Palladium Complexes of 2-Pyridin-2-yl Substituted 1,3-Bis(diphenylphosphino)propane: Highly Active Catalysts for the Room-Temperature Copolymerization of Carbon Monoxide with Ethene

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The 2,2′-disubstituted 1,3-bis(diphenylphosphino)propane derivatives [XC(Me)(CH_2PPh_2)$_2$] (X = 2-py, **1a**; X = CH_2OMe, **1b**; X = Ph, **1c**) and their corresponding palladium complexes [(P−P)$PdCl_2$] (**2a**−**c**), [(P−P)Pd$(OAc)_2$] (**3a**−**c**), [{2-methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane}PdClMe] (**4a**), and [{(*S*)-(+)-*N*,*N*-dimethyl-α-methylbenzylamine-C,N}-Pd{2-$MeOCH_2CMe(CH_2PPh_2)_2$}][ClO_4] (**5b**) have been prepared and characterized. Palladium(II) complexes of 2-methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane (**1a**) are highly active for the room-temperature copolymerization of ethene and carbon monoxide and, under our conditions, markedly more active than systems based on 1,3-bis(diphenylphosphino)propane (dppp), **1b** and **1c**. Catalysts formed from dppp, **1b**, and **1c** all show the expected increase in activity at elevated temperature (90 °C), while that formed from **1a** is highly temperature-sensitive and rapidly decomposes.

Introduction

In the early 1980s Drent discovered that the selectivity of the reaction between ethene and carbon monoxide in methanol depends markedly on the nature of the catalyst,[1] those based on triphenylphosphine resulting in alkoxycarbonylation to give methyl propanoate, a potential intermediate in the manufacture of acrylic esters, large volume chemical intermediates used annually on a multimillion ton scale,[2] while, under similar conditions, those based on the bidentate diphosphine 1,3-bis(diphenylphosphino)propane (dppp) result in the perfectly alternating copolymerization of ethene and carbon monoxide to give high molecular weight polyketone, a tough flexible wear-resistant, high impact strength environmentally friendly thermoplastic.[3] Since the discovery that palladium(II) complexes of diphosphines efficiently catalyze the perfectly alternating copolymerization of CO and ethene and the terpolymerization of CO, ethene, and propene, polyketone has become a commercial reality in the form of Carilon for Shell[4] and Ketonex for BP,[5] with other companies showing a keen interest, as evidenced by the escalating number of patents in this area. Despite some drawbacks, polyketone offers a combination of useful chemical and physical characteristics including photodegradability, biodegradability, chemical resistance, ease of functionalization, and impermeability to hydrocarbons, properties that can be fine-tuned/modified by changing the nature of the comonomer.

In his early studies, Drent demonstrated that the CO/ethene copolymerization activity of catalysts based on diphosphines of the type $Ph_2P(CH_2)_nPPh_2$ (n = 1−6) was sensitive to the length of the backbone, the most active catalyst corresponding to that with n = 3, i.e., a six-membered chelate ring, while those based on a four-membered chelate (n = 1, dppm) were essentially inactive. Since these pioneering studies, a wide range of palladium(II) complexes of diphosphines have been shown to catalyze the copolymerization of α-olefins with carbon monoxide, including *cis*,*trans*,*cis*-1,2,3,4-tetrakis(diphenylphosphino)cyclobutane (*cyclo*-tetraphos),[6] 1,2-bis(diphenylphosphino)ethene,[7] 1,2-bis(diarylphosphinomethyl)benzene,[8] 1,2-bis(2,3,4,5-tetramethylphospholylmethyl)benzene,[9] and numerous derivatives of dppp substituted either at the aryl ring or on the

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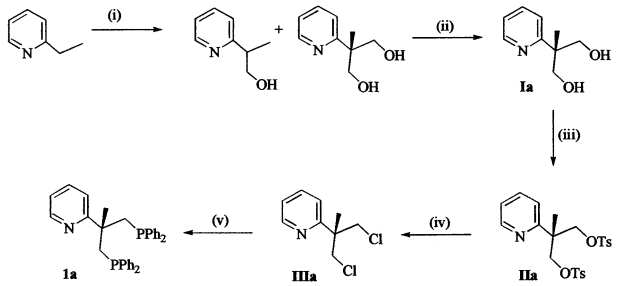
backbone.[10] For instance, workers at Shell discovered that incorporation of *polar* substituents, such as halide, alkoxy groups, amides, and esters, at the ortho position of the phenyl rings in dppp improves the relation between reaction rate and polymer molecular weight such that high molecular weight co- and terpolymers can be prepared at acceptable reaction rates.[10a] Interestingly, Pringle has recently reported that the activity of palladium(II) complexes with four-membered chelates ($Ar_2PCH_2PAr_2$) is dramatically increased by the presence of *bulky* ortho substituents on the aryl groups, and rates comparable to the best commercial catalysts have been obtained.[11] In addition to diphosphines, selectivity for copolymerization has also been reported for palladium(II) catalysts based on mixed phosphole−oxazolines and other P,N donors,[12] planar-at-nitrogen bidentate ligands such as 1,10-phenanthroline,[13] 2,2-bipyridine,[14] and bisoxazolines,[15] unsymmetrical phosphine−phosphites,[16] bisphospholes,[17] and bidentate N-heterocyclic carbenes.[18] Despite the large number of palladium(II) chelates that have been reported as catalysts, dppp-based chelates remain the ligand of choice since they outperform all others in terms of activity and selectivity.

In an attempt to improve catalyst performance and lifetime, Bianchini has investigated the influence of introducing substitutents onto the saturated backbone of dppp. Introduction of alkyl substituents at the 2-position did not significantly improve catalyst performance, whereas the introduction of methyl groups at both 1-positions resulted in a remarkable increase in polymer productivity, particularly in the case of the *R*,*S* (*S*,*R*) diastereoisomer, *meso*-2,4-bis(diphenylphosphino)pentane (*meso*-bdpp), which was considerably more active than its *rac*-2,4-bis(diphenylphosphino)pentane counterpart, generating 24 and 17 kg polymer (g palladium)$^{-1}$, respectively. For comparison, under comparable conditions catalysts based on dppp gave 16 kg polymer (g palladium)$^{-1}$ in 3 h.[19] At the time, no definitive explanation for the enhanced productivity of catalysts based on *meso*-2,4-bis(diphenylphosphino)pentane was provided. However, subsequent reports have appeared that support the generality of a *meso*-effect enhancing the productivity of palladium diphosphine catalysts. In particular, palladium(II) complexes of *meso*-[(C_6H_4)(CH(Me)$PPh_2)_2$]$_2$][20] and *meso*-2,3-bis(diphenylphosphino)-butane[21] are markedly more active for CO/propene copolymerization than their *rac* counterparts. We have recently begun to examine the effect on catalyst performance of introducing additional donor substituents onto the saturated backbone of dppp. In particular, we are interested in establishing whether these additional pendent groups interact with the metal center during copolymerization and the influence of such interactions on catalyst stability, activity, and selectivity as well as polymer properties. Herein we report that introduction of a pyridin-2-yl substituent at the 2-position has a marked effect on catalyst activity and stability. Specifically, catalysts based on 2-methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane are significantly more active for the room-temperature copolymerization of ethene and carbon monoxide than those based on dppp, but are highly temperature-sensitive and decompose rapidly at 90 °C.

Scheme 1[a]



[a] (i) 40% CH_2O, (ii) 40 % CH_2O, (iii) TsCl, pyridine, (iv) LiCl, HMPA, (v) $LiPPh_2$, THF, reflux.

Results and Discussion

Synthesis and Coordination Chemistry of Diphosphines 1a−c. Diphosphines **1a−c** were prepared according to the procedures described in Schemes 1 and 2. The diol 2-methyl-2-pyridin-2-yl-propane-1,3-diol, **Ia**, was prepared from 2-ethylpyridine and an aqueous solution of formaldehyde, according to the method of Gade and co-workers,[22] and converted into 2-methyl-2-pyridin-2-yl-1,3-dichloropropane, **IIIa**, by reaction of the corresponding tosylate, **IIa**, with lithium chloride in the presence of HMPA (Scheme 1).[23,24] Addition of chloro-

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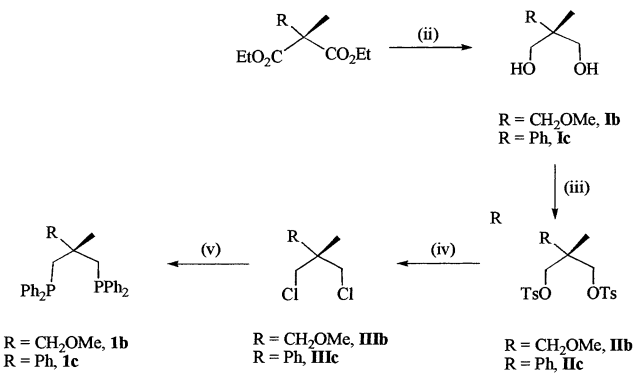
Scheme 2[a]

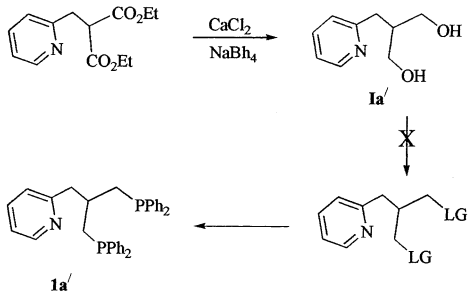


[a] (i) $LiAlH_4$, THF, (ii) TsCl, pyridine, (iv) LiCl, HMPA, (v) $LiPPh_2$, THF, reflux.

