Remarkable Differences in Catalyst Activity and Selectivity for the Production of Methyl Propanoate versus CO−Ethylene Copolymer by a Series of Palladium Complexes of Related C_4-Bridged Diphosphines

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The C_4-bridged diphosphines *cis*- and *trans*-1,2-bis(diphenylphosphinomethyl)cyclohexane (*cis*, **1a**; *trans*, **1b**) and *endo,endo*-2,3-bis(diphenylphosphinomethyl)norbornane and *exo,endo*-2,3-bis(diphenylphosphinomethyl)norbornane (*endo,endo*, **1c**; *exo,endo*, **1d**) and their corresponding palladium complexes [(P−P)$PdCl_2$] (**2a**−**d**), [(P−P)$Pd(OAc)_2$] (**3a**−**d**), and [(P−P)PdMeCl] (P−P = **1a**, **4a**; P−P = **1c**, **4c**) have been prepared and characterized. Single-crystal X-ray analysis of **2a** reveals that **1a** forms a seven-membered chelate ring with the *cis*-disubstituted cyclohexyl ring in the expected chair conformation. Variable-temperature $^{31}P\{^1H\}$ NMR studies of **2a** have revealed a dynamic process that interchanges stereoisomers via conformational changes in the six-membered ring, often characteristic of *cis*-disubstituted cyclohexane derivatives. The free energy of activation associated with this exchange has been determined ($\Delta G^{\ddagger}$ = 48 kJ mol^{-1}, **2a**). Variable-temperature $^{31}P\{^1H\}$ and ^{31}P NOESY NMR studies have shown that **4a** exist as an interconverting mixture of isomers which differ in the position of the Pd−Me, *trans* either to an axial or to an equatorial diphenylphosphinomethyl group. The free energy of activation associated with this interchange ($\Delta G^{\ddagger}$ = 44.2 kJ mol^{-1}), as determined from a line shape analysis of the $^{31}P\{^1H\}$ NMR spectra in the temperature range 213−308 K, is similar to that for **2a** and consistent with a process involving inversion of the cyclohexane ring. At 213 K, the equilibrium population of these isomers is surprisingly disparate. Full energy minimization calculations at the ZINDO(1) level gave an energy difference between the two minimized structures of 4 kJ mol^{-1}, which corresponds to an equilibrium constant of 5 and is fully consistent with that obtained using NMR spectroscopy. Single-crystal X-ray analysis of **4a** has revealed a square-planar geometry, such that the axial diphenylphosphinomethyl group occupies the site *trans* to the methyl and the equatorial diphenylphosphinomethyl group occupies the position *trans* to the chloride. The single-crystal X-ray structures of compounds **2d** and **4c** are also reported. Methanol solutions of **3a**−**c** and methane sulfonic acid are selective for the copolymerization of ethylene with carbon monoxide, generating low molecular weight polymers. Surprisingly, the activity of catalyst systems based on *cis*-1,2-bis(diphenylphosphinomethyl)cyclohexane (**1a**) is markedly higher than those based on its *trans*-isomer **1b**. In contrast, catalyst systems formed from *exo,endo*-2,3-bis(diphenylphosphinomethyl)norbornane (**1d**) are highly selective for the production of methyl propanoate (>90%).

Introduction

A wide range of catalyst systems based on a palladium precursor and phosphorus or nitrogen donor ligands such as bisphosphines,[1] bisphospholes,[2] mixed phosphole−oxazolines, and other P,N donors,[3] N_2-donors,[4] unsymmetrical phosphine−phosphites,[5] and chelating N-heterocyclic carbenes[6] have been used to catalyze the copolymerization of α-olefins with carbon monoxide. Interest in the copolymerization of CO and olefins has escalated in recent years because of the useful properties of polyketone, which has been heralded as a new engineering thermoplastic, a tough, flexible, wear resistant, high impact strength polymer.[7] A closely related process, the alkoxycarbonylation of olefins, is of immense industrial importance since methyl propanoate, the product of ethylene methoxycarbonylation, is a potential intermediate in the synthesis of acrylic polymers.[8] In addition, alkoxycarbonylation of nonconjugated dienes has been used to synthesize γ-keto esters

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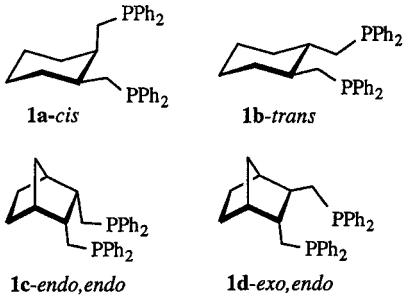
for use in the synthesis of natural products.[9] In the vast majority of cases, catalysts formed from a palladium precursor and a monodentate phosphine are selective for alkoxycarbonylation, while those based on a bidentate phosphine give high molecular weight copolymer. The process of alkoxycarbonylation is clearly intimately related to copolymerization and is thought to involve similar initiation and termination steps, but without chain propagation; that is, chain termination occurs after only a single turnover.[1,4] Given the intimate relationship between these two processes, it would not be surprising to find that subtle modifications in catalyst structure could influence selectivity. For instance, workers at INEOS Acrylics have reported that treatment of $[L_2Pd(dba)]$, where L_2 = the C_4-bridged 1,2-bis(di-*tert*-butylphosphinomethyl)benzene, generates a complex capable of converting ethylene, carbon monoxide, and methanol to methyl propanoate, at a rate of 440 000 g of product per mol of catalyst per hour with a selectivity of 99.98%.[10] In contrast, we have recently discovered that palladium complexes of the C_4-bridged diphosphine, 1,2-bis(2,3,4,5-tetramethylphospholylmethyl)benzene, form highly active catalysts for the selective production of polyketone and that, under our conditions, the activity of this catalyst compares favorably with that based on dppp.[2] The disparate selectivity of these two catalyst systems, both containing an *o*-xylyl backbone, suggests that the origin of selectivity in the palladium-catalyzed carboxylation of ethylene is likely to be more subtle than monodentate versus bidentate coordination.

Chart 1



In an extension of our preliminary studies we have begun to investigate the potential of related C_4-bridged diphosphines, such as 1,2-bis(diphenylphosphinomethyl)cyclohexane and 2,3-bis(diphenylphosphinomethyl)-norbornane derivatives, to catalyze the carboxylation of ethylene, to gain a clearer understanding of the factors that control catalyst selectivity. Reports of catalysis using such ligands are rare and are limited to asymmetric allylic aminations,[11a] hydrogenations,[11b] Diels–Alder reactions,[11c] hydroformylation,[11d] and cross coupling.[11e] We report here two discoveries: first, markedly disparate CO–ethylene copolymerization activities for palladium catalysts based on *cis*- and *trans*-1,2-bis-(diphenylphosphinomethyl)cyclohexane and, second, a dramatic dependence of catalyst selectivity on the stereochemistry of the norbornane-based ligands. *exo,endo*-2,3-Bis(diphenylphosphinomethyl)norbornane generates mainly methyl propanoate, while its *endo,endo* counterpart shows only low copolymerization activity.

Results and Discussion

Synthesis and Characterization of $[(P-P)PdX_2]$ (X = Cl, OAc) and [(P−P)PdMeCl]. Ligands **1a**−**b** and **1d** (Chart 1) were prepared by reacting the corresponding dibromide with lithium diphenyl phosphide, using a modification of the procedure reported for analogous compounds.[12] Unexpectedly, bromination of *endo,endo*-2,3-norbornanedimethanol did not give the corresponding dibromide. However, the corresponding diphosphine, **1c**, could be prepared from the dimesylate of the diol. Dropwise addition of a dichloromethane solution of **1a**−**d** into a dichloromethane solution of

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[(cycloocta-1,5-diene)$PdCl_2$] resulted in a gradual color change from yellow to orange with the formation of [(P−P)$PdCl_2$] (**2a**−**d**), in yields of up to 85%. The $^{31}P\{^1H\}$ NMR spectrum of **2a** contains a single broad resonance at δ 32.0; that of **2b** and **2c**, sharp singlets at δ 24.3 and 30.7, respectively; and that of **2d**, two doublets at δ 32.1 and 27.3 ($^2J_{PP}$ = 7.5 Hz), the latter corresponding to the *endo*- and *exo*-diphenylphosphinomethyl groups. The catalyst precursors [(P−P)Pd(OAc)$_2$] (**3a**−**d**) were prepared by the addition of a concentrated solution of the corresponding diphosphine to a rapidly stirred suspension of [$Pd_3(OAc)_6$], to give a yellow precipitate, which was filtered and washed with toluene and hexane to afford **3a**−**d** as spectroscopically pure solids.[13] In each case the spectroscopic characteristics of compounds **3a**−**d** were similar to those of **2a**−**d**. Complexes **4a** and **4c** were prepared by slow addition of a dichloromethane solution of **1a** and **1c**, respectively, to a dichloromethane solution of [cycloocta-1,5-diene)PdClMe]. The room-temperature $^{31}P\{^1H\}$ NMR spectrum of **4a** contains broad signals at δ 49.0 and 4.0, with a half-height line width of 600 Hz, while that of **4c** contains sharp doublets at δ 38.6 ($^2J_{PP}$ = 38.0 Hz) and 12.1 ($^2J_{PP}$ = 38.0 Hz). The ^1H NMR spectra of **4a** and **4c** each contain high-field doublets of doublets at δ 0.61 ($^3J_{PH}$ = 3.9 Hz, $^3J_{PH}$ = 7.7 Hz) and 0.64 ($^3J_{PH}$ = 3.7 Hz, $^3J_{PH}$ = 7.7 Hz), respectively, characteristic of the palladium-bound methyl.

