes copolymerize propylene with CO under milder conditions to yield perfectly alternating copolymers despite reaction conditions where $P_{\mathrm{olefin}} > P_{\mathrm{CO}}$. Recently, highly reactive polymerization catalysts have been reported which consist of a cationic Pd^{2+} species with a noncoordinating anion[6] and either bipyridine-type or bidentate phosphine ligands.[2] The best bisphosphine-type ligands bear a 3-carbon chain between the two phosphorus atoms.[2]

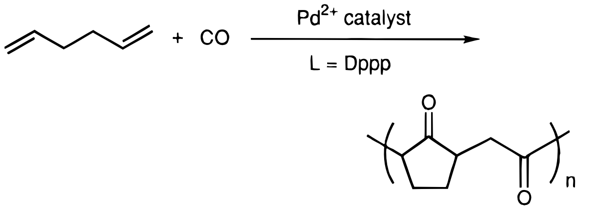
The perfectly alternating structure of the ethylene/CO copolymer produced with these catalysts is responsible for its high crystallinity and melting point of approximately 260 °C. For α-olefin copolymers, both the regio- and stereochemistry of insertion need to be controlled in order to prepare regular crystalline polymers. The copolymerization of styrene with CO in the presence of bipyridine-type ligands leads to a highly crystalline regioregular and stereoregular copolymer which has been assigned a *syndiotactic* structure.[7] Brookhart and co-workers have used chiral *C*2-symmetric cationic bis(oxazoline)palladium catalysts to obtain chiral *isotactic p-tert*-butylstyrene/CO copolymers.[8] For this system, it was shown that the regioregularity of these materials is due to a secondary (or 2,1) insertion of styrene.[9]

For aliphatic α-olefins, the regioselectivity of insertion is typically lower and much more highly dependent on the nature of the ligands.[10,11] While there have been some recent dramatic advances in the regio- and stereoselective/enantioselective polymerization of CO and propene,[12−16] the factors which govern the regioselectivity are still poorly understood.[10]

In this paper, we report our studies on the regioselective cyclocopolymerization[17] of 1,5-hexadiene and CO[18] to give regioregular cyclopolymers.[19,20] Here we have taken advantage of a diolefin as a mechanistic probe to study the factors which govern the regioselectivity in aliphatic α-olefin/CO copolymerization. The regioselectivity of this cyclocopolymerization has provided insight into the factors which influence the regioselectivity of olefin insertion into Pd−acyl bonds.

Results and Discussion

Drent at Shell has reported that the copolymerization of 1,5-hexadiene with CO using a catalyst system containing Pd^{2+}/1,3-bis(dibutylphosphino)propane (the general system contains $Pd(OAc)_2$, an alkyl or aryl bisphosphine $R_2PCH_2CH_2CH_2PR_2$, $Ni(ClO_4)_2\cdot 6H_2O$, and 1,4-naphthaquinone) at 50 °C in methanol solvent yielded a cyclocopolymer (eq 1).[18] A microstructure comprised predominantly of 5-membered ring ketones **1** was assigned to the product on the basis of ^{13}C NMR measurements. Attempts to substitute 1,3-bis(diphenylphosphino)propane in place of 1,3-bis(dibutylphosphino)propane under otherwise similar conditions yielded a catalyst system which was inactive for copolymerization of 1,5-hexadiene and CO.[18]



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We now report the cyclocopolymerization of 1,5-hexadiene with CO in chloroform solvent in the presence of a Shell-type catalyst system[21] containing the bisphosphine ligand $R_2PCH_2CH_2CH_2PR_2$ where R is isopropyl or phenyl. Under *dilute* monomer conditions (≤0.6 M) in *chloroform* solvent, both the bis(dialkylphosphino)-propane- and the bis(diarylphosphino)propane-derived catalysts are active and yield *soluble* polymers (Table 1).