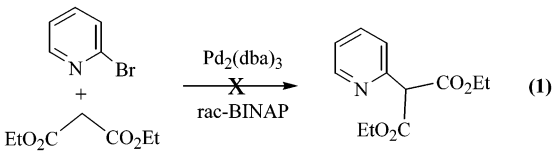
methyl methyl ether to a THF solution of diethyl methylmalonate and sodium hydride gave 2-methoxymethyl-2-methyl malonic acid diethyl ester, which was reduced to the corresponding diol **Ib** and converted into its tosylate **IIb** and finally into 1,3-dichloro-2-methoxymethyl-2-methylpropane, **IIIb**, according to Scheme 2. Diphosphine **1c** was prepared from commercially available diethyl phenylmalonate, which was first converted into diethyl methyl(phenyl)malonate by reaction with sodium hydride followed by methyl iodide and then reduced to **Ic** and subsequently converted into the desired chloride, **IIIc** (Scheme 2). The chlorides were chosen since all attempts to convert either the mesylate or tosylate into the corresponding diphosphine resulted in the formation of a number of byproducts, which prevented purification. Thermolysis of a THF solution of the appropriate chloride and lithium diphenylphosphide, generated in situ by deprotonation of diphenylphosphine with butyllithium, gave **1a**−**c**, as evidenced by the slow disappearance of the intense color associated with the lithium phosphide. In all cases, diphosphines **1a**−**c** were isolated as colorless or pale yellow moderately air-sensitive oils, which have been characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy and which could be used without further purification. The $^{31}P\{^1H\}$ NMR spectra of **1a**−**c** each contains a single resonance in the region expected for an uncoordinated diphosphine. The ^1H NMR spectra of **1a**−**c** contain resonances characteristic of a 2,2′-disubstituted 1,3-bis(diphenylphosphino)propane; in particular, the ^1H NMR spectrum of **1a** contains a doublet of AB quartets at δ 2.87 and 2.66 (J_{HH} = 14.1 Hz, J_{PH} = 3.5 Hz) and a singlet at δ 1.42, associated with the methylene protons and the methyl group, respectively. The ^1H NMR spectra of diphosphines **1b**−**c** both contain similar multiplets associated with the methylene protons and are fully consistent with the expected formulation.

The lengthy and somewhat arduous procedure required to convert 2-ethylpyridine into 2-methyl-2-pyridin-2-ylpropane-1,3-diol, **Ia**, prompted us to investigate an alternative synthesis involving the palladium-catalyzed coupling of 2-bromopyridine with diethyl malonate according to eq 1, following a protocol recently reported for the preparation of diethyl phenylmalonate.[25] If successful, diethyl (pyridin-2-yl)malonate would

Scheme 3



be methylated and converted into **1a** using a procedure identical to that described for the synthesis of **1c** from diethyl methyl(phenyl)malonate, shown in Scheme 2. Unfortunately, we found no evidence for the formation of the desired diethyl pyridin-2-ylmalonate using this strategy and have not attempted to investigate alternative catalyst systems and conditions.



The impressive performance of the catalyst precursor based on diphosphine **1a** at room temperature (vide infra) prompted us to investigate the synthesis of the related pyridin-2-yl-substituted dppp derivative **1a′**, which differs from **1a** in the proximity of the pyridyl ring with respect to the metal center. Access to this and related pyridyl-substituted diphosphines would enable us to systematically evaluate the effect of this substituent on catalyst performance. However, the synthesis of **1a′** proved unexpectedly challenging and ultimately unsuccessful. Reaction of sodium diethyl malonate, generated in situ from diethyl malonate and sodium hydride, with 2-chloromethylpyridine gave diethyl (pyridin-2-ylmethyl)malonate, which was subsequently reduced to the corresponding 1,3-diol, **Ia′**, by a combination of $CaCl_2$ and $NaBH_4$ in diethyl ether (Scheme 3). However, we have not been able to convert diol **Ia′** into an appropriate electrophile, such as its corresponding mesylate, tosylate, triflate, or 1,3-dibromide, for reaction with an alkali metal diphenylphosphide.

Addition of a dichloromethane solution of **1a**−**c** to a dichloromethane solution of [(cycloocta-1,5-diene)$PdCl_2$] resulted in a gradual color change from pale yellow to orange with the formation of [(P−P)$PdCl_2$] (**2a**−**c**) in yields of up to 75% (Chart 2). For each compound **1a**−**c**, the $^{31}P\{^1H\}$ NMR spectrum contains a sharp singlet shifted downfield relative to that of the uncoordinated diphosphine and in the range characteristic of a coordinated diphosphine. Compound **2a** was insoluble in chloroform and dichloromethane, but could be crystallized from a concentrated pyridine solution at room temperature. The ^1H NMR spectrum of **2a**, recorded in pyridine, contains a second-order doublet of doublets at δ 2.82 (J_{HH} = 14.9 Hz, J_{PH} = 9.4 Hz) and a broad ill-defined signal at δ 3.10, both of intensity 2H, associated with the diastereotopic methylene protons of the back-

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Chart 1

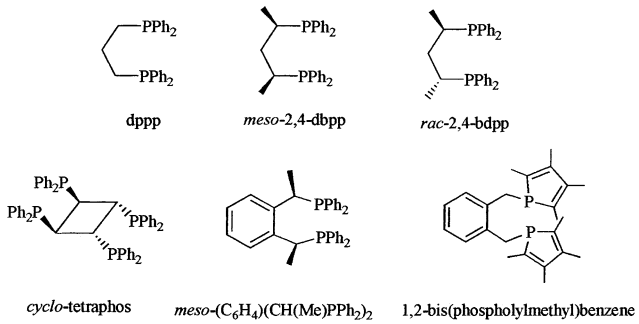
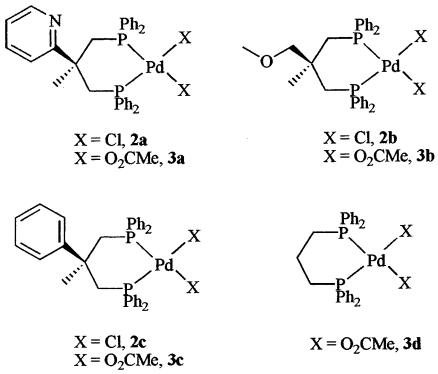
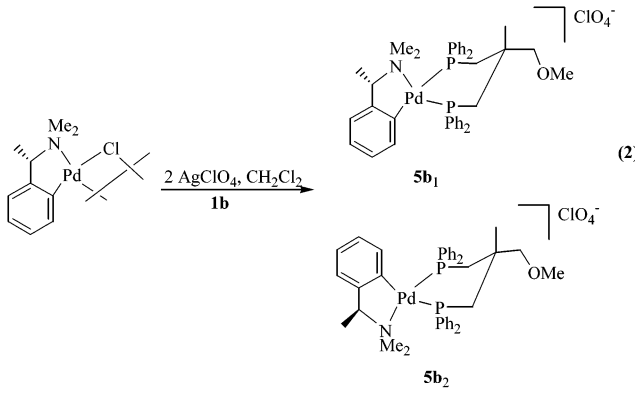


Chart 2



bone, and a low-field singlet at δ 0.83 for the methyl substituent. In contrast, the ^{1}H NMR spectrum of **2b** contains a well-resolved doublet of AB quartets at δ 2.40 and 2.18 (J_{HH} = 15.3 Hz, J_{PH} = 8.8 Hz) for the diastereotopic methylene protons in addition to two singlets at δ 2.6 and 2.5 ppm that correspond to the methyl and methylene protons of the 2-methoxymethyl group, and a singlet at δ 0.6 which belongs to the methyl group attached to the 2-position of the three-carbon backbone. The ^{1}H NMR spectrum of **1c** is similar to that of **2b** in that the diastereotopic protons appear as a well-resolved doublet of AB quartets, characteristic of a 2,2′-disubstituted dppp. The catalyst precursors [(P−P)Pd(OAc)$_2$] (**3a**−**c**) were prepared by addition of a concentrated toluene solution of the corresponding diphosphine to a rapidly stirred toluene suspension of [Pd$_3$(OAc)$_6$] to give a pale yellow-brown suspension, which was filtered and washed with toluene and hexane to afford **3a**−**c** as spectroscopically pure solids (Chart 2).[26a] Compounds **3a**−**d** were prepared and used immediately prior to catalyst testing to avoid decomposition that occurrs during crystallization.[26b] In each case the ^{1}H and ^{13}C{^{1}H} NMR spectroscopic characteristics of compounds **3a**−**c** are similar to those of their palladium dichloride counterparts **2a**−**c**. The low solubility of **2a** in common chlorinated solvents prompted us to prepare [{2-methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)-propane}PdClMe] (**4a**) by dropwise addition of a dichloromethane solution of **1a** into a dichloromethane solution of [(cyclocta-1,5-diene)PdClMe] at room temperature. As expected, the ^{31}P{^{1}H} NMR spectrum of **4a** contains a pair of well-separated doublets at δ 29.4 and 1.29 (J_{PP} = 48.6 Hz), which correspond to the diphenyphosphino groups trans to methyl and chloride, respectively, and a high-field doublet of doublets in the ^{1}H NMR spectrum (δ 0.57, $^2J_{PP}$ = 7.8 and 3.6 Hz) is characteristic of a palladium-bound methyl.[27] The diastereotopic methylene protons of **4a** appear as four distinct well-separated signals, two doublets of doublets ($^2J_{HH}$ = 15.3 Hz, $^2J_{PH}$ = 6.3/5.0 Hz) and two triplets ($^2J_{HH}$ = $^2J_{PH}$ = 15.3 Hz), the assignment of which has been confirmed by a combination of ^{1}H, ^{1}H{^{31}P}, and ^{1}H−^{1}H COSY NMR studies.

Although **2b** has been isolated and characterized using conventional spectroscopic methods, its poor solubility in common organic solvents prevented us from obtaining crystals suitable for analysis by single-crystal X-ray crystallography. A similarly low solubility of the palladium methyl chloride derivative prompted us to prepare [{(*S*)-(+)-*N*,*N*-dimethyl-α-methylbenzylamine-*C*,*N*}Pd{2-pyCMe{CH$_2$PPh$_2$}$_2$}][ClO$_4$] (**5b**), reasoning that it would have markedly different solubility properties. Complex **5b** was obtained in high yield by treatment of a dichloromethane solution of (*S*)-(+)-bis(μ-chloro)bis-[*N*,*N*-dimethyl-α-methylbenzylamine-*C*,*N*]dipalladium with 2 equiv of silver perchlorate at room temperature, followed by filtration to remove the AgCl byproduct and addition of a dichloromethane solution of **1b** (eq 2). The



(2)

most characteristic spectroscopic feature of **5b** is its ^{31}P{^{1}H} NMR spectrum, which contains two pairs of doublets of equal intensity, one at δ 29.0 and 1.75 ($^2J_{PP}$ = 46.0 Hz), the other at δ 28.5 and 1.55 ($^2J_{PP}$ = 46.0 Hz), consistent with the formation of a 1:1 mixture of diastereoisomers, tentatively assigned as **5b$_1$** and **5b$_2$** based on chairlike conformations. In each case the low-field signal corresponds to the diphenylphosphino group trans to Pd-aryl, while the high-field signal belongs to the phosphine trans to the dimethylamino group. Alternative possible conformations for a six-membered chelate include the chiral skew and boat, each of which has previously been identified for palladium(II) complexes of dppp-based diphosphines. However, we cannot dismiss the possibility that these two sets of signals

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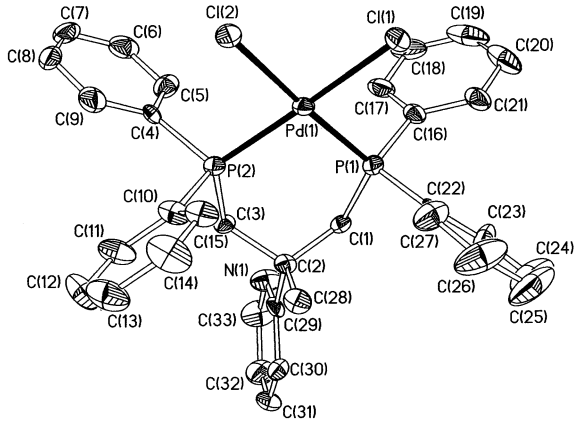

Figure 1. Molecular structure of **2a**. Ellipsoids are at 50% probability. Hydrogen atoms and solvent molecule omitted for clarity.