Variable-Temperature NMR Studies of 2a and 4a. As noted above, the room-temperature $^{31}P\{^1H\}$ NMR spectrum of **2a** contains a single broad resonance, which is not consistent with the solid state structure (vide infra). To investigate further the nature of this line broadening, a variable-temperature $^{31}P\{^1H\}$ NMR study was undertaken, the result of which is shown in Figure 1. The axial and equatorial diphenylphosphinomethyl groups should appear as distinct resonances; yet at room temperature there is only a single broad resonance at δ 32.0, which suggests a time-averaged structure with C_2 symmetry. As the temperature was lowered, this resonance broadens, disappears into the baseline, and reappears as two distinct, well-separated singlets as δ 47.0 and 16.5. While the low-temperature limiting spectrum of **2a** is consistent with the solid state structure, the temperature dependence of the $^{31}P\{^1H\}$ spectrum clearly shows that isomers **2a$_1$** and **2a$_2$** rapidly interconvert on the NMR time scale. The free energy of activation ($\Delta G^{\ddagger}$ = 48 kJ mol^{-1}) has been determined from an analysis of the coalescence behavior in the temperature range 278−283 K and is consistent with conformational changes of the cyclohexane ring, i.e., inversion of a *cis*-disubstituted cyclohexane ring as shown in Chart 2. Such a process generates time-averaged C_2-symmetry to give equivalent diphenylphosphinomethyl substituents. In contrast, there is no noticeable change in the $^{31}P\{^1H\}$ NMR spectrum of **2b** between 298 and 223 K, since the chelating nature of the diphosphine constrains the cyclohexane ring in its diequatorial conformation, preventing it from undergoing ring inversion into its diaxial counterpart. Moreover, the presence of two sharp doublets in the room-temperature $^{31}P\{^1H\}$ NMR spectrum of **2d** is also taken as evidence that the line broadening in the $^{31}P\{^1H\}$ spectrum of **2a** results from axial−equatorial exchange, since ring inversion cannot occur in norbornane derivatives.

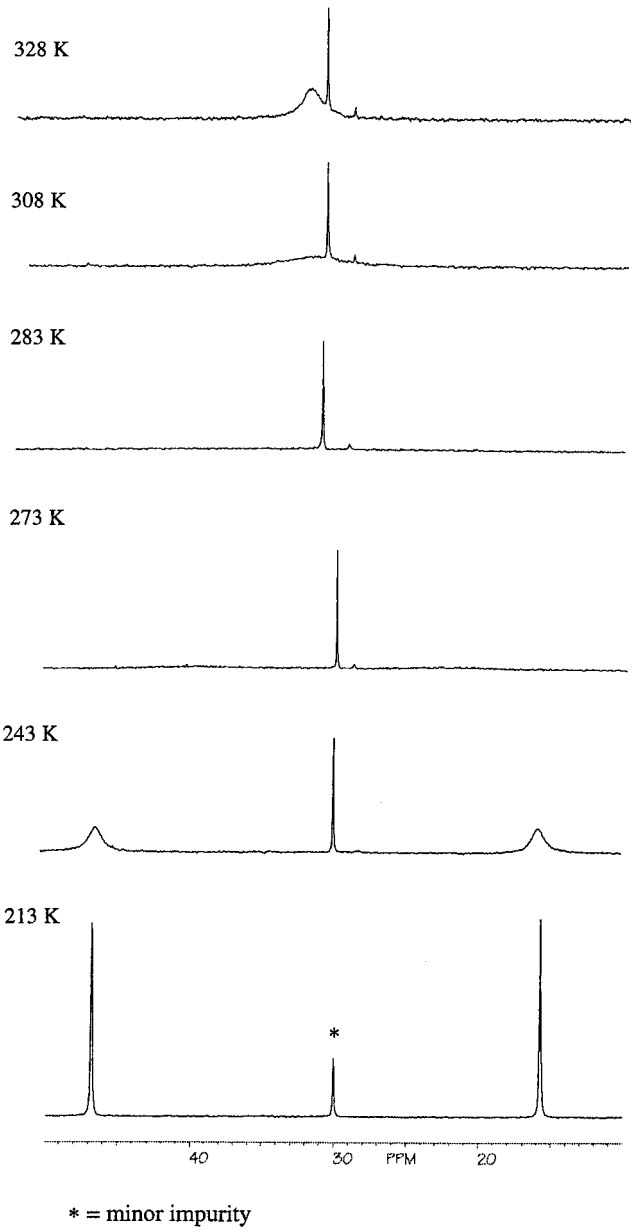
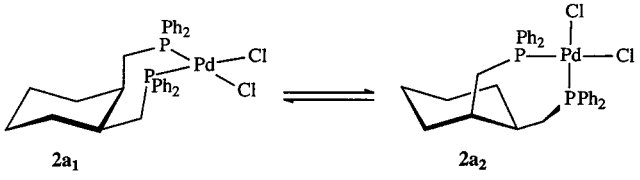


Figure 1. Variable-temperature $^{31}P\{^1H\}$ spectra of [*cis*-1,2-bis(diphenylphosphinomethyl)cyclohexanePdCl_2] (**2a**) recorded in THF.

Chart 2



As expected, the room-temperature $^{31}P\{^1H\}$ NMR spectrum of [*cis*-1,2-bis(diphenylphosphinomethyl)cyclohexanePdMeCl] (**4a**) contains two signals at δ 45.0 and 12.1, which correspond to diphenylphosphinomethyl *trans* to methyl and chloride, respectively. As for **2a**, the signals in the room-temperature $^{31}P\{^1H\}$ NMR spectrum appear as broad, ill-defined resonances, and

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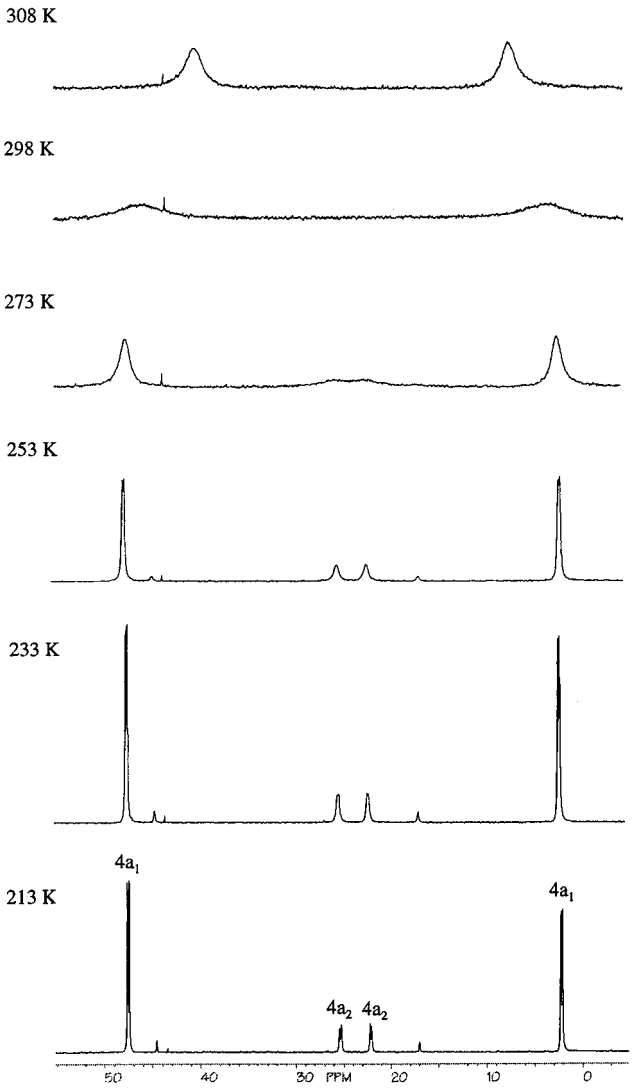


Figure 2. Variable-temperature $^{31}P\{^1H\}$ spectra of [*cis*-1,2-bis(diphenylphosphinomethyl)cyclohexanePdMeCl] (**4a**) recorded in THF.