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Table 1. Summary of Polymerization Results

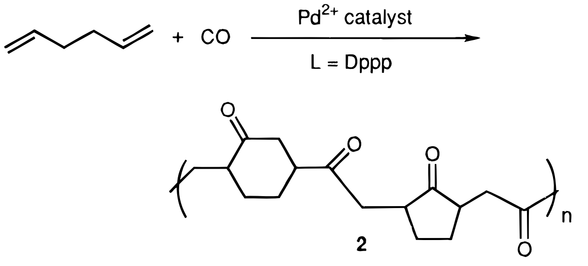
entry	ligand	[Pd^{2+}]/10^4 M	[hexadiene]/M	time/h	yield/g (%)	M_w[a]	M_n	M_w/M_n
1	Dppp[b]	3.7	0.22	7	0.13 (2)	6000	1900	3.17
2	Dppp[b]	3.7	0.22	21	0.28 (4)	5500	1900	2.86
3	Dppp[b]	3.7	0.22	22.5	2.9 (42)	85400	49800	1.72
4	(*S*,*S*)-DIOP[c]	3.7	0.25	23	0.99 (14)	10500	3500	3.04
5	(*S*)-BDPP[c]	4.0	0.25	22	2.1 (30)	33000	5570	5.92
6	Dipp[c]	3.4	0.22	17.5	0.24 (4)	8700	4000	2.14
7	Dipp[c]	6.7	0.67	40	3.6 (52)	nd	nd	nd

[a] GPC vs polystyrene. [b] Methanol solvent. [c] Chloroform/methanol solvent. All polymerizations were done at ambient temperature. Ligand abbreviations: Dppp =1,3-bis(diphenylphosphino)propane; (*S*)-BDPP = 2,4-bis(diphenylphosphino)pentane; (*S*,*S*)-DIOP = (2*S*,3*S*)-(+)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane; Dipp = 1,3-bis(diisopropylphosphino)propane.

Polymerization of hexadiene/CO using the Dppp ligand in methanol solvent afforded a very low yield (ca. 3%) of a low-MW copolymer (entries 1 and 2, Table 1). When a solvent system of 95:5 chloroform:methanol is used under similar conditions (entry 3, Table 1), we observe a 10-fold increase in the yield and a 25-fold increase in the molecular weight of the resulting polymer. Drent and others have shown that methanol acts both as an initiator and as a chain transfer agent for the polymerization.[2] The higher molecular weights observed in chloroform are consistent with a lower rate of chain transfer by methanol under these conditions.

We have not optimized yields for the production of soluble products; nevertheless, it is clear that monomer concentration is important for obtaining soluble polymers.[17] Part of the material isolated at monomer concentrations of 0.67 M (entry 7) was insoluble and presumably cross-linked hexadiene/CO polymer products (they are insoluble and they swelled when we attempted to dissolve them).

Polymer 2 from 1,3-Bis(diphenylphosphino)propane (Dppp). The cyclopolymerization of 1,5-hexadiene with CO with a Shell catalyst system containing the Dppp ligand (Table 1, entry 3) yielded a copolymer which was soluble in chloroform and assigned the structure **2** (eq 2) based on the following analysis of IR and NMR spectroscopic data. We could detect only traces of unsaturation by ^1H or ^{13}C NMR. As the polymer is soluble in chloroform, the extent of cross-linking (which would also eliminate olefinic resonances to give saturated peaks) must be small. Thus, we conclude that the low level of residual unsaturation is due to a high selectivity for cyclization to form a linear cyclopolymer.[17]



2

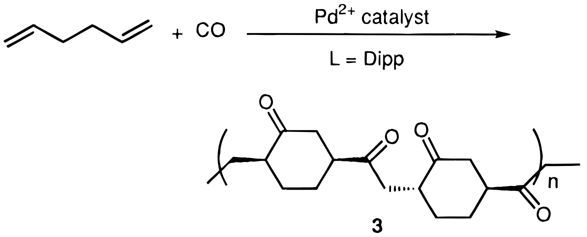
(2)

The IR spectrum of **2** displays two CO stretching bands, one at 1710 cm^{-1} and a higher frequency band of lower intensity at 1738 cm^{-1}. The band at 1710 cm^{-1} is characteristic of unstrained carbonyl groups[22] and is assigned to exocyclic carbonyl groups along the polymer backbone and endocyclic carbonyl groups contained in 6-membered rings. The higher frequency band at 1738 cm^{-1} is characteristic of a carbonyl contained in a 5-membered ring (cyclopentanone ν(CO) = 1751 cm^{-1}).[22]

Further evidence for the presence of both 5- and 6-membered rings is provided by the ^{13}C NMR spectra. The carbonyl region of the ^{13}C NMR spectrum of **2** contains two sets of resonances, one at 206−210 ppm and the other at 219−220 ppm. The first set occurs in a region expected for unstrained carbonyl groups (cyclohexanone δ = 211 ppm);[22] the set at higher field (219−220 ppm) are diagnostic for a cyclopentanone-type structure (cyclopentanone δ = 218 ppm).[22] The presence of 6-membered rings in **2** was also indicated by comparison of ^{13}C resonances of **2** with those of the related polymer **3**, prepared from 1,3-bis(diisopropylphosphino)propane (Dipp; vide infra). In particular, resonances at δ = 51.8 and 49.0 ppm in the ^{13}C NMR spectra (Figure 1a vs Figure 1b) were assigned to methine carbons of 6-membered rings adjacent to the carbonyl group.