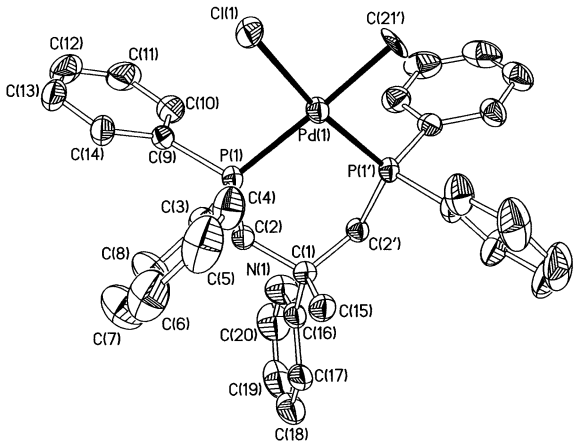

Figure 2. Molecular structure of **4a**. Ellipsoids are at 50% probability. Hydrogen atoms and solvent molecule omitted for clarity.

belong to two rigid noninterconverting conformations of a single diastereoisomer, most likely **5b$_1$**, which has been characterized by a single-crystal X-ray study (vide infra). A variable-temperature ^{31}P NMR study of compound **5b** showed no evidence for a fluxional process between room temperature and 60 °C, which supports the former suggestion that the two sets of signals belong to two distinct diastereoisomers and not to two different conformations of a single diastereoisomer. However, Herrmann has recently noted that the six-membered chelate ring of the *N*-heterocyclic carbene complex [*cis*-$CH_2\{N(H)C{=}C(H)N(Me)C\}_2Pd(CH_3CN)_2][BF_4]_2$ is conformationally rigid and undergoes a ring flipping process only at elevated temperatures (T_c = 95 °C), as evidenced by coalescence of the signals associated with the diasterotopic protons.[18] The ^{1}H NMR spectrum of compound **5b** is complex and contains resonances consistent with the presence of two diastereoisomers, as evidenced by two singlets at δ 2.93 and 2.75 and another two at δ 0.61 and 0.38, all of intensity 3H, which correspond to the 2-methoxymethyl and the methyl substituent attached to the central carbon atom of the C_3 backbone, respectively; four doublets between δ 2.29−2.17 (J_{PH} = 1.6 Hz) associated with the dimethylamino groups; two doublets of quartets at δ 3.57 (J_{HH} = J_{PH} = 6.1 Hz) and 3.54 (J_{HH} = J_{PH} = 6.1 Hz) belonging to the methine protons; and two doublets at δ 1.74, appearing as a triplet due to accidental equivalence, for the α-methyl substituent of the orthometalated *N*,*N*-dimethyl-α-methylbenzylamine.

X-ray Crystal Structures of [{2-Methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane}-$PdCl_2$] (2a), [{2-Methyl-2-pyrdin-2-yl-1,3-bis(diphenylphosphino)propane}PdMeCl] (4a), and [{(*S*)-(+)-*N*,*N*-Dimethyl-α-methylbenzylamine-*C*,*N*}Pd-{2-pyCMe{CH_2PPh_2}$_2$][ClO_4] (5b). The marked temperature sensitivity of catalysts formed from 2-methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane, **1a**, and the unexpectedly high activity in the room-temperature copolymerization of ethene and carbon monoxide prompted us to undertake single-crystal X-ray structure determinations of **2a** and **4a** to provide precise structural details. Single crystals of **2a** and **4a** suitable for X-ray analysis were grown from a concentrated pyridine solution at room temperature and by slow diffusion of diethyl ether into a dichloromethane solution, respectively. The molecular structures of **2a** and **4a** are shown in Figures 1 and 2, respectively, and a selection of bond lengths and angles for both compounds are listed in Table 1, while crystal data are provided in Table 4. The structure of **4b** has the methyl and chloride ligands disordered, which makes a detailed description of the geometry involving these groups less reliable than that

Table 1. Selected Bond Distances (Å) and Angles (deg) for 2a and 4a

compound **2a**		compound **4a**	
Pd(1)−P(1)	2.2466(17)	Pd(1)−P(1)	2.2716(6)
Pd(1)−P(2)	2.2455(17)	Pd(1)−Cl(1)	2.348(3)
Pd(1)−Cl(1)	2.3486(16)	Pd(1)−C(21)	2.072(8)
Pd(1)−Cl(2)	2.3489(16)	P(1)−C(2)	1.831(2)
P(1)−C(1)	1.841(6)	C(1)−C(2)	1.550(3)
P(2)−C(3)	1.828(6)		
C(1)−C(2)	1.527(9)		
C(2)−C(3)	1.554(9)		
P(1)−Pd(1)−P(2)	95.63(5)	P(1)−Pd(1)−P(1′)	96.18(3)
Cl(1)−Pd(1)−Cl(2)	90.76(5)	C(21′)−Pd(1)−Cl(1)	86.9(4)
P(1)−Pd(1)−Cl(1)	86.50(6)	P(1′)−Pd(1)−C(21′)	85.5(4)
P(2)−Pd(1)−Cl(2)	87.11(6)	P(1)−Pd(1)−Cl(1)	91.36(9)
P(1)−Pd(1)−Cl(2)	177.26(6)	P(1′)−Pd(1)−Cl(1)	172.46(9)
P(2)−Pd(1)−Cl(1)	177.66(7)	P(1)−Pd(1)−C(21′)	177.8(5)
P(1)−C(1)−C(2)	118.2(4)	P(1)−C(2)−C(1)	118.75(19)
P(2)−C(3)−C(2)	117.4(4)	C(2)−C(1)−C(2′)	111.4(3)
C(1)−C(2)−C(3)	110.4(4)	C(2)−C(1)−C(15)	111.34(18)
C(1)−C(2)−C(28)	111.2(5)	C(2)−C(1)−C(16)	105.35(19)
C(1)−C(2)−C(29)	106.2(5)	C(15)−C(1)−C(16)	111.8(3)
C(3)−C(2)−C(28)	112.2(6)		
C(3)−C(2)−C(29)	105.8(5)		
C(28)−C(2)−C29)	110.8(4)		

Table 2. Selected Bond Distances (Å) and Angles (deg) for 5b

Pd(1)−P(1)	2.2516(7)	P(1)−C(1A)	1.835(3)
Pd(1)−P(2)	2.3690(7)	P(2)−C(2A)	1.842(3)
Pd(1)−N(3)	2.189(2)	C(1A)−C(3A)	1.545(4)
Pd(1)−C(11)	2.085(3)	C(2A)−C(3A)	1.529(4)
P(1)−Pd(1)−P(2)	93.11(3)	C(1)−N(3)−C(4)	107.9(2)
N(3)−Pd(1)−C(11)	79.88(10)	C(2)−N(3)−C(4)	109.2(2)
P(1)−Pd(1)−C(11)	90.60(8)	P(1)−C(1A)−C(3A)	119.66(19)
P(2)−Pd(1)−N(3)	96.48(6)	P(2)−C(2A)−C(3A)	117.77(19)
P(1)−Pd(1)−N(3)	170.22(7)	C(1A)−C(3A)−C(2A)	109.4(2)
P(2)−Pd(1)−C(11)	175.85(8)	C(1A)−C(3A)−C(5A)	107.9(2)
Pd(1)−N(3)−C(1)	107.52(17)	C(1A)−C(3A)−C(4A)	112.1(2)
Pd(1)−N(3)−C(2)	121.85(18)	C(4A)−C(3A)−C(5A)	106.4(2)
Pd(1)−N(3)−C(4)	103.45(16)	C(2A)−C(3A)−C(4A)	112.5(2)
C(1)−N(3)−C(2)	106.3(2)	C(2A)−C(3A)−C(5A)	108.3(2)

Table 3. Summary of Ethene Carbon Monoxide Copolymerization Results Using Precursors 3a−c[a]

entry	ligand/ precursor	temp (°C)	mass of polymer (g)[a]	activity/g of polyketone (mol cat)$^{-1}$ h^{-1}	n[c]	M_n[c]
1	**1a/3a**	25	7.27	42 800	2000	112 000
2	**1a/3a**	40	4.85	28 500	455	25 600
3	**1a/3a**	90	0.70	4150	60	3600
4	**1b/3b**	25	2.05	12 000	800	45 600
5	**1b/3b**	90	5.08	29 900	25	1400
6	**1c/3c**	25	3.66	21 500	840	47 200
7	**1c/3c**	90	4.76	28 000	35	2000
8	dppp	25	3.97	23 400	1970	110 700
9	dppp	90	10.16	59 700	40	1600
10	dppp + py	25	2.13	12 500	230	13 000

[a] All reactions were performed in methanol pressurized to 25 bar with an equimolar mixture of CO/C_2H_4 for 2 h. [b] Average mass of polymer obtained over three runs. [c] The average degree of polymerization (n) and the average molecular weight, estimated by integration of the end group signals in the $^{13}C\{^1H\}$ NMR spectra.