a variable-temperature NMR study was undertaken to investigate the cause of this line broadening (Figure 2). At 213 K, **4a** exists as a 5.5:1 mixture of two conformers in slow exchange. The major isomer appears as a pair of doublets at δ 47.5 and 2.2 ($^2J_{PP} = 34.7$ Hz); the minor isomer, as doublets at δ 25.4 and 22.1 ($^2J_{PP} = 36.0$ Hz). The temperature dependence of the $^{31}P\{^1H\}$ NMR spectra shows that these two isomers interconvert, and a low temperature (253 K) ^{31}P NOESY spectrum confirmed that the signals corresponding to the major isomer at δ 47.4 and 2.2 undergo pairwise exchange with those belonging to the minor isomer at δ 25.4 and 22.1, respectively (Figure 3). Above room temperature the major (491) and minor (492) isomers interconvert rapidly (Chart 3) to give an averaged spectrum. The free energy of activation for this exchange ($\Delta G^{\ddagger} = 44.2$ kJ mol^{-1}) was determined from a line shape analysis of the spectra shown in Figure 2 and is similar to that calculated for **2a**, strongly suggesting that the same dynamic process is responsible for the line broadening, i.e., interconversion of isomers in which the Pd−Me is *trans* to axial and equatorial diphenylphosphino methyl groups via cyclohexane ring inversion. Low-temperature

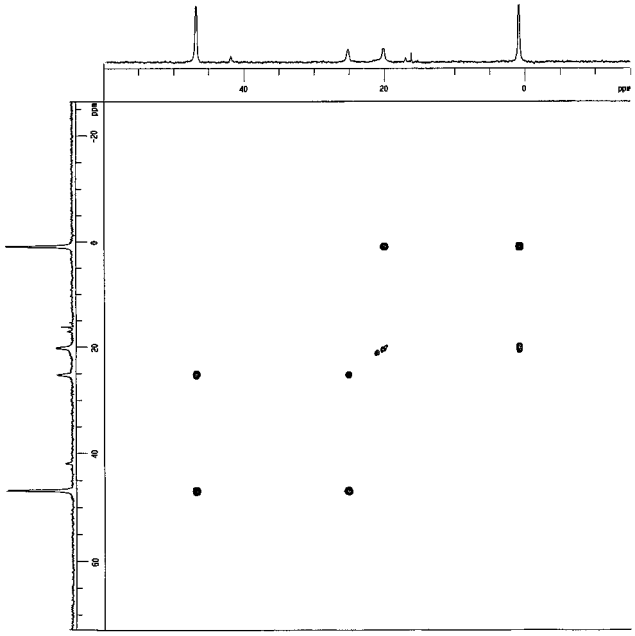
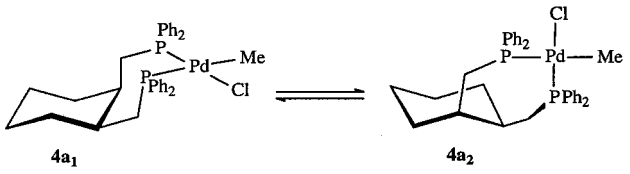


Figure 3. ^{31}P NOESY spectrum of [*cis*-1,2-bis(diphenylphosphinomethyl)cyclohexanePdMeCl] (**4a**) recorded at 243 K.

Chart 3



$^1H\{^{31}P\}$ NMR spectra, selectively decoupled at δ 47.6 and 2.2, confirm that the former signal corresponds to the phosphine *trans* to Pd−methyl, since irradiating at this frequency removed the large phosphorus−hydrogen coupling constant ($^3J_{PH} = 7.7$ Hz), while that the latter signal belongs to the phosphine *trans* to chloride, since irradiating at δ 2.2 removed the smaller phosphorus−hydrogen coupling constant ($^3J_{PH} = 3.9$ Hz).

The most surprising feature of the NMR studies on **4a** is the disparate populations of these two isomers, indicating a discernible energy difference between **4a$_1$** and **4a$_2$**. The molecular system **4a** was drawn using the SPARTAN software package, and the structure was minimized using MM2 methods. The coordination geometry around the metal center was constrained as square planar, but no other constraints were imposed. After obtaining an energy-minimized structure in this way more detailed conformation searches were made using the semiempirical methods with ZINDO(1) parameters. A full geometry optimization was made for the molecule in vacuo, and the various bond lengths and angles were measured. The methyl and chloride substituents were exchanged, and a full energy minimization was made at the ZINDO(1) level. The two minimized structures are shown in Figure 4. An energy difference between the two minimized structures of 4 kJ mol^{-1} was obtained, which corresponds to an equilibrium constant, K, of 5 ($\Delta E = -RT \ln K$) at room temperature and 7.8 at 233 K. This value is supported by the low-temperature $^{31}P\{^1H\}$ NMR spectrum of **4a**, from which an equilibrium ratio of 5.5:1 was calculated

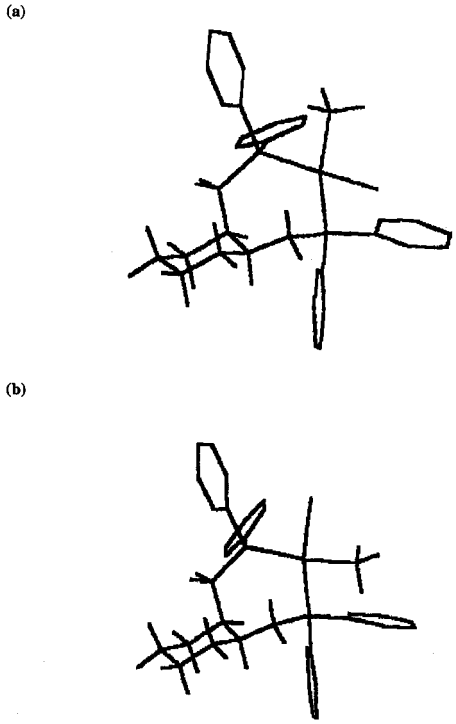


Figure 4. Energy-minimized conformations for (a) **4a$_1$** and (b) **4a$_2$** using ZINDO(1) parameters. Hydrogen atoms on the phenyl rings have been omitted for clarity.

for **4a$_1$** and **4a$_2$**. The main structural difference between the two forms concerns the P−Pd−Cl angle, this being 88.5° in **4a$_1$** and 93.5° in **4a$_2$**. Of the two forms, calculations imply that **4a$_1$** is the more stable. Molecular dynamics simulations run over 1 ns indicate that the two species interconvert. Using the intrinsic reaction coordinate method, an approximate transition state (TS) structure was determined. The energy of this hypothetical TS was calculated at the ZINDO(1) level to be 38 kJ mol^{-1} above that of **4a$_1$**. It was subsequently confirmed that the TS structure could relax into either **4a$_1$** or **4a$_2$**, suggesting that it is a genuine TS. The results obtained from energy minimization at the ZINDO(1) level lend further support to our interpretation of the $^{31}P\{^1H\}$ NMR studies described above.

X-ray Structures of [*cis*-1,2-Bis(diphenylphosphinomethyl)cyclohexanePdCl$_2$] (2a) and [*exo,endo*-2,3-Bis(diphenylphosphinomethyl)norbornanePdCl$_2$] (2d). The lack of structural data for palladium(II) complexes of *cis*-1,2-bis(diphenylphinomethyl)cyclohexane and *exo,endo*-2,3-bis(diphenylphosphinomethyl)-norbornane prompted us to undertake single-crystal X-ray analyses of **2a** and **2d**. Single-crystals of **2a**·$CHCl_3$ and **2d** suitable for X-ray analysis were grown from a chloroform solution layered with diethyl ether and a dichloromethane solution layered with *n*-hexane, respectively. Perspective views of the molecular structures of **2a** and **2d**, together with the atomic numbering scheme, are illustrated in Figures 5 and 6, respectively, a selection of bond lengths and angles is listed in Table 1, and crystal data are presented in Table 4. Since the structures of both compounds are based on a palladium complex of a C_4-bridged diphosphine and are clearly related, they will be discussed in parallel. In both **2a** and **2d** the coordination sphere around Pd(1) is close to square planar, as indicated by a dihedral angle of 2.8°

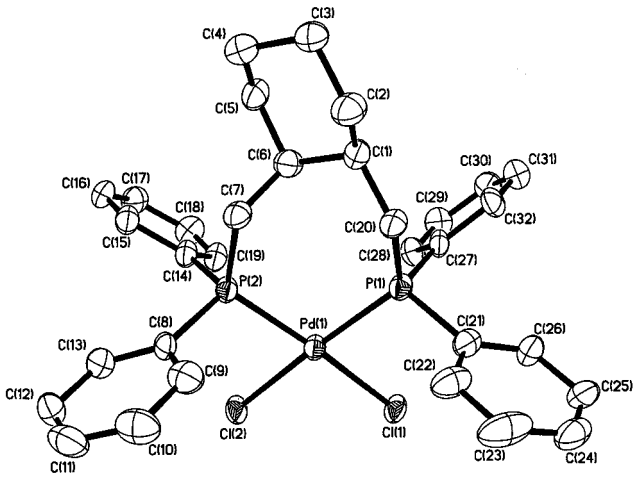


Figure 5. Molecular structure of **2a**. Hydrogen atoms and the $CHCl_3$ molecule of crystallization have been omitted. Ellipsoids are at the 50% probability level.