Polymers obtained from DIOP and BDPP ligands (entries 4 and 5) show a similar microstructure to those obtained with Dppp. The polymer obtained from (*S*,*S*)-DIOP showed a small but measurable optical rotation $[\alpha]_{589}$ = +6.7° (*c* = 0.016, $CHCl_3$, 20 °C).[23,24]

Polymer 3 from 1,3-Bis(diisopropylphosphino)propane (Dipp). The cyclopolymerization of 1,5-hexadiene with CO with a Shell catalyst system containing the 1,3-Dipp ligand (Table 1, entries 6 and 7) yielded a copolymer which was soluble in chloroform and assigned the structure **3** (eq 3) based on the following analysis of IR and NMR spectroscopic data. The absence of resonances in the ^1H and ^{13}C NMR corresponding to olefins and the solubility in $CHCl_3$ indicate a high selectivity for cyclization to give a linear cyclopolymer.



3

(3)

The IR spectrum of **3** contains a single strong carbonyl stretching band at 1708 cm^{-1} and no evidence of a shoulder at 1738 cm^{-1}. Furthermore, in the carbonyl region of the ^{13}C NMR spectra, we detected a series of resonances in the region δ = 208−211 ppm, but no resonances in the region δ = 219−220 ppm corresponding to cyclopentanone carbonyl groups. On the basis of this evidence, we conclude that this soluble cyclopolymer contains predominantly 6-membered cyclic ketones.

The aliphatic region of the ^{13}C NMR spectra of **3** contains 12 prominent peaks as well as several smaller peaks (Figure 1b). A ^{13}C DEPT spectrum of **3** indicated that the peaks between 51.8 and 45.3 ppm were due to CH type carbons and the peaks between 42.7 and 26.1 ppm were due to CH_2 type carbons. This chemical shift and DEPT data are consistent with 4 *C*HC=O reso-

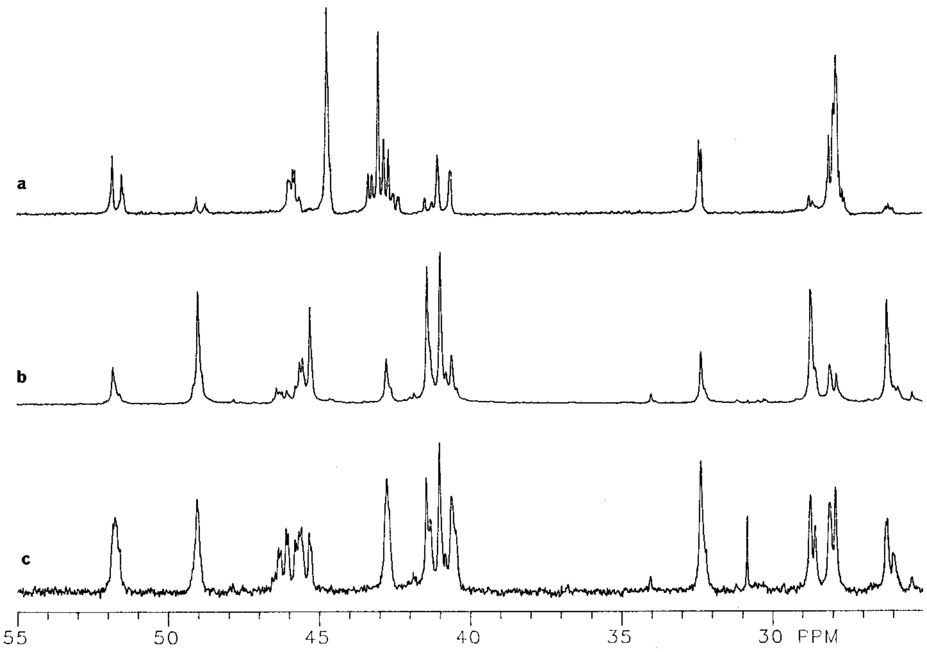


Figure 1. ^{13}C NMR of aliphatic region for 1,5-hexadiene copolymers: (a) polymer **2** from Dppp; (b) polymer **3** from Dipp; (c) 50% epimerized polymer **3** from Dipp.