in the ordered structure. Refinement details are given in the Experimental Section. Since both structures are based on the 2-methyl-2-pyridin-2-yl-substituted dppp, **1a**, and are clearly related, they will be described together. In both **2a** and **4a** the geometry at Pd(1) is close to square planar, as evidenced by the dihedral angles of 1.0° and 1.4° between the planes containing P(1)−Pd(1)−P(2)/Cl(1)−Pd(1)−Cl(2) and P(1)−Pd(1)−P(1′)/Cl(1)−Pd(1)−C(21′), respectively. In both cases the six-membered chelate ring adopts a chairlike conformation with the pyridin-2-yl substituent equatorial and the methyl group axial, presumably to avoid unfavorable 1,3-diaxial interactions with the axial phenyl rings of the diphenylphosphino groups. The Pd−P bond lengths in **2a** are similar [Pd(1)−P(1) = 2.2466(17) Å, Pd(1)−P(2) = 2.2455(17) Å] and comparable to those reported for related palladium complexes of three-carbon-bridged diphosphines including [Pd(dppp)(SCN)$_2$] [1.241(1) Å][28] and [Pd(dppp)Cl$_2$] [2.244(1) Å].[29] The P−Pd−P natural bite angles of 95.63(5)° (**2a**) and 96.18(3)° (**4a**) are significantly larger than those of 89.32(3)° and 90.58(5)° in [Pd(dppp)(SCN)$_2$][28] and [Pd(dppp)Cl$_2$],[29] respectively, and much closer to those of 93.74(4)° and 94.5(5)° in [CH(CH$_2$PPh$_2$)$_2$PdCl$_2$]$_2$.[30] The Cl(1)−Pd(1)−Cl(2) angle of 90.76(5)° in **2a** is close to the ideal value of 90°, and the large natural bite angle of the diphosphine manifests itself in the compression of the two P−Pd−Cl angles, which are both significantly smaller than 90° [P(1)−Pd(1)−Cl(1) = 86.50(6)°, P(2)−Pd(1)−Cl(2) = 87.11(6)°]. Interestingly, the pyridin-2-yl rings in **2a** and **4a** are oriented perpendicular to the P$_2$Pd plane, most probably to minimize unfavorable steric interactions between the H atoms attached to C(30) (**2a**) and C(17) (**4a**) of the pyridin-2-yl ring and the methylene protons on the dppp backbone.

Although the $^{31}P\{^1H\}$ and ^1H NMR spectra of several crystallized samples of **5b** were found to contain two pairs of doublets, of equal intensity, consistent with the bulk crystallized sample containing a 1:1 mixture of both diastereoisomers, a single-crystal X-ray analysis was undertaken to unequivocally establish whether the diastereoisomers cocrystallize. X-ray quality crystals of a single diastereoisomer of **5b** were grown from a concentrated methanol solution at room temperature. The molecular structure together with the atomic numbering scheme is shown in Figure 3, and a selection of bond lengths and angles are listed in Table 2. The molecular structure clearly shows that the crystal chosen corresponds to diastereoisomer **5b$_1$** (vide supra) and that the methoxymethyl ether-substituted diphosphine coordinates in a bidentate manner. The coordination sphere around Pd(1) is distorted square planar, as indicated by the marked deviations of P(1) and P(2) [P(1) = 0.0364 Å, P(2) = −0.0322 Å] and N(3) and C(11) [N(3) = 0.0403 Å, C(11) = −0.0436 Å] from the Pd(1), P(1), P(2), N(3), C(11) mean plane and the dihedral angle of 2.9° between the planes containing Pd(1)P(1)P(2) and Pd(1)N(3)C(11). The difference of 0.1174 Å between the bond lengths Pd(1)−P(1) [2.2516(7) Å] and Pd(1)−P(2) [2.3690(7) Å] reflects the much stronger trans influence of the σ-bonded aryl ring compared to the dimethylamino group. The Pd−P bond lengths are unexceptional and within the range reported for related palladium complexes of 1,3-bis(diphenylphosphino)propane derivatives including [(C$_6$H$_4$CH$_2$NMe$_2$-*C*,*N*)Pd(dppp)] [2.247(5) Å, 2.395(5) Å],[31] [Pd(dppp)(Ph)Cl] [2.2385(5) Å, 2.3504(5) Å],[32] [Pd(dppp){C(O)^{t}Bu}Cl] [2.254(1) Å, 2.409(2) Å],[7] and [1,4-{Pd[2,4-(OMe)$_2$C$_6$H$_2$C(H)=N]}$_2$-C$_6$H$_4$-{PPh$_2$-(CH$_2$)$_3$PPh$_2$-*P*,*P*}$_2$][PF$_6$]$_2$ [2.254(3) Å, 2.352(3) Å].[33] The Pd(1)−C(11) bond length of 2.085(3) Å is slightly longer than the typical value of ca. 1.98 Å[34] and similar to that of 2.050(2) Å recently reported for [{*o*-C$_6$H$_4$(CH$_2$)NMe$_2$}-Pd(dppp)][PF$_6$].[35] The five-membered chelate ring adopts a puckered envelope conformation, and the six-membered chelate ring has a chairlike conformation with the methyl group axial and the methoxymethyl ether substituent occupying the equatorial site, presumably to minimize unfavorable steric interactions with the phenyl rings of the diphenylphosphino groups. The natural bite angle of 93.11(3)° for P(1)−Pd(1)−P(2) is considerably greater than that of 89.3(2)° in [(C$_6$H$_4$CH$_2$NMe$_2$-*C*,*N*)Pd(dppp)][31] and closer to those in the 2,3-bis-{(diphenylphosphino)methyl}1,4-bis(diphenylphosphino)-butane complex [CH(CH$_2$PPh$_2$)$_2$PdCl$_2$]$_2$.[29] The N(3)−Pd(1)−C(11) angle of 79.88(10)° is unexceptional and typical of palladium complexes of cyclometalated *N*,*N*-dimethyl-α-methylbenzylamine.[36] The remaining cis angles of 96.48(6)° and 90.60(8)° for N(3)−Pd(1)−P(2) and C(11)−Pd(1)−P(1), respectively, reflect the relative steric bulk associated with the dimethylamino group and the metalated phenyl ring.

Catalytic Studies: Copolymerization of Ethene and CO. Diphosphines **1a−c** all form catalysts that are

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Table 4. Summary of Crystal Data and Structure Determination for Compounds 2a, 4a, and 5b

	2a	4a	5b
mol form	$C_{33}H_{31}Cl_2NP_2Pd\cdot 4C_5H_5N$	$C_{34}H_{34}ClNP_2Pd\cdot CH_2Cl_2$	$C_{40}H_{47}NO_5P_2Pd\cdot ClO_4$
fw	997.23	745.34	825.58
cryst size, mm	0.40 × 0.30 × 0.04	0.40 × 0.30 × 0.30	0.45 × 0.34 × 0.19
temperature, K	160(2)	160(2)	153(2)
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$P2_1/m$	$P2_12_12_1$
a, Å	9.8853(8)	9.8597(6)	10.4101(8)
b, Å	16.9646(14)	17.5391(10)	18.4749(14)
c, Å	28.654(2)	10.7622(6)	19.7509(15)
β, deg		112.590(1)	
V, Å^3	4805.3(7)	1718.32(17)	3798.6(5)
Z	4	2	4
μ, mm^{-1}	0.606	0.890	0.688
θ range, deg	1.4−25.0	2.0−28.5	1.5−28.6
no. reflns measd	34 516	14 687	35 878
no. unique reflns	8462	4162	8734
transmn coeff range	0.806−0.928	0.734−0.928	0.852−0.928
R_{int} (on F^2)	0.0735	0.0192	0.0520
no. of params	625	234	456
R^a	0.0484	0.0361	0.0321
$R_w{}^b$	0.1071	0.1090	0.0682
GOF^c on F^2	1.073	1.094	1.003
max., min. diff map (e Å^{-3})	0.69, −1.22	1.14, −1.39	0.52, −0.37

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

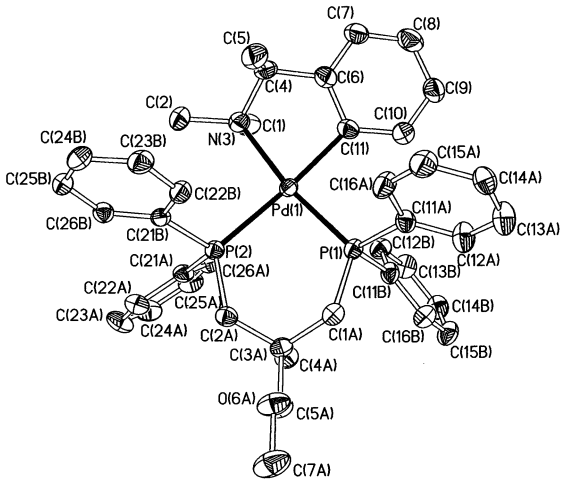
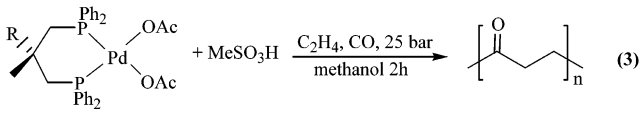


Figure 3. Molecular structure of **5b**. Ellipsoids are at 50% probability. Hydrogen atoms and perchlorate anion omitted for clarity.

highly active for the palladium-catalyzed copolymerization of ethene and carbon monoxide (eq 3). Initial



(3)

R = 2-py, **3a**
R = CH_2OMe, **3b**
R = Ph, **3c**

catalyst testing was conducted in methanol under 12.5 bar each of CO and ethene at 90 and 25 °C. After 2 h the reactor was vented and cooled, if necessary, and the polymer isolated by filtration. We have not made any attempt to optimize catalyst conditions, either via the use of oxidizing additives such as 1,4-benzoquinone or by varying the Brønsted acid. Rather, we have relied on comparative results obtained using dppp as a standard under our conditions in order to relate the results of our studies to those reported in the literature. The $^{13}C\{^1H\}$ NMR spectra of copolymer generated using catalysts based on **1a**−**c** and dppp have been recorded in 1,1,1,3,3,3-hexafluoroisopropyl alcohol and found to contain signals associated with the methylene and carbonyl carbons at δ 35.0 and 212.1 ppm, respectively, in addition to resonances at δ 217.0 (CH_3CH_2CO), 176.4 (MeOCO), 6.5 (CH_3CH_2), 52.0 (CH_2OCH_3), and 27.5 (CH_2−C(O)OMe), which correspond to keto and ester end groups of the polymer; that is, the principal chain termination step involves alcoholysis with no evidence for chain termination via β-elimination. The average molecular weights (M_n) of the copolymers have been estimated by end group analysis of their $^{13}C\{^1H\}$ NMR spectra, according to the procedure reported by Drent.[1b] The copolymers produced at 90 °C using catalyst precursors **3a**−**c** are all off-white powders, whereas those produced at room temperature are considerably less dense and have a fluffy fibrous morphology.