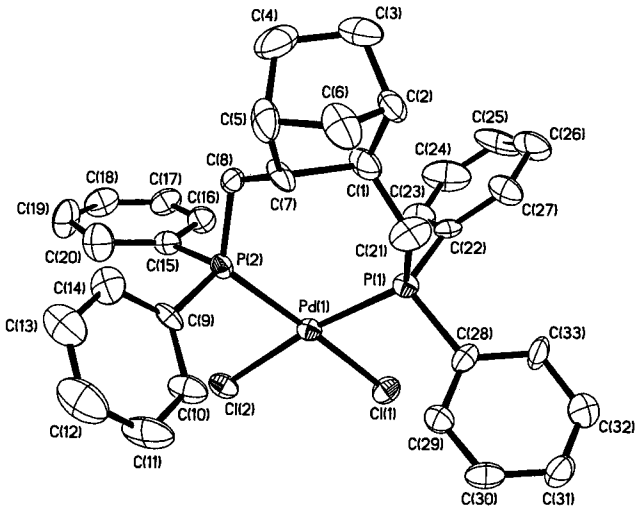


Figure 6. Molecular structure of **2d**. Hydrogen atoms have been omitted. Ellipsoids are at the 40% probability level.

(**2a**) and 5.8° (**2d**) between the planes containing P(1)-Pd(1)P(2) and Cl(1)Pd(1)Cl(2). The Pd−P bond lengths in **2a** [Pd(1)−P(2) = 2.2532(17), Pd(1)−P(1) = 2.2647-(17) Å] are similar to those in **2d** [Pd(1)−P(1) = 22694-(16), Pd(1)−P(2) = 2.2734(17) Å] and are within the range expected for related palladium diphosphine complexes such as [Pd(dppe)Cl$_2$][14] and [Pd(dppb)Cl$_2$].[15] The natural bite angles of 100.53(6)° (**2a**) and 102.46(3)° (**2d**) for P(1)−Pd(1)−P(2) are similar to that reported for [Pd(dppf)Cl$_2$] (∠PPdP = 99.10°)[16,17] and slightly larger than that in the palladium dichloride complex of the C_4-bridged diphosphine 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane (∠PPdP = 96.78°).[18] The cyclohexane ring in **2a** adopts the familiar chair conformation, with one diphenylphosphinomethyl axial and one equatorial. In both **2a** and **2d** the angle Cl(1)Pd-

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Table 1. Selected Bond Distances (Å) and Angles (deg) for 2a and 2d

2a		2d	
Pd(1)−Cl(1)	2.3539(16)	Pd(1)−Cl(1)	2.3347(17)
Pd(1)−Cl(2)	2.3552(16)	Pd(1)−Cl(2)	2.3313(16)
Pd(1)−P(1)	2.2647(17)	Pd(1)−P(1)	2.2694(16)
Pd(1)−P(2)	2.2532(17)	Pd(1)−P(2)	2.2734(17)
P(1)−C(20)	1.833(6)	P(1)−C(21)	1.854(5)
P(2)−C(7)	1.826(7)	P(2)−C(8)	1.803(7)
C(1)−C(20)	1.534(9)	C(1)−C(21)	1.492(9)
C(1)−C(6)	1.533(9)	C(1)−C(7)	1.560(4)
C(6)−C(7)	1.559(10)	C(7)−C(8)	1.536(8)
P(1)−Pd(1)−P(2)	100.53(6)	P(1)−Pd(1)−P(2)	102.46(3)
Cl(1)−Pd(1)−Cl(2)	90.66(6)	Cl(1)−Pd(1)−Cl(2)	89.83(3)
P(1)−Pd(1)−Cl(1)	84.77(6)	P(1)−Pd(1)−Cl(1)	83.71(7)
P(2)−Pd(1)−Cl(2)	83.98(6)	P(2)−Pd(1)−Cl(2)	84.32(7)
Pd(1)−P(1)−C(20)	122.9(2)	Pd(1)−P(1)−C(21)	124.1(2)
P(1)−C(20)−C(1)	120.7(5)	P(1)−C(21)−C(1)	115.8(4)
C(20)−C(1)−C(6)	113.9(6)	C(21)−C(1)−C(7)	111.9(5)
C(1)−C(6)−C(7)	112.5(6)	C(1)−C(7)−C(8)	115.3(5)
C(6)−C(7)−P(2)	111.9(5)	C(7)−C(8)−P(2)	114.9(4)
C(7)−P(2)−Pd(1)	119.6(2)	C(8)−P(2)−Pd(1)	123.73(19)

Table 2. Selected Bond Distances (Å) and Angles (deg) for 4a and 4c

4a		4c	
Pd(1)−Cl(1)	2.3577(9)	Pd(1)−Cl(1)	2.350(2)[a]
Pd(1)−C(33)	2.160(3)	Pd(1)−C(18)	2.0504(10)[a]
Pd(1)−P(1)	2.3487(7)	Pd(1)−P(1)	2.2760(9)[a]
Pd(1)−P(2)	2.2463(8)	P(1)−C(5)	1.837(3)
P(1)−C(20)	1.845(3)	C(4)−C(5)	1.528(5)
P(2)−C(7)	1.836(3)	C(4)−C(4A)	1.584(6)
C(1)−C(20)	1.531(4)		
C(1)−C(6)	1.543(4)		
C(6)−C(7)	1.550(4)		
P(1)−Pd(1)−P(2)	101.00(3)	P(1)−Pd(1)−P(1A)	102.03(5)
Cl(1)−Pd(1)−C(33)	82.48(8)	C(18)−Pd(1)−Cl(1)	86.2(7)[a]
P(1)−Pd(1)−Cl(1)	88.63(3)	C(18)−Pd(1)−P(1)	85.2(9)[a]
P(2)−Pd(1)−C(33)	87.84(8)	P(A)−Pd(1)−Cl(1)	86.5(2)[a]
Pd(1)−P(1)−C(20)	122.08(9)	Pd(1)−P(1)−C(5)	121.17(11)
P(1)−C(20)−C(1)	116.06(9)	P(1)−C(5)−C(4)	113.4(2)
C(20)−C(1)−C(6)	114.2(2)	C(5)−C(4)−C(4A)	118.42(18)
C(1)−C(6)−C(7)	112.2(2)		
C(6)−C(7)−P(2)	112.48(19)		
C(7)−P(2)−Pd(1)	118.29(9)		

[a] Note: restraints applied to geometry due to methyl/chloride interchange disorder.

(1)Cl(2) is close to 90° (**2a**, 90.66(6)°; **2d**, 89.83(3)°), and the large natural bite angle of the diphosphine manifests itself in the compression of the two P−Pd−Cl angles, which are significantly lower than 90° [P(2)−Pd(1)−Cl(2) = 83.98(6)°, P(1)−Pd(1)−Cl(1) = 84.77(6)°, **2a**; P(1)−Pd(1)−Cl(1) = 83.71(7)°, P(2)−Pd(1)−Cl(2) = 84.32(7)°, **2d**]. A diphosphine bridged by an *endo,endo*-1,4-substituted norbornyl tether, prepared by Casey, has an estimated natural bite angle of 126.1° and a calculated 12.2 kcal mol^{-1} increase in steric energy upon chelation.[19] Not surprisingly, there are no examples of monomeric complexes of this diphosphine. In contrast, the 2,3-*endo,exo*-norbornyl-bridged diphosphine, **1d**, coordinates to palladium through both phosphorus atoms, presumably because the increase in steric energy upon chelation associated with a natural bite angle of 102.46(3)° is significantly lower than 12.2 kcal mol^{-1}. However, under conditions of catalysis, **1d** may not act solely as a bidentate ligand and several active species may be present (vide infra).

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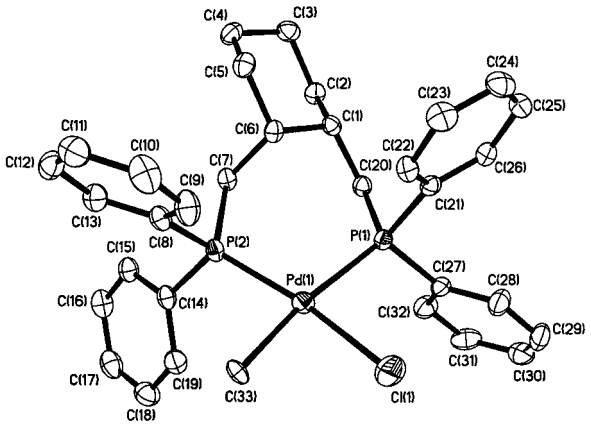


Figure 7. Molecular structure of **4a**. Hydrogen atoms have been omitted. Ellipsoids are at the 50% probability level.

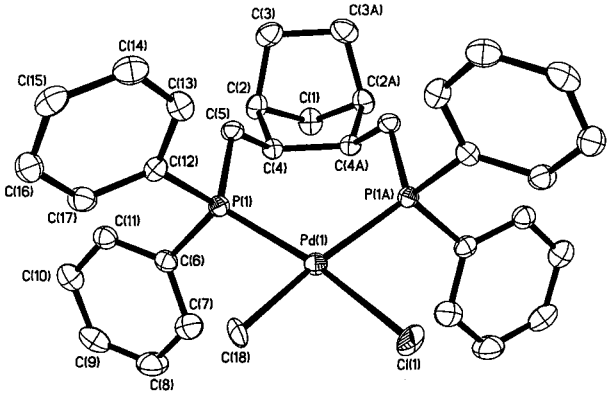


Figure 8. Molecular structure of **4c**. Hydrogen atoms and CH_2Cl_2 molecule of crystallization have been omitted. Ellipsoids are at the 50% probability level. Note C(18)/Cl(1) subject to interchange disorder.