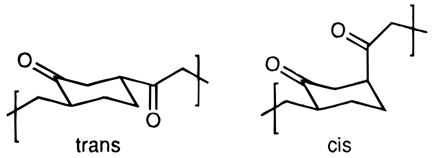
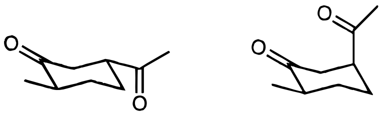


Figure 2. *trans-* and *cis*-cyclohexanone repeating units.



4 **5**

Figure 3. Conformations of *cis*- and *trans*-1,3-disubstituted cyclohexanone diastereomers.

nances at 51.8, 49.0, 45.6/45.5, and 45.3 ppm; 4 CH_2CO resonances at 41.3, 40.7, 42.7, and 40.5; and 4 high-field CH_2 resonances at 32.2, 28.6, 28.0, and 26.1 ppm. The number and type of resonances observed are consistent with the presence of both *cis*- and *trans*-2,5-disubstituted 6-membered ring ketones. In addition, from the relative intensities of the resonances at 51.8 vs 49.0 ppm ($CH_2CHC{=}O$); 45.5,45.6 vs 45.3 ppm ($CH_2CHC{=}O$); and 42.7/40.5 vs 41.3/40.7 ppm ($CH_2CH_2C{=}O$), we conclude that there is an unequal ratio of 6-membered ring diastereomers formed in this cyclocopolmerization. The ratio of diastereomers is approximately 1:3, although we were unable to assign which are the major and minor diastereomers from these data.

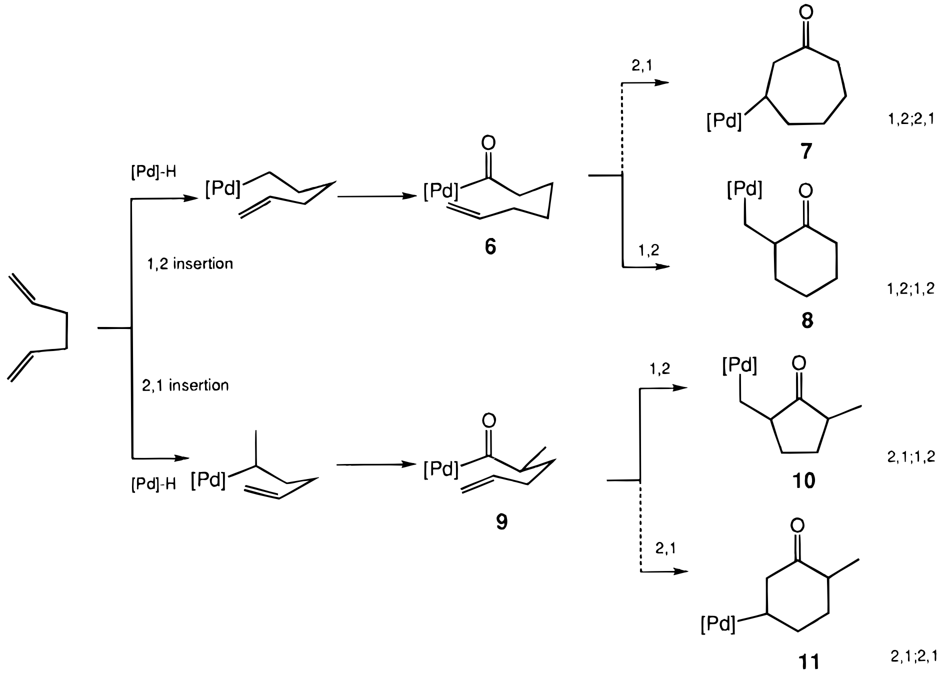
In an effort to provide further information on the structural assignment of these polymers, we carried out epimerization studies of **3**. For 2,5-disubstituted cyclohexanones the *trans* isomer has diequatorial substituents whereas the *cis* isomer has one axial and one equatorial substituent (Figure 2). If the kinetically formed ratio of diasteromers is different from the thermodynamically preferred ratio of diastereomers, then epimerization of the polymer should lead to a change in the diastereomeric ratio.