The results of the polymerization experiments and polymer properties are summarized in Table 3 and Charts 3 and 4. Preliminary catalyst testing, conducted at 90 °C, revealed that methanol solutions of **3b** or **3c** and methane sulfonic acid are highly active for the copolymerization of ethene and carbon monoxide with activities of 29 000 and 28 000 g polymer (mol of cat)$^{-1}$ h^{-1}, respectively, somewhat lower than that of 59 700 g polymer (mol of cat)$^{-1}$ h^{-1} obtained with the dppp-based Pd(II) precursor (entry 9). The reduced productivity of catalysts based on these 2,2′-disubstituted dppp derivatives is perhaps not surprising in the light of the recent studies of Bianchini, which demonstrated that substitution at the 2-position of the carbon backbone of dppp could reduce catalyst performance.[19] Under identical conditions the 2-methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane-based catalyst is unstable and rapidly decomposes at 90 °C, each catalytic run typically producing ca. 0.7 g of polymer (entry 3). The polymer produced during these catalytic runs is most likely generated in the early stages of the reaction below

Chart 3. Comparison of CO−Ethene Copolymerization Activities at 25 and 90 °C for Catalyst Precursors 3a−d

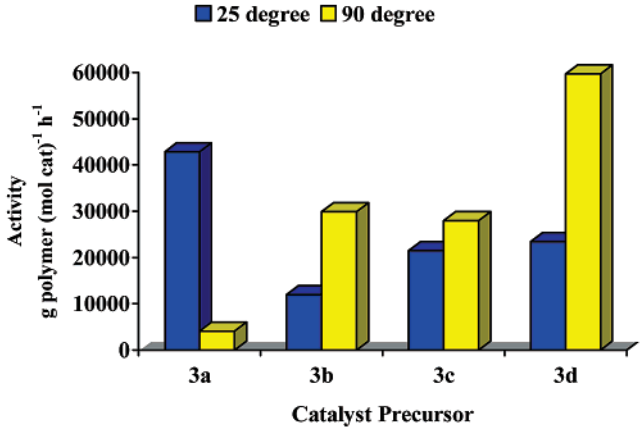
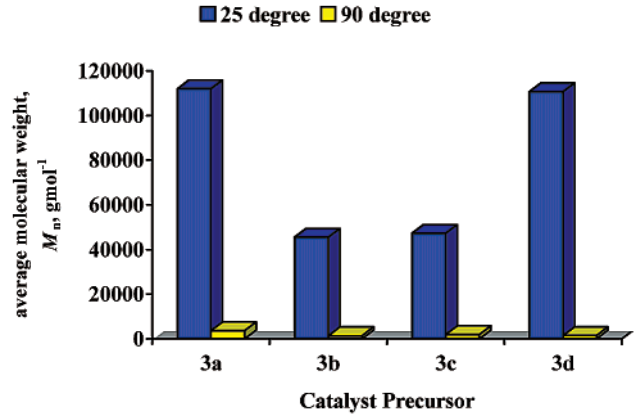


Chart 4. Comparison of Molecular Weight (M_n) of Polyketone Generated at 25 and 90 °C with Catalyst Precursors 3a−d



90 °C, as evidenced by a rapid uptake of gas before the reactor temperature stabilizes. However, gas consumption ceases shortly after the reactor reaches 90 °C, a clear indication that catalyst decomposition has occurred. Since the introduction of a phenyl and methyl substituent at the 2-position of the dppp backbone does not significantly affect catalyst performance, as evidenced by comparison of the activity obtained using catalyst precursor **3c** (entry 7) with that of [(dppp)Pd(OAc)$_2$] (entry 9), it is clear that the pyridin-2-yl ring must be responsible for the poor performance of catalyst mixtures formed from **3a**. Since oxidants such as benzoquinone are commonly used as additives to improve catalyst activity by increasing the number of active sites through oxidation of either Pd(0) or Pd(I) to Pd(II),[3a,f] we have examined the effect of added benzoquinone on the activity of precatalyst **3a** and found that the presence of benzoquinone has no noticeable effect on catalyst performance, as evidenced by the generation of dark gray polymer with an average activity of ca. 4000 g polymer (mol of cat)$^{-1}$ h^{-1}.

The rapid uptake of gas between room temperature and 90 °C for catalyst mixtures based on **3a** prompted us to evaluate the performance of each catalyst system at room temperature. As expected, polymerization rates obtained using catalyst precursors **3b**, **3c**, and [(dppp)Pd(OAc)$_2$] are significantly lower at room temperature than at 90 °C, with average activities of 12 000 (**3b**), 21 500 (**3c**), and 23 400 [(dppp)Pd(OAc)$_2$]. In contrast, catalyst mixtures formed from **3a** are an order of magnitude more active at RT than at 90 °C, are markedly more active than those based on [(dppp)Pd(OAc)$_2$] and consistently outperform those formed from **3b** and **3c** (Chart 3). In a comparative study at room temperature, catalysts based on **3a** consistently produce ca. twice as much polymer as those based on dppp, with an average activity of 42 800 g polymer (mol of cat)$^{-1}$ h^{-1} compared with 23 400 g polymer (mol of cat)$^{-1}$ h^{-1}, respectively. The disparate activity and stability of catalysts based on **3a** and **3c**, which differ solely in the substitution of a pyridin-2-yl ring for a phenyl ring, confirms that the nature of the substituent at the 2-position of the backbone of dppp has a marked effect on catalyst performance. In this regard, Bianchini has reported that introduction of alkyl substituents at the 2-position of the carbon backbone of dppp does not significantly improve catalyst performance, whereas introduction of methyl groups at both 1-positions results in a marked increase in productivity, particularly for *meso*-2,4-bis(diphenylphosphino)pentane (*meso*-bdpp).[19] A combination of electronic and steric factors has been suggested to contribute to the enhanced productivity of the *meso*-bdpp catalyst. It was proposed that the increased activity might be due to the more facile reoxidation of the one-electron-reduced species by either benzoquinone or H$^+$, which ultimately results in a larger number of active palladium centers. In addition, recent kinetic and thermodynamic studies suggest that a greater rigidity of the ligand backbone in [{*meso*-2,4-bis(diphenylphosphino)pentane}Pd] favors the propagation step by decreasing the stability of the β-chelate resting state [(P−P)Pd(CH$_2$CH$_2$COR)]$^+$.[3f] In an attempt to investigate the role of the pyridin-2-yl substituent, we have examined the effect of adding pyridine to a catalyst mixture of **3d** and methane sulfonic acid and found that, under comparable conditions, addition of 1 equiv of pyridine results in a reduction in activity from 23 400 to 12 500 g polymer (mol of cat)$^{-1}$ h^{-1}, for catalyst mixtures of **3d** and **3d**/pyridine, respectively. The poor performance of the **3d**/pyridine mixture (entry 10) compared with the impressive productivity obtained using **3a** (entry 1) implies that it is necessary for the pyridin-2-yl ring to be proximate to the metal center in order to influence catalyst performance. However, at this stage we are unable to provide a definitive explanation for the role of the pyridin-2-yl ring in determining catalyst stability and productivity but note that it is likely to be protonated in the presence of excess methane sulfonic acid. Clearly, further studies are required in order to understand how the pyridin-2-yl ring enhances catalyst performance at room temperature, compared to dppp, while markedly reducing its stability at higher temperatures, such that catalyst decomposition is rapid at 90 °C.

End group analysis of the ^{13}C{^{1}H} NMR spectra revealed that polyketone produced at 90 °C has a markedly lower average molecular weight than that produced at 25 °C. The end groups of polymers generated at 25 °C appear as low intensity resonances and when integrated correspond to average molecular weights (M_n) of 45−112 kg mol^{-1} (n = 800−2000), whereas the average molecular weights of polymers generated at 90

°C are significantly lower and range from 1.6 to 3.5 kg mol^{-1} (Chart 4). In his early studies Drent reported that a reaction rate of $\sim 10^4$ mol converted ethene (mol Pd)$^{-1}$ h^{-1} gave polymer with an average molecular weight (M_n) of $\sim$20 kg mol^{-1}.[1] He found that high molecular weight polymer could be produced using a combination of dppp and toluenesulfonic acid in methanol at 65 °C, whereas polymer generated at higher temperatures (90 and 115 °C) generally had a much lower average molecular weight. Herrmann has reported that dicationic palladium(II) complexes of chelating *N*-heterocyclic carbenes catalyze the perfectly alternating copolymerization of ethene and carbon monoxide to give polyketone under mild conditions and low pressure.[18] The polymer molecular weights could not be determined as a result of the low intensity of the end group resonances in the $^{13}C\{^1H\}$ NMR spectrum, but were assumed to be significantly greater than those generated by Drent et al. Given the large molecular weight of the polymer and the relatively modest TONs, it was concluded that only a small percentage of palladium was active. By analogy, the high molecular weight of polyketone generated by precursors **3a**−**c** at 25 °C, in combination with the productivity, suggests that a smaller percentage of the palladium precatalysts **3a**−**c** produce polymer compared to that at 90 °C. Since the average molecular weight of copolymer is determined by the relative rates of chain propagation, via alternating insertions of ethene into metal−acyl bonds and carbon monoxide into metal−alkyl bonds, and chain termination, via attack by methanol, the high molecular weight of copolymer produced at 25 °C must be due to an increase in the ratio of the rates of these two processes, which we tentatively suggest to involve a reduction in the rate of termination relative to that of propagation. The opposing influence of reaction temperature on the rate of polymerization and the molecular weight of the polyketone is well documented.[10a] Introduction of heteroatoms/polar substituents, in particular a methoxy group, at the position ortho to phosphorus in dppp results in a dramatic enhancement of the rate of copolymerization compared to the unmodified catalyst, which offers the possibility of preparing polymers of high molecular weight at a high reaction rate. In this regard, further studies aimed at optimizing the performance of the catalyst formed from **3a** would be worthwhile.