X-ray Structures of [*cis*-1,2-Bis(diphenylphosphinomethyl)cyclohexanePdMeCl] (4a) and [*endo,endo*-2,3-Bis(diphenylphosphinomethyl)norbornanePdMeCl] (4c). A single-crystal X-ray analysis of **4a** was determined, which corresponds to isomer 491, the major isomer observed in the low temperature limiting $^{31}P\{^1H\}$ NMR spectrum. As no examples of palladium complexes of *endo,endo*-2,3-norbornyl-bridged diphosphines have previously been reported, a single-crystal X-ray study of [*endo,endo*-2,3-bis(diphenylphosphinomethyl)norbornanePdMeCl] (**4c**) was also undertaken to provide precise structural details. The structure of **4c** is disordered, with the methyl and chloride ligands interchanging. Refinement details are given in the Experimental Section. Note that this disorder makes a detailed description of the geometry involving these groups less reliable than that in the ordered structure, **4a**. The molecular structures of **4a** and **4c** are shown in Figures 7 and 8, respectively, and a selection of bond lengths and angles is listed in Table 2. The molecular structure of **4a** clearly shows that the diphosphine binds in a chelating manner, with the equatorial diphenylphosphinomethyl group *trans* to Pd−Me and the axial diphenylphosphinomethyl *trans* to Pd−Cl. The difference of 0.1024 Å between the bond lengths Pd(1)−P(1) [2.3487(7) Å] and Pd(1)−P(2) [2.2463(8) Å] reflects the much stronger *trans* influence of methyl compared

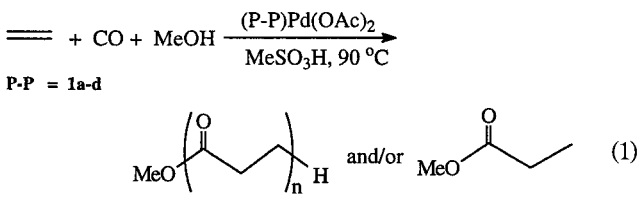
Table 3. Summary of Ethylene Carbon Monoxide Copolymerization Results Using Catalyst Precursors 3a−d

entry	ligand	mass of polymer (g)[a]	mass of propanoate (g)[b]	productivity/g polyketone (mol cat)$^{-1}$ h^{-1}	n[c]	productivity/g methyl propanoate (mol cat)$^{-1}$ h^{-1}
1	**3a**	7.3	0	33 000	16	0
2	**3b**	2.7	0	7 260	20	0
3	**3c**	1.5	0	6 060	13	0
4	**3d**	1.1	13.7	5 000	14	62 270

[a] All reactions were performed in methanol pressurized to 10 bar with an equimolar mixture of CO/C_2H_4 at 90 °C for 1 h. [b] Average mass of product obtained over 3 runs. [c] The average degree of polymerization (n) determined by end-group analysis of the $^{13}C\{^1H\}$ NMR spectra.

to chloride.[20] The Pd−P bond lengths are comparable to those reported for other $[L_2PdRCl]$ (L_2 = diphosphine, R = alkyl, aryl) complexes such as [{bis(dicyclohexylphosphino)ethane}PdCl(CH_2Cl)] [2.255(2) Å, 2.317(2) Å],[21] [(dppe)PdCl($CHCl_2$)] [2.232(1) Å, 2.309(1) Å],[22] and [(dppp)PdCl(Ph)] [2.239(1) Å, 2.350(1) Å].[23] The natural bite angles P(1)−Pd(1)−P(2) of 101.00(3)° and 102.03(5)° in **4a** and **4c**, respectively, are similar to that in **2a** [100.53(6)°]. In both **4a** and **4c**, the coordination sphere about Pd(1) is close to square planar, clearly evident from the dihedral angles of 2.6° and 4.0°, respectively, between the planes containing P(1), Pd(1), P(2) and Cl(1), Pd(1), C(33)/C(18) in **4a** and **4c**, respectively. The preference for square-planar coordination is not unusual, although interestingly palladium complexes of C_4-bridged diphosphines such as $[Pd(dpbp)Cl_2]$ (dpbp = 2,2′-bis(diphenylphosphino)-1,1′-biphenyl)[24] and $[Pd(dppb)Cl_2]$ (dppb = 1,4-bis(diphenylphosphino)butane)[16] have been reported to show a pronounced distortion toward tetrahedral coordination.

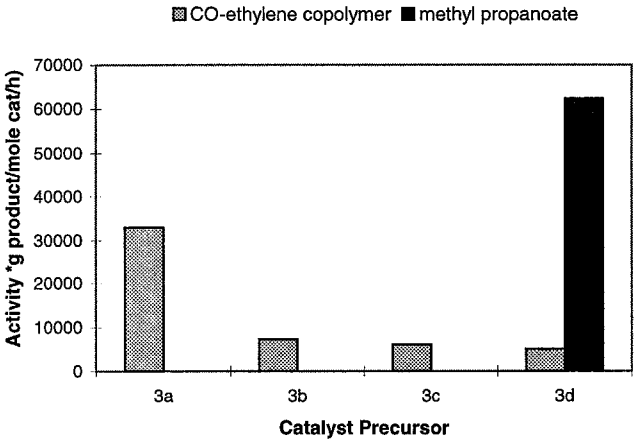
Catalytic Studies. Preliminary studies on the carbonylation of ethylene (eq 1) have shown that methanol



(1)

solutions of $[(P-P)Pd(OAc)_2]$ (**3a**,**b**) and methane sulfonic acid are active for the copolymerization of ethylene and carbon monoxide, generating low molecular weight polymers. The average degree of polymerization, (n), determined by end group analysis of the $^{13}C\{^1H\}$ NMR spectra, reveals that the products are in fact co-oligomers with n ranging from 14 to 20. The results of these initial studies and polymer properties are given in Table 3 and summarized in Chart 4. The polyketone isolated using these catalysts is an off-white powder, which is consistent with catalyst decay, suggesting that the active species is not stable under these conditions.

Chart 4. Productivity/Selectivity of Catalysts Formed from Phosphines 1a−d



The most surprising feature of these catalyst systems is their disparate productivity. In a comparative study catalysts formed from *cis*-[{*cis*-1,2-bis(diphenylphosphinomethyl)cyclohexane}$Pd(OAc)_2$] (**3a**) repeatedly produced at least three times as much polymer as its *trans* counterpart, *cis*-[{*trans*-1,2-bis(diphenylphosphinomethyl)cyclohexane}$Pd(OAc)_2$] (**3b**), under similar conditions (entries 1 and 2, Table 3).

The selectivity of catalysts based on **1a**,**b** is perhaps not unexpected since the vast majority of diphenylphosphino-substituted phosphines form catalysts that are selective for copolymerization, differing mainly in their activity. For instance, Drent has examined the effect of varying the length of the tether in diphosphines of the type $Ph_2P(CH_2)_nPPh_2$ (n = 1−6) and established a marked dependence of both reaction rate and the molecular weight of the copolymer, the most efficient catalyst system corresponding to 1,3-bis(diphenylphosphino)propane, while those formed from diphosphines with chain lengths greater than 3 generated methanol-soluble co-oligomer. In contrast, under our conditions, co-oligomer generated using catalysts based on **1a**−**d** precipitated from solution and was typically isolated by filtration.

Interestingly, the selectivity of the norbornyl-derived catalyst systems, based on **1c** and **1d**, is strongly influenced by the ligand stereochemistry. Under the same conditions, catalyst mixtures based on *endo,endo*-2,3-bis(diphenylphosphinomethyl)norbornane, **1c**, generate polyketone (entry 3), while those formed from *exo,endo*-2,3-bis(diphenylphosphinomethyl)norbornane, **1d,** are highly active and selective (>90%) for the production of methyl propanoate (entry 4). Such a difference in *selectivity* for diphenylphosphino-substi-

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Table 4. Summary of Crystal Data and Structure Determination for Compounds 2a·$CHCl_3$, 2d, 4a, and 4c·CH_2Cl_2