A solution of **3** was refluxed in $CHCl_3$ with 4-(dimethylamino)pyridine (DMAP). This yielded considerable insoluble material, which was likely crosslinked polymer due to intramolecular aldol condensations mediated by DMAP. The soluble fraction was isolated and dissolved in tetrachloroethane-d_2. Analysis by ^{13}C NMR at 75 °C revealed a decrease in the intensity of peaks at 49.0, 45.2, 41.3, 40.7, 28.6, and 26.1 ppm (the original major isomer) and a corresponding increase in the intensity of peaks at 51.8, 45.4, 42.7, 40.5, 32.2, and 28.0 ppm (the original minor isomer). Shown in Figure 1c is the spectrum of the polymer obtained after approximately 50% epimerization. The reaction was monitored at several stages until the ^{13}C NMR spectrum of the remaining soluble material exhibited a major:minor ratio in favor of the original minor isomer (ca. 4:1). Although we were unable to independently confirm which diastereomer is the thermodynamically more stable, it is reasonable to assign the diequatorial *trans* isomer as the more stable diastereomer. The results of a molecular mechanics calculation[25] on compounds **4** (a model compound for the *trans*-substituted cyclic ketone) and **5** (a model compound for the *cis*-substituted ketone) appear to support this assumption; the lowest energy conformation for *trans*-**4** is thermodynamically more stable than that for the *cis*-**5** by about 1 kcal/mol (Figure 3). Although this energy difference is not great, it does imply that the *trans* ring structure is thermodynamically more stable than the *cis* structure.

The epimerization results would imply that the NMR signals at 49.0, 45.2, 41.3, 40.7, 28.6, and 26.1 ppm are due to the less stable *cis* isomer, which upon epimerization isomerizes to the *trans* isomer. Thus, we tentatively assign the microstructure of **3** to be a 3:1 mixture of *cis* and *trans* 6-membered rings. These results would suggest that the diastereoselectivity for the formation of 6-membered rings is predominantly *cis* in the presence of the Dipp ligand. In contrast, if one compares the ratio of resonances at 51.8 and 49.0 ppm in Figure 1a for polymer **2** obtained from the Dppp ligand, it appears that the diastereoselectivity for the 6-membered rings in this case favors the *trans* rings. It is not possible at this time to determine the diastereoselectivity for the 5-membered rings.

Regioselectivity. While the factors controlling the regio- and stereoselectivity for the copolymerization of

Scheme 1. Regioselectivity of Olefin Insertion



styrene and CO are reasonably well understood,[7-9] the situation for α-olefin/CO copolymers is less well defined.[10] End-group analysis, which is generally a powerful method for establishing the regioselectivity of addition,[11] is not always straightforward for these olefin/CO copolymers since the chains can initiate or terminate with both ketones and esters.[2,11,26] Consiglio[10,12,13] and Sen[14,15,27] have recently reported highly regio- and stereoselective copolymerization of propylene and CO, but in these cases they were unable to unambiguously establish the regioselectivity of addition of propylene. The only case where the regiochemistry of addition of an α-olefin has been unambiguously established was in Takaya's recent elegant study of the enantioselective polymerization of propylene and CO with Pd(II) complexes of (*R*,*S*)-BINAPHOS.[16,28] In this case, Takaya spectroscopically identified intermediates which showed that the high regioselectivity for these chiral ligands was due to a primary 1,2-insertion of propylene.

At the time that we had initiated our studies, Consiglio[29] had reported that propylene/CO copolymers obtained with catalysts containing 1,3-bis(diphenylphosphino)propane (Dppp) are regioirregular due to both 1,2- and 2,1-insertion of propylene. However, propylene/CO copolymers obtained with catalysts containing 1,3-bis(diisopropylphosphino)propane (Dipp) or 1,3-bis(dicyclohexylphosphino)propane are regioregular. In this case, it was not possible to establish if regioregularity was due to 1,2- or 2,1-insertion of propylene. The present studies on the cyclocopolymerization of 1,5-hexadiene and CO utilizing the same ligands shed some light on the factors which govern the regioselectivity of olefin insertion with these ligands.