In conclusion, several 2,2′-disubstituted dppp derivatives have been prepared that form catalysts that are active for the copolymerization of ethene and carbon monoxide. Contrary to previous reports, our studies clearly demonstrate that substitution at the 2-position of the carbon backbone of dppp can exert a marked influence on catalyst activity and stability. The most striking feature of these catalyst systems is the effect that a pyridin-2-yl group has on both catalyst stability and productivity. Under identical conditions catalysts based on [{2-phenyl-2-methyl-1,3-bis(diphenylphosphino)propane}$Pd(OAc)_2$] and [{2-methoxymethyl-2-methyl-1,3-bis(diphenylphosphino)propane}$Pd(OAc)_2$] are slightly less active than that of dppp, whereas catalyst mixtures formed from [{2-methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane}$Pd(OAc)_2$] are unstable and rapidly decompose at 90 °C. In contrast, the 2-methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane-based catalyst is stable at room temperature and consistently outperforms those based on **3b**−**c** and most notably has an activity approximately twice that of its unsubstituted counterpart dppp. The average molecular weight of polyketone produced at room temperature is markedly higher than that at 90 °C and, taking into account the average catalyst productivity, is consistent with an increase in the ratio of the rate of chain termination to the rate of chain propagation. Clearly, evaluation of the factors that influence the performance of 2,2′-disubstituted dppp-based catalysts is not straightforward, and further studies are required to develop an understanding of the origin of these effects. In particular, investigations into the influence of ligand modification including the basicity of the 2-substituent, its steric bulk, and the proximity of the heteroatom donor on catalyst stability, activity, and polymer molecular weight are currently underway. It should also be possible to enhance polymer productivity by preparing well-defined cationic methyl and methoxycarbonyl precatalysts, which will enable us to undertake catalyst testing in dichloromethane and to investigate the mechanism using stoichiometric model reactions.

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 from potassium, toluene from sodium, dichloromethane and pyridine from calcium hydride, and ethanol from sodium ethoxide and stored over 3 Å molecular sieves. Deuteriochloroform was predried with calcium hydride, then vacuum transferred and stored over 4 Å molecular sieves. 1,1,1,3,3,3-Hexafluoropropan-2-ol was purchased from Aldrich and used as received. The palladium complexes [(cycloocta-1,5-diene)$PdCl_2$],[37] [(cycloocta-1,5-diene)PdClMe],[38] and (*S*)-(+)-bis(*μ*-chloro)bis[*N*,*N*-dimethyl-α-methylbenzylamine-*C*,*N*]dipalladium,[39] and 2-methyl-2-pyridin-2-yl-1,3-propanediol and 2-methyl-2-pyridin-2-yl-1,3-bis(toluene-4-sulfonyloxy)propane[22] were prepared as previously described.

Synthesis of 2-Methoxymethyl-2-methyl Malonic Acid Diethyl Ester. A tetrahydrofuran solution (40 mL) of diethyl phenylmalonate (5.0 g, 28.7 mmol) was cooled to −78 °C and treated with a 2.5 M solution of butyllithium in hexanes (11.48 mL, 28.7 mmol). The resulting mixture was stirred rapidly and, after warming to room temperature, was transferred dropwise to a tetrahydrofuran solution (30 mL) of chloromethyl methyl ether (2.31 g, 28.7 mmol). After stirring overnight the solvent was removed under vacuum and the residue extracted into diethyl ether (2 × 30 mL), washed with water (2 × 30 mL), dried over $MgSO_4$, and filtered, and the solvent was removed to afford the desired ester as a pale yellow/colorless oil in 84% yield (5.24 g, 24.01 mmol). ^1H NMR (300.0 MHz, $CDCl_3$, δ): 4.12 (quart, 4H, J = 7.1 Hz, CH_2CH_3), 3.66 (s, 2H, CH_2), 3.28 (s, 3H, OCH_3), 1.78 (s, 3H, CH_3), 1.42 (t, 6H, J = 7.1 Hz, CH_2CH_3).

Synthesis of Diethyl Methyl(phenyl)malonate. Diethyl phenylmalonate (7.50 g, 31.7 mmol) was added dropwise to a solution of sodium ethoxide, prepared by dissolution of sodium

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(1.0 g, 43.5 mmol) in ethanol (ca. 100 mL). After stirring the reaction mixture rapidly for ca. 30 min methyl iodide (6.25 g, 2.74 mL, 44.0 mmol) was added dropwise and stirring was continued for a further 2 h, after which time the solvent was removed under vacuum and the residue extracted into CH_2Cl_2 (2 × 50 mL). The organic phase was washed with water (2 × 50 mL), dried over $MgSO_4$, filtered, and concentrated under vacuum to give the desired ester as a yellow oil, which was distilled (116−118 °C, 0.1 mmHg) to afford diethyl methyl(phenyl)malonate as a pale yellow oil in 93% yield (7.39 g, 29.5 mmol). ^{1}H NMR (300.0 MHz, $CDCl_3$, δ): 7.24 (m, 5H, C_6H_5), 4.14 (q, 4H, J = 7.1 Hz, CH_2CH_3), 1.79 (s, 3H, CH_3), 1.17 (t, 6H, J = 7.1 Hz, CH_2CH_3).

Reduction of 2-Methoxymethyl-2-methyl Malonic Acid Diethyl Ester. A solution of 2-methoxymethyl-2-methyl malonic acid diethyl ester (6.43 g, 29.5 mmol) in tetrahydrofuran (20 mL) was added dropwise via cannula to a stirred suspension of $LiAlH_4$ (5.60 g, 147.6 mmol) in tetrahydrofuran (ca. 80 mL), at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for a further 4 h. After cooling to 0 °C, the resulting suspension was diluted with diethyl ether (ca. 100 mL) and quenched by addition of water (10 mL), followed by KOH (2.8 g in 10 mL of water) and finally water (10 mL), and stirred for a further 1 h. After hydrolysis was complete, the resulting mixture was filtered and the solids were washed with diethyl ether (2 × 25 mL). The organic fractions were combined, and dried over $MgSO_4$, and the solvent was removed to afford 2-methoxymethyl-2-methyl-1,3-propanediol (**Ib**) as a colorless oil in 83% yield (3.28 g, 24 mmol). ^{1}H NMR (300.0 MHz, $CDCl_3$, δ): 3.58 (d, 2H, J = 10.7 Hz, CH_2), 3.48 (d, 2H, J = 10.7 Hz, CH_2) 3.31 (s, 2H, CH_2), 3.28 (s, 3H, OCH_3), 0.75 (s, 3H, CH_3). ^{13}C{^{1}H} (125.7 MHz, $CDCl_3$, δ): 17.1 (s, CH_3), 40.8 (s, *C*Me), 59.5 (s,CH_3), 67.6 (s, CH_2OH), 78.4 (CH_2OMe).

Reduction of Diethyl Methyl(phenyl)malonate. 2-Methyl-2-phenyl-1,3-propanediol (**Ic**) was isolated as a white solid in 79% yield (1.80 g), according to the procedure described above for 2-methoxymethyl-2-methyl-1,3-propanediol. ^{1}H NMR (300.0 MHz, $CDCl_3$, δ): 7.35−7.10 (m, 5H, C_6H_5), 3.84 (d, 2H, J = 10.9 Hz, CH_2), 3.70 (d, 2H, J = 10.9 Hz, CH_2), 2.52 (br s, 2H, O*H*), 1.19 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, δ): 20.6 (s, CH_3), 52.9 (s, *C*Me), 69.7 (s, CH_2OH), 126.6 (s, C_6H_5), 128.6 (s, C_6H_5), 143.1 (s, C_6H_5).

Synthesis of 2-Methoxymethyl-2-methyl-1,3-bis(toluene-4-sulfonyloxy)propane (IIb). *p*-Toluenesulfonyl chloride (9.50 g, 50 mmol) was added portionwise to a stirred solution of 2-methoxymethyl-2-methyl-1,3-propanediol (2.68 g, 20 mmol) in dry pyridine (30 mL) at such a rate to maintain the temperature at 0 °C. After stirring at room temperature for ca. 12 h, the reaction mixture was poured onto ice/water (150 mL) and extracted with diethyl ether (2 × 50 mL). The organic phase was separated, dried over $MgSO_4$, and filtered, and the solvent was removed under vacuum to afford 2-methoxymethyl-2-methyl-1,3-bis(toluene-4-sulfonyloxy)propane as a colorless viscous oil in 72% yield (6.4 g). ^{1}H NMR (300.0 MHz, $CDCl_3$, δ): 7.66 (d, 4H, AA′XX′, $|J_{AX} + J_{A'X}| = 8.3$ Hz, *p*-C_6H_4), 7.28 (d, 4H, AA′XX′, $|J_{AX} + J_{AX'}| = 8.3$ Hz, *p*-C_6H_4), 3.75 (s, 4H, CH_2), 3.06 (s, 3H, OCH_3), 3.04 (s, 2H, CH_2), 2.39 (s, 6H, *p*-CH_3), 0.82 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, δ): 16.3 (s, CH_3), 21.6 (s, CH_3), 39.7 (s, *C*Me), 59.0 (s, OCH_3), 71.1 (s, CH_2OMe), 72.4 (s, CH_2O), 127.8 (s, C_6H_4), 129.8 (s, C_6H_4), 132.3 (s, C_6H_4), 144.9 (s, C_6H_4).

Synthesis of 2-Methyl-2-phenyl-1,3-bis(toluene-4-sulfonyloxy)propane (IIc). *p*-Toluenesulfonyl chloride (9.50 g, 50 mmol) was added portionwise to a stirred solution of 2-methyl-2-phenyl-1,3-propanediol (3.32 g, 20 mmol) in dry pyridine (30 mL) at such a rate to maintain the temperature at 0 °C. After stirring at room temperature for ca. 12 h, the reaction mixture was poured onto ice/water (150 mL) and the resulting oil triturated to afford a white precipitate, which was isolated by filtration, washed with water (3 × 30 mL) and then petroleum ether (2 × 30 mL), and dried under vacuum to afford 2-methyl-2-phenyl-1,3-bis(toluene-4-sulfonyloxy)propane as a white solid in 75% yield (6.6 g). ^{1}H NMR (300.0 MHz, $CDCl_3$, δ): 7.57 (d, 4H, AA′XX, $|J_{AX} + J_{A'X}| = 8.1$ Hz, *p*-C_6H_4), 7.23 (d, 4H, AA′XX′, $|J_{AX} + J_{AX'}| = 8.1$ Hz, *p*-C_6H_4), 7.15 (m, 3H, C_6H_5), 7.03 (m, 2H, C_6H_5), 4.04 (br s, 4H, CH_2), 2.37 (s, 6H, *p*-CH_3), 1.23 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, δ): 20.3 (s, CH_3), 21.6 (s, CH_3), 42.1 (s, *C*Me), 72.8 (s, CH_2O), 125.9 (s, $C_6H_5'C_6H_4$), 127.4 (s, $C_6H_5'C_6H_4$), 127.9 (s, C_6H_5/C_6H_4), 128.5 (s, C_6H_5/C_6H_4), 129.9 (s, C_6H_5/C_6H_4), 132.2 (s, C_6H_5/C_6H_4), 139.5 (s, C_6H_5/C_6H_4), 145.0 (s, C_6H_5/C_6H_4).