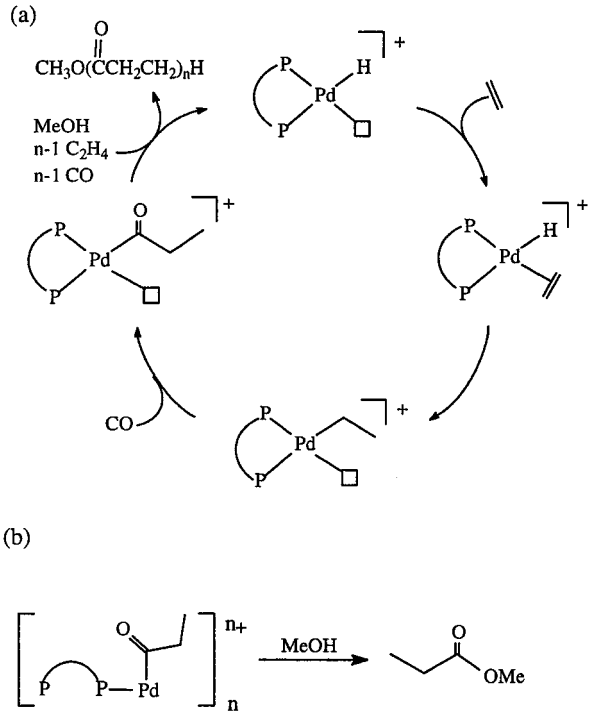
	2a·$CHCl_3$	**2d**	**4a**	**4c**·CH_2Cl_2
mol form	$C_{32}H_{34}Cl_2P_2Pd.CHCl_3$	$C_{33}H_{34}Cl_2P_2Pd$	$C_{33}H_{37}ClP_2Pd$	$C_{34}H_{37}ClP_2Pd.CH_2Cl_2$
fw	777.20	669.84	637.42	734.35
cryst size, mm	0.50 × 0.40 × 0.20	0.57 × 0.56 × 0.36	0.40 × 0.40 × 0.30	0.60 × 0.40 × 0.40
temp, K	160(2)	190(2)	160(2)	160(2)
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	Cc	$P2_1/c$	$Pnma$
a, Å	17.330(3)	12.935(2)	18.7036(8)	17.9616(15)
b, Å	9.9739(15)	15.291(4)	9.4279(4)	16.7307(14)
c, Å	20.038(3)	15.548(3)	18.0954(8)	11.1047(9)
β, deg	91.546(2)	98.392(15)	116.234(2)	
V, Å^3	3462.2(9)	3042.4(11)	2862.2(2)	3337.1(5)
Z	4	4	4	4
D_{calcd}, g cm^{-3}	1.491	1.462	1.479	1.462
μ, mm^{-1}	1.036	0.912	0.875	0.916
F(000)	1576	1368	1312	1504
θ range, deg	2.03−25.00	2.08−28.55	2.25−28.59	2.16−28.66
max. indices: h,k,l	20, 11, 23	17, 20, 19	25, 12, 23	24, 22, 14
no. reflns measd	21 390	12 800	24 119	25 016
no. unique reflns	6067	6826	6870	4216
no. reflns with $F^2 > 2\sigma(F^2)$	5065	5853	5506	3820
transmn coeff range	0.625−0.812	0.628−0.735	0.666−0.802	0.609−0.711
R_{int} (on F^2)	0.0534	0.0198	0.0360	0.0405
weighting params[a] a, b	0.0731, 24.0357	0.0339, 0	0.0403, 3.8281	0.0166, 10.1401
R[b]	0.0647	0.0264	0.0357	0.0578
R_w[c]	0.1754	0.0641	0.0932	0.1062
no. of params	371	344	335	206
GOF[d] on F^2	1.068	0.976	1.063	1.324
max, min diff map, e Å^{-3}	3.274, −1.262	0.717, −0.502	1.663, −0.893	0.918, −1.743

[a] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$. [b] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$. For "observed" reflections having $F_o^2 > 2\sigma(F_o^2)$. [c] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data. [d] GOF $= [\sum w(F_o^2 - F_c^2)^2/(\text{no. unique reflns} - \text{no. of params})]^{1/2}$.

tuted catalysts is unexpected and may be due to the large natural bite angle enforced by the *exo,endo* arrangement of the diphenylphosphinomethyl substituents. In this regard, a single-crystal X-ray study of [{*exo,endo*-2,3-bis(diphenylphosphinomethyl)norbornane}-$PdCl_2$] has revealed a natural bite angle of 102.46(3)°, slightly larger than that found in **2a** (∠PPdP = 100.53-(6)°). If selectivity, for a single site catalyst, is determined by the relative rates of termination after a single turnover, either via methanolysis or protonolysis, versus chain propagation, be it migratory insertion of CO or ethylene, it is difficult to understand how such a subtle change could have such a dramatic effect on the product distribution. In particular, if the selectivity of catalysts based on **1d** is the result of a large change in the rate of chain transfer relative to propagation upon a change in ligand structure, one would expect largely a single turnover (i.e., formation of methyl propanoate) with rapidly diminishing amounts of dimer and higher oligomers. If this were the case, the average degree of polymerization would be significantly lower than 14.

A more credible explanation involves the presence of two distinct catalytic species operating in parallel, one in which **1d** acts as a bidentate ligand and operates in the same way as **3a**−**c** to generate polyketone (Scheme 1a), the other in which one arm of the diphosphine dissociates and effectively serves in much the same manner as a monodentate phosphine to generate methyl propanoate (Scheme 1b). Indeed, it is well known that the tendency for bidentate diphosphines to open and form *trans* bridged complexes or oligomeric species increases with increasing natural bite angle.[25] This explanation is supported by the observed selectivity

Scheme 1



since the isolation of polyketone with an average degree of polymerization of 14 would not be expected for a catalyst with a selectivity for methyl propanoate of 90%. At this stage we are reluctant to speculate about the

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exact nature of this species, and further studies are clearly required to determine the precise structure of this entity.

In a recent study, Tooze and co-workers suggested that selectivity for methyl propanoate appears to be associated with ligands that are reluctant to adopt classical bidentate chelate structures with divalent palladium.[10] It was tentatively suggested that this may be related to the *cis*−*trans* isomerization thought to be responsible for the production of low molecular weight materials in palladium-catalyzed methoxycarbonylation using triphenylphosphine as the ligand. Indeed, a cyclic tetramer, [{1,3-bis(di-*tert*-butylphosphino)propanePd-$(OAc)_2]_4$, and the doubly orthometalated $[Pd_2(OAc)_2\{\mu$-$C_6H_2(CH_2PBut)_2\}]$ have been isolated from the reaction between palladium acetate and 1,3-bis(di-*tert*-butylphosphino)propane and 1,2-bis(di-*tert*-butylphosphinomethyl)benzene, respectively, although notably neither was conclusively shown to be a catalytic intermediate.

In conclusion, catalyst systems based on the C_4-bridged diphosphines *cis*- and *trans*-1,2-bis(diphenylphosphinomethyl)cyclohexane are selective for copolymerization of ethylene with carbon monoxide, polymer productivity depending markedly on the stereochemistry of the diphenylphosphinomethyl substituents on the cyclohexyl tether. In a remarkable reversal of selectivity, catalyst systems based on *exo,endo*-2,3-bis(diphenylphosphinomethyl)norbornane are highly selective for the production of methyl propanoate. In contrast, catalyst mixtures formed from its *endo,endo* counterpart are selective for copolymer, with a productivity similar to that of *trans*-1,2-bis(diphenylphosphinomethyl)cyclohexane. Clearly, within the series of phosphines **1a**−**d**, evaluation of the parameters that influence catalyst selectivity and activity is not straightforward and further studies are required to investigate fully the origin of these effects. In particular, investigations of the influence of ligand modification on catalyst selectivity, i.e., the formation of polyketone versus methyl propanoate, and on polymer molecular weight and detailed mechanistic investigations and molecular modeling studies are currently underway.

Experimental Section

General Procedures. All manipulations involving air-sensitive materials were carried out in an inert atmosphere glovebox or using standard Schlenk line techniques under an atmosphere of nitrogen or argon. Diethyl ether and hexane were distilled from potassium/sodium alloy, tetrahydrofuran was distilled from potassium, and dichloromethane was distilled from calcium hydride. Deuteriochloroform was predried with calcium hydride, then vacuum transferred and stored over 4 Å molecular sieves. Variable-temperature $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL LAMBDA 500. The diphosphines *cis*- and *trans*-1,2-bis(diphenylphosphinomethyl)cyclohexane (**1a**,**b**) were prepared from the corresponding dibromides, and *endo,endo*-2,3-bis(diphenylphosphinomethyl)norbornane (**1c**) and *exo,endo*-2,3-bis(diphenylphosphinomethyl)-norbornane (**1d**) from their corresponding dimesylates as described below.

Synthesis of *cis*-1,2-Bis(diphenylphosphinomethyl)-cyclohexane (1a). A solution of diphenylphosphine (2.92 g, 15.7 mmol) in THF (15 mL) was cooled in a dry ice/acetone bath and with rapid stirring treated with a 2.5 M solution of butyllithium in hexanes (6.28 mL, 15.7 mmol). The temperature was allowed to rise to 0 °C, and the reaction mixture stirred for 30 min, after which time a THF (20 mL) solution of *cis*-1,2-cyclohexane dimethylbromide (2.12 g, 7.85 mmol) was added dropwise. The reaction mixture was allowed to warm to ambient temperature and stirred for a further 2 h. The solvent was removed under reduced pressure, and the resulting oily residue was treated with degassed H_2O (30 mL) and then extracted into diethyl ether (60 mL). The organic phase was separated, dried over $MgSO_4$, and filtered, and the solvent was removed to afford *cis*-1,2-bis(diphenylphosphinomethyl)-cyclohexane (**1a**) as a spectroscopically pure oil in 80% yield (3.2 g). ^1H NMR (500.0 MHz, $CDCl_3$, δ): 7.32 (m, 8H, phenyl), 7.22 (m, 12H, phenyl), 1.84 (m, 4H, CH_2), 1.08−1.57 (m, 10H, Cy−*H*). $^{31}P\{^1H\}$ NMR (202.0 MHz, $CDCl_3$, δ): −18.0 (s, PPh_2).