Scheme 1 relates the regioselectivity of insertion to the nature of the ring formed in the cyclocopolymerization of 1,5-hexadiene and CO. An initial 1,2- or primary insertion of the diene yields a primary carbon bonded to Pd. Following insertion of CO to give **6**, there are two possibilities, a 2,1-insertion to generate a 7-membered ring **7** or a 1,2-insertion to generate a 6-membered ring **8**. Alternatively, an initial 2,1- or secondary insertion of the diene yields an intermediate with a secondary carbon bonded to Pd. In this case, CO insertion to give **9** followed by a 1,2-insertion yields a 5-membered ring **10**, whereas CO insertion followed by a second 2,1-insertion yields a 6-membered ring **11**. Thus, there is only one way to form a 5- or 7-membered ring, but two ways in which a 6-membered ring might form.

At present, our results are inconclusive with regard to the formation of 7-membered rings. They may be present, but we have no unambiguous evidence by IR or NMR for their occurrence in these copolymers. The presence of both 5- and 6-membered rings in copolymers **2** derived from Dppp suggests quite strongly that an initial 2,1-insertion is a facile process with this ligand since the only way to produce a 5-membered ring is by an initial 2,1-insertion. The formation of 6-membered rings can be rationalized either by a 1,2/CO/1,2-insertion sequence to give **8** or via a 2,1/CO/2,1-insertion sequence to give **11** (Scheme 1). Experimentally, it is impossible to determine whether 6-membered rings are derived from a 1,2/CO/1,2-insertion sequence or a 2,1/CO/2,1-insertion sequence. However, if one tries to construct molecular models to mimic the transition state for formation of the 6-membered ring **11** from the intermediate acyl **9**, it is difficult to arrange the pendant olefin in a geometry conducive to insertion into the Pd−acyl bond (Figure 4).[30]

Thus, if we conclude that 6-membered rings are not likely to be formed by a 2,1/CO/2,1-insertion sequence, then the presence of 6-membered rings is a signature for an initial 1,2-insertion of the diene and the presence of 5-membered rings in the polymer is a signature for an initial 2,1-insertion of the diene. This analysis would imply that the mixture of 5- and 6-membered rings observed in the polymer **2** derived from Dppp is a consequence of a lack of regioselectivity in the initial insertion of the olefin in the presence of this ligand. The high regioselectivity for 6-membered rings observed in the formation of polymer **3** derived from Dipp is indicative of a preference for an initial 1,2-insertion of the olefin into the Pd−acyl bond. Presumably, the greater steric demands imposed by the diisopropyl groups (or

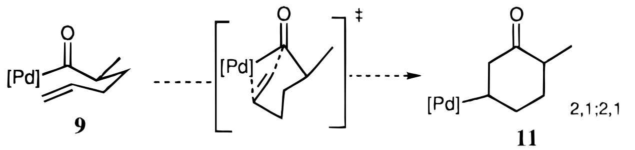


Figure 4. Transition state for 2,1/CO/2,1 insertion involves considerable strain.

the electron-donating character[12,31] of the Dipp ligand) favor a 1,2-insertion of the monomer.

Consiglio has obtained regioirregular propylene/CO copolymers with the 1,3-Dppp ligand containing catalyst, the same one which gives regioirregular **2**. By analogy, we propose that the high degree of regioregularity observed for the propylene/CO copolymer obtained by Consiglio with the catalyst containing the 1,3-Dipp ligand results from a high degree of regioselectivity for 1,2-insertion.

Conclusion

The reaction of 1,5-hexadiene with CO in the presence of a Shell-type Pd^{2+} catalyst system employing the 1,3-Dppp ligand produces a regioirregular copolymer **2** which contains both 5- and 6-membered ring ketones. By changing the ligand to the more basic and sterically more demanding Dipp, we obtain the more regioregular copolymer **3** containing almost entirely 6-membered ring ketones. The formation of 6-membered ring ketones in both **2** and **3** is most consistent with a mechanism involving initial 1,2-insertion of hexadiene into an intermediate Pd−acyl species, whereas the formation of 5-membered ring ketones in **2** involves an initial 2,1-insertion of hexadiene. The initial 1,2-insertion regiochemistry with the Dipp catalyst gives the least sterically hindered insertion product due to an unfavorable steric interaction between the bulky isopropyl groups on the phosphine ligand and the alkyl substituent on the α-olefin. By analogy, we propose that the mechanism for the formation of highly regioregular propylene/CO copolymer obtained using a Dipp-containing catalyst system similarly involves a 1,2-insertion regiochemistry of propylene into an intermediate Pd−acyl species.