Synthesis of 1,3-Dichloro-2-methyl-2-pyridin-2-ylpropane (IIIa). A suspension of 2-methyl-2-pyridin-2-yl-1,3-bis-(toluene-4-sulfonyloxy)propane (4.43 g, 10.0 mmol) and anhydrous lithium chloride (3.53 g, 83.0 mmol) in hexamethyl phosphoramide (HMPA) (ca. 20 mL) was stirred and heated to 110 °C for ca. 12 h. After cooling to room temperature, the mixture was diluted with water (100 mL) and extracted with *n*-pentane (4 × 100 mL). The combined organic phase was further washed with water (2 × 100 mL) and brine (1 × 100 mL), dried over $MgSO_4$, and filtered, and the solvent was removed to afford 1,3-dichloro-2-methylpyridin-2-yl-propane as a viscous oil in 75% yield (1.53 g). ^{1}H NMR (300.0 MHz, $CDCl_3$, δ): 8.59 (ddd, 1H, J = 4.8 Hz, 0.9 Hz, C_5H_4N), 7.71 (dt, 1H, J = 1.9 Hz, 7.8 Hz, C_5H_4N), 7.31 (d, J = 8.0 Hz, C_5H_4N), 7.19 (m, 1H, C_5H_4N), 4.01 (AB, 4H, CH_2), 1.56 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, δ): 21.9 (s, CH_3), 47.6 (s, *C*Me), 51.4 (s, CH_2Cl), 121.5 (s, C_5H_4N), 122.5 (s, C_5H_4N), 136.9 (s, C_5H_4N), 149.5 (s, C_5H_4N), 161.5 (s, C_5H_4N).

Synthesis of 1,3-Dichloro-2-methoxymethyl-2-methylpropane (IIIb). 1,3-Dichloro-2-methoxymethyl-2-methylpropane was isolated as a pale yellow oil in 73% yield (1.21 g), according to the procedure described above for **IIIa**. ^{1}H NMR (300.0 MHz, $CDCl_3$, δ): 3.48 (AB, J_{HH} = 12.8 Hz, 2H, CH_2Cl), 3.46 (AB, J_{HH} = 11.3 Hz, 2H, CH_2Cl), 3.27 (s, 3H, OCH_3), 3.23 (s, 2H, CH_2), 1.02 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, δ): 18.6 (s, CH_3), 41.1 (s, CMe), 48.8 (s, CH_2Cl), 59.4 (OCH_3), 74.9 (OCH_2).

Synthesis of 1,3-Dichloro-2-methyl-2-phenylpropane (IIIc). 1,3-Dichloro-2-methyl-2-phenylpropane was prepared according to the procedure described above for **IIIa** and isolated as a pale yellow oil in 84% yield (2.30 g). ^{1}H NMR (300.0 MHz, $CDCl_3$, δ): 7.32−7.18 (m, 5H, C_6H_5), 3.80 (AB, J_{HH} = 11.3 Hz, 2H, CH_2Cl), 3.77 (AB, J_{HH} = 11.3 Hz, 2H, CH_2Cl), 1.45 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, δ): δ 22.6 (s, CH_3), 44.4 (s, *C*Me), 51.4 (s, CH_2Cl), 126.2 (s, C_6H_5), 127.4 (s, C_6H_5), 128.6 (s, C_6H_5), 141.8 (s, C_6H_5).

Synthesis of 2-Methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane (1a). A solution of diphenylphosphine (2.98 g, 16.0 mmol) in THF (20−30 mL) was cooled to −78 °C and was treated with a 2.5 M solution of butyllithium in hexanes (6.40 mL, 16.0 mmol) with rapid stirring. After warming to room temperature the solution was cooled in an ice bath, and a tetrahydrofuran solution of 2-methylpyridin-2-yl-1,3-dichloropropane (1.53 g, 8.0 mmol) added dropwise. The resulting mixture was heated to reflux overnight, during which time the color changed from deep orange to a pale yellow/colorless. The solvent was removed under vacuum, and the resulting oily residue was extracted into diethyl ether (70 mL) and washed with degassed water (40−50 mL). The organic phase was separated, dried over $MgSO_4$, and filtered, and the solvent was removed to afford 2-methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane as a colorless oil in 75% yield (3.0 g). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, δ): −22.2 (s). ^{1}H NMR (300.0 MHz, $CDCl_3$, δ): 8.17 (m, 1H, C_6H_5), 7.32 (m, 8H, C_6H_5), 7.25−7.05 (m, 14H, C_6H_5), 6.74 (m, 1H, C_6H_5), 2.87 (ABd, 2H, J = 3.5 Hz, 14.1 Hz, CH_2), 2.66 (ABd, 2H, J = 3.5 Hz, 14.1 Hz, CH_2), 1.45 (s, 3H, CH_3).

Synthesis of 2-Methoxymethyl-2-methyl-1,3-bis(diphenylphosphino)propane (1b). 2-Methoxymethyl-2-methyl-1,3-bis(diphenylphosphino)propane was isolated as a pale yellow,

viscous oil in 80% yield (1.72 g), according to the procedure described above for **1a**. $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, δ): −24.3 (s). ^1H NMR (300.0 MHz, $CDCl_3$, δ): 7.35 (m, 8H, C_6H_5), 7.10 (m, 12H, C_6H_5), 3.02 (s, 2H, CH_2), 2.75 (s, 3H, CH_3), 2.32 (dd, 2H, J = 14.3, 2.5 Hz, CH_2), 2.27 (dd, 2H, J = 14.3 Hz, 2.5 Hz, CH_2), 0.90 (s, 3H, CH_3).

Synthesis of 2-Methyl-2-phenyl-1,3-bis(diphenylphosphino)propane (1c). 2-Methyl-2-phenyl-1,3-bis(diphenylphosphino)propane was isolated as a colorless, viscous oil in 79% yield (1.39 g), according to the procedure described above for **1a**. $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, δ): −23.0 (s). ^1H NMR (300.0 MHz, $CDCl_3$, δ): 7.34−6.94 (m, 25H, C_6H_5), 2.71 (dd, 2H, J = 14.4 Hz, 4.0 Hz, CH_2), 2.62 (dd, 2H, J = 14.4 Hz, 4.0 Hz, CH_2), 1.42 (s, 3H, CH_3).

Synthesis of [{2-Methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane}PdCl$_2$] (2a). A solution of [(cycloocta-1,5-diene)$PdCl_2$] (0.202 g, 0.71 mmol) in dichloromethane (4−5 mL) was treated with a dichloromethane solution (5 mL) of 2-methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane (0.365 g, 0.725 mmol) and stirred vigorously for ca. 1−2 h. The reaction mixture was filtered and the precipitate washed with hexane (2 × 10 mL) and dried under vacuum to give **2a** as a yellow solid in 81% yield (0.392 g). Crystallization from a pyridine solution layered with hexane gave X-ray quality crystals of **2a**. $^{31}P\{^1H\}$ NMR (121.4 MHz, C_5D_4N, δ): 19.0 (s, PPh_2). ^1H NMR (300.0 MHz, $CDCl_3$, δ): 8.23 (m, 4H, C_6H_5), 8.13 (dm, 1H, C_6H_5), 7.79 (m, 4H, C_6H_5), 7.28−7.04 (m, 13H, C_6H_5), 6.87 (m, 1H, C_6H_5), 6.77 (m, 1H, C_6H_5), 3.10 (br m, 2H, CH_2), 2.82 (dd, J_{HH} = 14.9 Hz, 9.4 Hz, 2H, CH_2), 0.83 (s, 3H, CH_3). Anal. Calcd for $C_{33}H_{31}Cl_2NP_2Pd\cdot 4C_5H_5N$: C, 63.83; H, 5.15; N, 7.02. Found: C, 64.33; H, 5.43; N, 7.41.

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

Synthesis of [{2-Methoxymethyl-2-methyl-1,3-bis(diphenylphosphino)propane}PdCl$_2$}] (2b). Compound **2b** was isolated as a yellow solid in 80% yield (0.254 g) from a dichloromethane solution layered with hexane. $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, δ): 18.0 (s, PPh_2). ^1H NMR (300.0 MHz, $CDCl_3$, δ): 7.88 (m, 4H, C_6H_5), 7.80 (m, 4H, C_6H_5), 7.40 (m, 12H C_6H_5), 2.60 (s, 3H, CH_3), 2.50 (s, 2H, CH_2), 2.40 (ABd, J_{HH} = 15.3 Hz, 8.8 Hz, 2H, CH_2), 2.18 (ABd, J_{HH} = 15.3 Hz, 8.8 Hz, 2H, CH_2), 0.60 (s, 3H, CH_3). Anal. Calcd for $C_{30}H_{32}Cl_2OP_2Pd$: C, 55.64; H, 4.98. Found: C, 55.91; H, 4.72.

Synthesis of [{2-Methyl-2-phenyl-1,3-bis(diphenylphosphino)propane}PdCl$_2$}] (2c). Compound **2c** was prepared according to the procedure described above and was isolated as a pale yellow solid in 68% yield (0.277 g). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, δ): 21.2 (s, PPh_2). ^1H NMR (300.0 MHz, $CDCl_3$, δ): 7.79−6.78 (m, 25H, C_6H_5), 2.96 (dd, J_{HH} = 14.9 Hz, 9.4 Hz, 2H, CH_2), 2.88 (dd, J_{HH} = 14.9 Hz, 9.4 Hz, 2H, CH_2), 0.87 (s, 3H, CH_3). Anal. Calcd for $C_{34}H_{33}Cl_2P_2Pd$: C, 59.99; H, 4.89. Found: C, 60.23; H, 5.03.