Synthesis of *trans*-1,2-Bis(diphenylphosphinomethyl)-cyclohexane (1b). *trans*-1,2-Bis(diphenylphosphinomethyl)-cyclohexane (**1b**) was isolated in 77% yield from *trans*-1,2-cyclohexane dimethylbromide, according to the procedure described above for **1a**. ^1H NMR (500.0 MHz, $CDCl_3$, δ): 7.32 (m, 4H, phenyl), 7.23 (m, 4H, phenyl), 7.16 (m, 12H, phenyl), 2.30 (d, J = 14.0 Hz, 2H), 1.95 (d, J = 12.8 Hz, 2H), 1.50 (m, 4H), 1.20 (m, 2H), 1.05 (m, 2H), 0.90 (m, 2H). $^{31}P\{^1H\}$ NMR (202.0 MHz, $CDCl_3$, δ): −18.7 (s, PPh_2).

Synthesis of 2,3-*endo,endo*-Bis(diphenylphosphino-methyl)norbornane (1c). A solution of diphenylphosphine (3.0 g, 16.1 mmol) in THF (20 mL) was cooled in a dry ice/acetone bath and with rapid stirring treated with a 2.5 M solution of butyllithium in hexanes (6.45 mL, 16.1 mmol). After warming to room temperature and stirring for a further 30 min the solution was cooled in an ice bath, and a THF solution (30 mL) of the dimesylate of 2,3-*endo,endo*-norbonanedimethanol (2.59 g, 8.0 mmol) added dropwise. The reaction mixture was warmed to room temperature and stirred overnight, during which time there was a color change from deep orange-red to pale yellow. The solvent was removed under reduced pressure, and the resulting oily residue was dissolved in diethyl ether (120 mL) and washed with degassed water (30−40 mL). The organic phase was separated, dried over $MgSO_4$, and filtered, and the solvent was removed to afford 2,3-*endo,endo*-bis(diphenylphosphinomethyl)norbornane (**1c**) in 74% yield (2.90 g). ^1H NMR (500.0 MHz, $CDCl_3$, δ): 7.40 (m, 4H, phenyl), 7.32 (m, 4H, phenyl), 7.24 (m, 12H, phenyl), 2.27 (br s, 4H, CH_2), 1.86 (m, 4H, CH_2), 1.48 (m, 2H, CH_2), 1.23 (m, 4H, C*H*). $^{31}P\{^1H\}$ NMR (202.0 MHz, $CDCl_3$, δ): −16.3 (s, PPh_2).

Synthesis of 2,3-*exo,endo*-Bis(diphenylphosphino-methyl)norbornane (1d). 2,3-*endo,exo*-Bis(diphenylphosphinomethyl)norbornane (**1d**) was isolated in 82% yield, according to the procedure described above for **1c**. ^1H NMR (500.0 MHz, $CDCl_3$, δ): 7.39 (m, 4H, phenyl), 7.32 (m, 4H, phenyl), 7.22 (m, 12H, phenyl), 2.18 (br s, 1H), 2.05 (br s, 1H), 1.95 (m, 1H), 1.85 (m, 1H), 1.50 (br m, 1H), 1.38 (m, 3H), 1.22 (m, 2H), 1.08 (m, 1H), 0.95 (m, 2H), 0.81 (m, 1H). $^{31}P\{^1H\}$ NMR (202.0 MHz, $CDCl_3$, δ): −18.3 (s, PPh_2), −0.18.9 (s, PPh_2).

Synthesis of [{*cis*-1,2-Bis(diphenylphosphinomethyl)-cyclohexane}$PdCl_2$] (2a). A solution of (cycloocta-1,5-diene)-$PdCl_2$] (1.2 g, 4.2 mmol) in toluene (4−5 mL) was treated with a toluene solution (7−10 mL) of *cis*-1,2-bis(diphenylphosphinomethyl)cyclohexane (2.02 g, 4.2 mmol) and stirred vigorously for ca. 1−2 h. The reaction mixture was filtered, and the precipitate was washed with hexane (2 × 10 mL) and dried under vacuum to give **2a** as a pale yellow solid (2.23 g, 81%). Crystallization from a chloroform solution layered with *n*-hexane gave X-ray quality crystals of **2a**. ^1H NMR (500.0 MHz, CD_2Cl_2, δ): 7.82 (m, 4H, phenyl), 7.64 (m, 4H, phenyl), 7.42 (m, 12H, phenyl), 2.26 (m, 2H), 2.09 (m, 2H), 1.85 (br s, 2H), 1.26 (m, 2H), 1.10 (m, 6H). $^{31}P\{^1H\}$ NMR (202.0 MHz, $CDCl_3$, 298 K, δ): 32.0 (br s, PPh_2). $^{31}P\{^1H\}$ NMR (202.0 MHz, $CDCl_3$, 213 K, δ): 46.0 (d, $^2J_{PP}$ = 40.0 Hz, PPh_2), 16.5 (d, $^2J_{PP}$ = 40.0 Hz, PPh_2). Anal. Calcd for $C_{32}H_{34}Cl_2P_2Pd{\cdot}CH_2Cl_2$: C, 53.36; H, 4.88. Found: C, 53.54; H, 4.72.

Compounds **2b**−**d** were prepared according to the procedure described above.

Synthesis of [{*trans*-1,2-Bis(diphenylphosphinomethyl)cyclohexane}$PdCl_2$] (2b). 2b was isolated as yellow crystals in 55% yield from a concentrated dichloromethane solution at room temperature. ^{1}H NMR (500.0 MHz, $CDCl_3$, 298 K, δ): 7.89 (m, 4H, phenyl), 7.42 (m, 12H, phenyl), 7.29 (m, 4H, phenyl), 2.26 (m, 5H), 1.44 (m, 9H), 0.84 (m, 6H). ^{31}P{^{1}H} NMR (202.0 MHz, $CDCl_3$, 298 K, δ): 24.3 (s, PPh_2). Anal. Calcd for $C_{32}H_{34}Cl_2P_2Pd{\cdot}CH_2Cl_2$: C, 53.36; H, 4.88. Found: C, 53.80; H, 4.81.

Synthesis of [{2,3-*endo*,*endo*-Bis(diphenylphosphinomethyl)norbornane}$PdCl_2$] (2c). 2c was isolated as yellow crystals in 55% yield by diffusion of diethyl ether into a concentrated dichloromethane solution at room temperature. ^{1}H NMR (500.0 MHz, $CDCl_3$, 298 K, δ): 7.84 (m, 4H, phenyl), 7.49 (m, 4H, phenyl), 7.33 (m, 12H, phenyl), 2.55 (m, 2H), 2.21 (m, 4H), 1.74 (m, 2H), 1.60 (m, 1H), 1.38 (m, 2H), 1.22 (m, 2H), 1.10 (m, 1H). ^{31}P{^{1}H} NMR (202.0 MHz, $CDCl_3$, δ): 30.7 (s, PPh_2). Anal. Calcd for $C_{33}H_{34}Cl_2P_2Pd.CH_2Cl_2$: C, 54.11; H, 4.81. Found: C, 53.64; H, 4.72.

Synthesis of [{2,3-*exo*,*endo*-Bis(diphenylphosphinomethyl)norbornane}$PdCl_2$] (2d). 2d was isolated as yellow crystals in 67% yield from a dichloromethane solution layered with *n*-hexane. ^{1}H NMR (500.0 MHz, $CDCl_3$, 298 K, δ): 7.89 (m, 4H, phenyl), 7.47 (m, 4H, phenyl), 7.32 (m, 12H, phenyl), 2.60 (m, 1H), 2.45 (m, 1H), 2.23 (m, 1H), 1.80 (m, 3H), 1.10 to 1.50 (m, 7H), 0.95 (m, 1H). ^{31}P{^{1}H} NMR (202.0 MHz, $CDCl_3$, δ): 32.1 (d, $^2J_{PP}$ = 7.5 Hz, PPh_2), 27.3 (d, $^2J_{PP}$ = 7.5 Hz, PPh_2). Anal. Calcd for $C_{33}H_{34}Cl_2P_2Pd{\cdot}CH_2Cl_2$: C, 54.10; H, 4.81. Found: C, 53.84; H, 4.81.