Experimental Section

Polymerization solvents $CHCl_3$ and methanol were not dried but were degassed prior to use. 1,5-Hexadiene (Wiley Organics, 99%) and CO (Liquid Carbonic, 99.5%) were used as received. $Pd(OAc)_2$ (Strem Chemicals), $[Ni(ClO_4)_2 \cdot 6H_2O]$ (Aldrich), 1,4-naphthaquinone (Aldrich), and 4-(dimethylamino)pyridine (Aldrich) were used as received. 1,3-Bis(diisopropylphosphino)propane was prepared as in the literature.[32] Polymerization reactions were performed in a 1-L Autoclave (Autoclave Engineers). The bomb was connected to a stainless steel vacuum manifold equipped with steel-reinforced Teflon hoses for bomb evacuation and purging with argon and pressurization with CO. IR spectra were obtained using KBr pellets on a Perkin-Elmer Model 1600 FT-IR spectrometer. NMR spectra were obtained at 75 °C in CD_2ClCD_2Cl (using residual protons for reference) on a Varian 400 MHz spectrometer operating at 100 MHz for ^{13}C. Calculations were performed with Macromodel (W. C. Still, Columbia) by Rich Taylor in the Wender Group. Analyses were performed by E+R Microanalytical Laboratory, Corona, NY.

1,5-Hexadiene/CO Copolymer (Entry 7). The catalyst solution was prepared as follows: A solution of $CHCl_3$ (24 mL) and methanol (1 mL) was prepared and degassed at −72 °C. To this were added 1,3-bis(diisopropylphosphino)propane (0.1110 g, 0.4016 mmol), $Pd(OAc)_2$ (0.0901 g, 0.4016 mmol), $Ni(ClO_4)_2 \cdot 6H_2O$ (0.2006 g, 0.5485 mmol), and 1,4-naphthaquinone (0.4004 g, 2.55 mmol). To this solution was added 100 mL of degassed $CHCl_3$. To a previously degassed 1-L bomb, the catalyst solution was transferred via cannula under an argon counterflow. Similarly, 1,5-hexadiene (10 mL) was transfered to the bomb, which was then sealed and pressurized with CO (520 psig). The reaction was stirred (stirbar, magnetic stirrer) for 2 days at ambient temperature during which the pressure dropped to about 420 psig. The CO was released, and the product mixture was filtered through a glass frit, leaving a small amount of dark insoluble precipitate which contained black Pd^0 metal particles. To the filtrate was added 400 mL of methanol, resulting in a white precipitate, which was filtered and dried over high vacuum. Yield: 3.62 g of solid white powder. $\{^1H\}^{13}C$ NMR (100 MHz, $CDCl_2CDCl_2$, 75 °C) major resonances: ($CH_2\mathit{C}HC{=}O$) 49.0, 45.2; ($CH_2\mathit{C}H_2C{=}O$) 41.3, 40.7; ($CH\mathit{C}H_2\mathit{C}H_2CH$) 28.6, 26.1; minor resonances: ($CH_2\mathit{C}HC{=}O$) 51.6, 45.4; ($CH_2\mathit{C}H_2C{=}O$) 42.7, 40.5; ($CH\mathit{C}H_2\mathit{C}H_2CH$) 32.2, 28.0). Anal. Calcd: C, 69.54; H, 7.29. Found: C, 69.36; H, 7.46.

Epimerization of Copolymer. A solution of the copolymer (0.136 g, 1.23 mmol) and 4-(dimethylamino)pyridine (0.210 g, 1.72 mmol) in $CHCl_3$ was heated to reflux for 3.5 h. The mixture was filtered through a coarse frit, and 100 mL of methanol was added to the filtrate, producing a white precipitate, which was washed 1 × 5 mL of methanol and dried over high vacuum. A $\{^1H\}^{13}C$ spectrum (15 mg of polymer, $CDCl_2CDCl_2$, 75 °C) revealed that the original *cis*:*trans* ratio of 3:1 was now 1:1 (Figure 1c). To the tube was added additional 4-(dimethylamino)pyridine (14.3 mg, 0.12 mmol), and the tube was heated to a bath temperature of 100 °C for 2 h. Additional solid formed during this time. The major resonances in the $\{^1H\}^{13}C$ spectrum of the treated polymer now correspond to the minor resonances for the original copolymer.

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Supporting Information Available: ^{13}C NMR spectra of the carbonyl region for polymers **2** and **3** (1 page). Ordering information is given on any current masthead page.

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