Synthesis of [{2-Methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane}Pd(OAc)$_2$] (3a). A suspension of palladium acetate (0.61 g, 2.98 mmol) in toluene (∼1−2 mL) was treated with a toluene solution (∼5−6 mL) of 2-methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane (1.50 g, 2.98 mmol) and stirred vigorously for ca. 30 min, during which time a pale-colored solid precipitated from solution. The reaction mixture was filtered, and the precipitate was washed with toluene (2 × 2 mL) and hexane (3 × 10 mL) and dried under vacuum to give **3a** as a salmon pink solid in 77% yield (1.62 g). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, δ): 17.4 (s, PPh_2). ^1H NMR (300.0 MHz, $CDCl_3$, δ): 8.49 (m, 1H, C_5H_4N/C_6H_5), 7.94 (m, 4H, C_5H_4N/C_6H_5), 7.64 (m, 4H, C_5H_4N/C_6H_5), 7.45−7.15 (m, 13H, C_5H_4N/C_6H_5), 7.02 (m, 2H, C_5H_4N/C_6H_5), 3.09 (dd, 2H, J = 7.9 Hz, 15.2 Hz, CH_2), 2.39 (dd, 4H, J = 8.9 Hz, 15.2 Hz, CH_2), 1.43 (br s, 6H, O_2CCH_3), 1.27 (s, 3H, 2-py-CCH_3).

Compounds **3b**−**c** were prepared according to the procedure described above.

Synthesis of [{2-Methoxymethyl-2-methyl-1,3-bis(diphenylphosphino)propane}Pd(OAc)$_2$] (3b). Compound **3b** was prepared according to the procedure described above for **3a** and was isolated as a tan solid in 87% yield (1.31 g). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, δ): 16.3 (s, PPh_2). ^1H NMR (300.0 MHz, $CDCl_3$, δ): 7.82 (m, 8H, C_6H_5), 7.36 (m, 12H, C_6H_5), 2.97 (s, 3H, OCH_3), 2.78 (s, 2H, OCH_2), 2.46 (m, 2H, CH_2), 2.10 (m, 2H, CH_2), 1.48 (br s, 6H, O_2CCH_3), 0.82 (s, 3H, CH_3).

Synthesis of [{2-Methyl-2-phenyl-1,3-bis(diphenylphosphino)propane}Pd(OAc)$_2$] (3c). Compound **3c** was prepared according to the procedure described above and was isolated as a white solid in 83% yield (0.9 g). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, δ): 16.8 (s, PPh_2). ^1H NMR (300.0 MHz, $CDCl_3$, δ): 8.06 (m, 4H, C_6H_5), 7.63 (m, 4H, C_6H_5), 7.45−7.05 (m, 17H, C_6H_5), 2.67 (dd, 2H, J = 7.6 Hz, 14.9 Hz, CH_2), 2.55 (dd, 2H, J = 7.6 Hz, 14.9 Hz, CH_2), 1.45 (br s, 6H, O_2CCH_3), 1.10 (s, 3H, CH_3).

Synthesis of [{1,3-Bis(diphenylphosphino)propane}-Pd(OAc)$_2$}] (3d). Compound **3d** was prepared according to the procedure described above and isolated as a white solid in 77% yield (2.24 g). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, δ): 10.5 (s, PPh_2). ^1H NMR (300.0 MHz, $CDCl_3$, δ): 7.33−7.18 (m, 20H, C_6H_5), 2.12 (m, 4H, CH_2), 1.59 (m, 2H, CH_2).

Synthesis of [{2-Methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane}PdMeCl] (4a). A dichloromethane solution of [(cycloocta-1,5-diene)PdMeCl] (0.072 g, 0.27 mmol) was treated with a dichloromethane solution of 2-methyl-2-pyridin-2-yl-1,3-bis(diphenylphosphino)propane (0.137 g, 0.27 mmol) and stirred rapidly for ca. 2−3 h. The reaction mixture was filtered and the residue washed with hexane (2 × 10 mL) and crystallized from a dichloromethane solution layered with hexane to give **4a** as yellow crystals in 69% yield (0.122 g). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, δ): 29.4 (d, $^2J_{PP}$ = 48.6 Hz, PPh_2), −1.79 (d, $^2J_{PP}$ = 48.6 Hz, PPh_2). ^1H NMR (300.0 MHz, CD_2Cl_2, δ): 8.44 (m, 1H, C_5H_4N/C_6H_5)), 8.14 (m, 2H, C_5H_4N/C_6H_5), 8.03 (m, 2H, C_5H_4N/C_6H_5), 7.72 (m 2H, C_5H_4N/C_6H_5), 7.62 (m 2H, C_5H_4N/C_6H_5), 7.58−7.52 (m 7H, C_5H_4N/C_6H_5), 7.44 (m, 6H, C_5H_4N/C_6H_5), 3.03 (dd, $^2J_{HH}$ = 15.3 Hz, $^2J_{PH}$, 6.3 Hz, 1H, CH_aCH_b), 2.91 (dd, $^2J_{HH}$ = 15.3 Hz, $^2J_{PH}$ = 5.0 Hz, 1H, CH_cCH_d), 2.82 (dd, $^2J_{HH}$ = $^2J_{PH}$ = 15.3 Hz, 1H, CH_aCH_b), 2.72 (dd, 1H, $^2J_{HH}$ = $^2J_{PH}$ = 15.3 Hz, CH_cCH_d), 0.94 (s, 3H, CH_3), 0.57 (dd, $^3J_{PH}$ = 7.8, 6.6 Hz, 3H, Pd−CH_3). Anal. Calcd for $C_{34}H_{34}ClNP_2Pd\cdot CH_2Cl_2$: C, 57.18; H, 4.87. Found: C, 57.44; H, 4.57.

Synthesis of [{(*S*)-(+)-*N*,*N*-Dimethyl-α-methylbenzylamine-*C*,*N*}Pd{MeOCH$_2$}CMe{CH$_2$PPh$_2$}$_2$][ClO$_4$] (5b). A solution of (*S*)-(+)-bis(μ-chloro)bis[*N*,*N*-dimethyl-α-methylbenzylamine-*C*,*N*]dipalladium (0.78 g, 0.13 mmol) in dichloromethane (ca. 5 mL) and silver perchlorate (0.056 g, 0.26 mmol) was stirred at room temperature in the dark for ca. 2 h. The resulting cloudy reaction mixture was filtered and then treated with a dichloromethane solution (5 mL) of 2-methoxymethyl-2-methyl-1,3-bis(diphenylphosphino)propane (0.127 g, 0.27 mmol) and stirred for a further 1 h. The solvent was removed to give **5b** as an off-white solid in 70% yield (0.152 g). Crystallization from warm methanol afforded X-ray quality crystals of **5b**, as a 1:1 mixture of diastereoisomers. $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, δ): 29.0 (d, J_{PP} = 46.0 Hz), 28.6 (d, J = 46.0 Hz), 1.75 (d, J = 46.0 Hz), 1.55 (d, J_{PP} = 46.0 Hz). ^1H NMR (300.0 MHz, $CDCl_3$, δ): 8.2−6.4 (m, 24H, C_6H_5/C_6H_4), 3.75 (dq, J_{HH} = J_{PH} = 6.1 Hz, 1H, C*H*Me), 3.54 (dq, J_{HH} = J_{PH} = 6.1 Hz, 1H, C*H*Me), 2.93 (s, 3H, CH_2OMe), 2.75 (s, 3H, CH_2OMe), 2.7−2.0 (m, 6H, PCH_2/CH_2OMe), 2.29 (d, J = 1.6 Hz, 3H, NMe_2), 2.27 (d, J = 1.6 Hz, 3H, NMe_2), 2.22 (s, 3H, NMe_2) 2.19 (s, 3H, NMe_2), 1.74 (d, J = 6.1 Hz, 3H, CH*Me*), 1.73 (d, J = 6.1 Hz, 3H, CH*Me*), 0.61 (s, 3H, C(*Me*)CH_2OMe), 0.38 (s, 3H, C(*Me*)CH_2OMe). Anal. Calcd for $C_{40}H_{46}ClNO_5P_2Pd$: C, 58.28; H, 5.62. Found: C, 58.66; H, 5.73.

Polymerization Procedure and Polymer Characterization. Polymerizations were conducted in methanol in a 300 mL autoclave. The catalyst precursors were prepared according

to the procedure reported for [(dppp)Pd(OAc)$_2$]. In a typical procedure, 0.17 mmol of [(P−P)Pd(OAc)$_2$] was dissolved in 120 mL of anhydrous methanol, 0.11 mL (1.7 mmol) of methane sulfonic acid was added, and the solution was transferred to a 300 mL autoclave under N_2. The reactor was pressurized to 25 bar with a 1:1 mixture of CO and ethene and heated at 90 °C while maintaining a pressure of ca. 25 bar by the continuous feeding of an equimolar mixture of CO and C_2H_4 from a gas reservoir. After stirring at 400 rpm for 2 h the reaction was quenched by release of CO/ethene pressure and the polymer isolated by filtration, washed with methanol and ether, dried, and weighed.

Crystal Structure Determination of 2a, 4a, and 5b. Data were collected on Bruker SMART CCD diffractometers with Mo Kα radiation (λ = 0.71073 Å) at low temperature; crystal data and other information are presented in Table 4. Absorption corrections were semiempirical, based on repeated and symmetry-equivalent reflections. The structures were determined by direct methods and refined by full-matrix least-squares techniques on all unique F^2 values. Hydrogen atoms were constrained with a riding model. **2a** was found to contain three ordered and one disordered pyridine molecule in the asymmetric unit; for the disordered molecule, two orientational components were refined, without H atoms and without distinction between C and N atoms. In **4a** there is a highly disordered dichloromethane molecule on a mirror plane, for which partially occupied atom sites were refined to fit the observed electron density peaks; the geometry of this fragment is meaningless. The main complex molecule is also disordered across a mirror plane, which exchanges the methyl and chloro ligands; these were refined with half-occupancy in each of the two positions and were subject to restraints because of the high degree of overlap of their electron density distributions. Complex **5b** is unsolvated and consists of a complex cation and an uncoordinated perchlorate anion in the asymmetric unit. The crystal of **2a** was found to be racemically twinned. Programs were standard Bruker SMART (diffractometer control) and SAINT (data integration), together with SADABS (absorption corrections and frame scaling), SHELXTL (structure solution, refinement, and graphics), and local software.

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Supporting Information Available: For **2a**, **4a**, and **5b** details of structure determination, non-hydrogen atomic positional parameters, full listings of bond distances and angles, anisotropic displacement parameters, and hydrogen atomic coordinates. ^{1}H and ^{31}P{^{1}H} NMR spectra for compounds **3a**−**d**. 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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