Synthesis of [{*cis*-1,2-Bis(diphenylphosphinomethyl)cyclohexane}$Pd(OAc)_2$] (3a). A suspension of palladium acetate (0.465 g, 2.07 mmol) in toluene (~1−2 mL) was treated with a toluene solution (~6−7 mL) of *cis*-1,2-bis(diphenylphosphinomethyl)cyclohexane (1.10 g, 2.29 mmol) and stirred vigorously for ca. 30 min, during which time a pale yellow solid precipitated from solution. The reaction mixture was filtered, and the precipitate was washed with toluene (3 × 2 mL) and hexane (2 × 10 mL) and dried under vacuum to give **3a** as a bright yellow solid (1.21 g, 83%), which was used without further purification. ^{1}H NMR (500.0 MHz, $CDCl_3$, δ): 7.72 (m, 4H, phenyl), 7.57 (m, 4H, phenyl), 7.32 (m, 12H, phenyl), 2.01 (m, 4H, CH_2PPh_2), 1.38 (m, 16H). ^{31}P{^{1}H} NMR (202.0 MHz, $CDCl_3$, δ): 26.4 (br s, PPh_2).

Catalyst precursors **3b**−**d** were prepared using a procedure similar to that described for **3a**.

Synthesis of [{*trans*-1,2-Bis(diphenylphosphinomethyl)cyclohexane}$Pd(OAc)_2$] (3b). 3b was isolated as a yellow powder in 83% yield. ^{1}H NMR (500.0 MHz, $CDCl_3$, 298 K, δ): 7.89 (m, 4H, phenyl), 7.42 (m, 12H, phenyl), 7.29 (m, 4H, phenyl), 2.26 (m, 5H), 1.44 (m, 9H), 0.84 (m, 6H). ^{31}P{^{1}H} NMR (202.0 MHz, $CDCl_3$, δ): 24.3 (s, PPh_2).

Synthesis of [{2,3-*endo*,*endo*-Bis(diphenylphosphinomethyl)norbornane}$Pd(OAc)_2$] (3c). 3c was isolated as a pale yellow-amber solid in 76% yield. ^{1}H NMR (500.0 MHz, $CDCl_3$, 298 K, δ): 7.77 (m, 4H, phenyl), 7.52 (m, 4H, phenyl), 7.30 (m, 12H, phenyl), 2.81 (br s, 2H), 2.26 (m, 4H), 2.10 (s, 2H), 1.57 (d, J = 9.0 Hz, 1H), 1.35 (m, 10H), 1.20 (m, 1H). ^{31}P{^{1}H} NMR (202.0 MHz, $CDCl_3$, δ): 22.5 (s, PPh_2).

Synthesis of [{2,3-*exo*,*endo*-Bis(diphenylphosphinomethyl)norbornane}$Pd(OAc)_2$] (3d). 3d was isolated as a lemon yellow powder in 69% yield. ^{1}H NMR (500.0 MHz, $CDCl_3$, 298 K, δ): 7.88 (m, 4H, phenyl), 7.42 (m, 4H, phenyl), 7.33 (m, 12H, phenyl), 2.52 (m, 1H), 2.33 (m, 2H), 2.15 (m, 1H), 1.85 (s, 1H), 1.80 (s, 1H), 1.43 (m, 2H), 0.98 to 1.38 (m, 12H). ^{31}P{^{1}H} NMR (202.0 MHz, $CDCl_3$, δ): 21.6 (d, $^2J_{PP}$ = 23.0 Hz, PPh_2), 26.6 (d, $^2J_{PP}$ = 23.0 Hz, PPh_2).

Synthesis of [{*cis*-1,2-Bis(diphenylphosphinomethyl)cyclohexane}PdMeCl] (4a). A solution of [(cycloocta-1,5-diene)PdMeCl] (0.250 g, 1.0 mmol) in dichloromethane (10 mL) was treated with a dichloromethane solution (7−10 mL) of *cis*-1,2-bis(diphenylphosphinomethyl)cyclohexane (0.48 g, 1.0 mmol) and stirred vigorously for ca. 3−4 h. The reaction mixture was filtered, and the residue was washed with hexane (2 × 10 mL) and crystallized from a dichloromethane solution layered with *n*-hexane to give **2a** as yellow crystals in 55% yield (0.350 g). ^{1}H NMR (500.0 MHz, CD_2Cl_2, δ): 7.84 (br, 2H, C_6H_5), 7.67 (ddd, J = 9.4, 7.6, 1.9 Hz, 1H, C_6H_5), 7.57 (m br, 4H, C_6H_5), 7.42−7.29 (m, 12H, C_6H_5), 2.26 (m, 1H, CH_2PPh_2), 2.26 (m, 3H, CH_2PPh_2), 1.94 (t, J = 11.0 Hz, 1H, Cy−*H*), 1.65 (br, 1H, Cy−*H*), 1.36 (br, 1H, Cy−*H*), 1.18−0.97 (m, 7H, Cy−*H*), 0.61 (dd, $^3J_{PH}$ = 3.9 Hz, $^3J_{PH}$ = 7.7 Hz, 3H, CH_3). ^{31}P{^{1}H} NMR (202.0 MHz, $CDCl_3$, 213 K, δ): 47.5 (d, $^2J_{PP}$ = 34.7 Hz, PPh_2, **4a$_1$**), 25.4 (d, $^2J_{PP}$ = 36.0 Hz, PPh_2, **4a$_2$**), 22.1 (d, $^2J_{PP}$ = 36.0 Hz, PPh_2, **4a$_2$**), 2.2 (d, $^2J_{PP}$ = 34.7 Hz, PPh_2, **4a$_1$**). Anal. Calcd for $C_{33}H_{37}ClP_2Pd.CH_2Cl_2$: C, 56.55; H, 5.44. Found: C, 56.81; H, 5.39.

Synthesis of [{2,3-*endo*,*endo*-Bis(diphenylphosphinomethyl)norbornane}PdMeCl] (4c). Compound **4c** was prepared according to the procedure described above for **4a**. It was isolated as yellow crystals in 55% yield from a concentrated dichloromethane solution layered with diethyl ether at room temperature. ^{1}H NMR (500.0 MHz, CD_2Cl_2, δ): 7.91 (ddd, J = 2.1, 5.8, 9.8 Hz, 2H, C_6H_5), 7.83 (ddd, J = 1.3, 7.4, 9.5 Hz, 2H, C_6H_5), 7.6 (m, 2H, C_6H_5), 7.52 (ddd, J = 1.8, 6.4, 8.2 Hz, 2H, C_6H_5), 7.47 (m, 2H, C_6H_5), 7.38−7.31 (m, 8H, C_6H_5), 2.45−1.15 (m, 14H, *norbornyl*, CH_2), 0.64 (dd, $^3J_{PH}$ = 7.7 Hz, $^3J_{PH}$ = 3.7 Hz, 3H, CH_3). ^{31}P{^{1}H} NMR (202.0 MHz, $CDCl_3$, δ): 38.6 ($^2J_{PP}$ = 38.0 Hz, PPh_2), 12.1 ($^2J_{PP}$ = 38.0 Hz, PPh_2). Anal. Calcd for $C_{34}H_{37}ClP_2Pd{\cdot}CH_2Cl_2$: C, 57.25; H, 5.35. Found: C, 56.83; H, 5.45.

Polymerization Procedure. Polymerizations were conducted in methanol in a 300 mL autoclave. The catalyst precursors were prepared according to the procedure reported for [(dppp)Pd(OAc)$_2$].[13] In a typical procedure, 0.10 g of [(P−P)Pd(OAc)$_2$] was dissolved in 50 mL of anhydrous methanol, 0.06 mL of CH_3SO_3H was added, and the solution was transferred to a 300 mL autoclave under N_2. The reaction mixture was pressurized to 10 bar with an equimolar mixture of CO and ethylene and heated at 90 °C for 1 h. The reaction was quenched by release of CO/ethylene pressure and the polymer isolated by filtration, dried, and weighed.

Crystal Structure Determinations of 2a, 2d 4a, and 4c. All measurements were made on a Bruker AXS SMART 1K CCD area-detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073) and narrow frame exposures (0.3° in ω). Cell parameters were refined from the observed ω angles of all strong reflections in each data set. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections. No significant intensity decay was observed. The structures were solved by direct methods (Patterson synthesis for **2d** and **4c**) and refined on F^2 values for all unique data by full-matrix least-squares. Table 4 gives further details. All non-hydrogen atoms were refined anisotropically. H atoms located in difference maps were constrained with a riding model; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Atoms C(18) and Cl(1) exhibited interchange disorder, and their geometry and isotropic displacement parameters were restrained during refinement. Refinement of **4c** in space group $Pna2_1$ did not resolve this disorder, so the simpler model in *Pnma* was used. Programs used were SHELXTL[26] for structure solution, refinement, and molecular graphics, Bruker AXS SMART (control) and SAINT (integration), and local programs.[27]

Acknowledgment. We gratefully acknowledge the University of Newcastle upon Tyne and the EPSRC for

(26) Sheldrick, G. M. *SHELXTL user manual, version* 5; Bruker AXS Inc.: Madison, WI, 1994.
(27) *SMART and SAINT software for CCD diffractometers*; Bruker AXS Inc.: Madison, WI, 1994.

funding (E.R.) and Johnson Matthey for loans of palladium salts.

Supporting Information Available: For **2a**·$CHCl_3$, **2d**, **4a**, and **4c**·CH_2Cl_2 details of structure determination, nonhydrogen atomic positional parameters, full listings of bond distances and angles, anisotropic displacement parameters, and hydrogen atomic coordinates. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor tables are available from the authors upon request.

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