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Palladium Complexes of C_2-, C_3-, and C_4-Bridged Bis(phospholyl) Ligands: Remarkably Active Catalysts for the Copolymerization of Ethylene and Carbon Monoxide

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*Summary: The C_2-, C_3-, and C_4-bridged bis(2,3,4,5-tetramethylphospholes) $[\{\overline{C(Me)C(Me)C(Me)C(Me)P}\}_2X]$ (**1a**, $X = C_2H_4$; **1b**, $X = C_3H_6$; **1c**, $X = (CH_2)_2C_6H_4$) and their corresponding palladium complexes $[(P\text{-}P)PdCl_2]$ (**2a**−**c**) have been prepared and characterized. A single-crystal X-ray analysis of [{bis(2,3,4,5-tetramethylphospholyl)-o-xylene}$PdCl_2$] (**2c**) reveals that **1c** forms a seven-membered chelate; the phosphole rings are oriented perpendicular to the PdP_2Cl_2 plane. Methanol solutions of $[(P\text{-}P)Pd(OAc)_2]$ (**3a**, P-P = **1b**; **3b**, P-P = **1c**) and methanesulfonic acid are active for the copolymerization of ethylene and carbon monoxide, generating high-molecular-weight polymers with narrow molecular weight distributions. Under our conditions, the activity of catalyst systems containing **1c** is comparable to that based on bis(diphenylphosphino)propane (dppp).*

Bidentate phosphines are among the most popular ligands used in platinum group catalysis,[1] primarily because of their steric, electronic, and geometric versatility. However, despite the immense number of novel diphosphines that are now available, our understanding of how factors such as chelate ring size, bite angle, and conformational flexibility influence catalyst activity and selectivity is rather limited.[2] In this regard, one of the most striking illustrations of the influence of the diphosphine on reactivity is the delicate balance of olefin alkoxycarbonylation versus CO/ethylene polymerization. For instance, cationic catalyst systems prepared from palladium acetate, bis(di-*tert*-butylphosphino)propane, and methanesulfonic acid are highly active for the alkoxycarbonylation of, for example, ethylene to give methyl proprionate.[3] Remarkably, the use of bis(diphenylphosphino)propane in place of bis(di-*tert*-butylphosphino)propane results in a change in product selectivity to give high-molecular-weight, perfectly alternating olefin/CO copolymer.[4] Two mechanisms have been proposed for the alkoxycarbonylation of olefins by Pd(II) salts. The first involves olefin insertion into Pd−H, followed by CO insertion and liberation of the product by alcoholysis, and the second, a carboalkoxide, which undergoes ethylene insertion followed by protonolysis to liberate the corresponding methyl propionate.[5,6] Similar steps appear to be integral to the alternating copolymerization of ethylene and carbon monoxide; in this case production of polyketone via successive alternating insertions of CO and ethylene is favored over termination after only a single turnover.[7] Given the intimate similarity between these two processes, it would not be surprising to find that subtle modifications in catalyst structure could influence selectivity.

In addition to dppp, selectivity for copolymerization is also achieved with catalyst systems based on planar-at-nitrogen bidentate ligands such as 1,10-phenanthroline, 2,2-bipyridine, and oxazoline derivatives,[8,9] the last of which has been used in the synthesis of stereoblock polyketone through ancillary ligand exchange.[9] We have recently begun to explore the potential of C_2-, C_3-, and C_4-bridged bis(2,3,4,5-tetramethylphospholyl)-based systems to catalyze the carboxylation of olefins, with an emphasis on understanding the factors that determine catalyst selectivity for alkoxycarbonylation versus copolymerization. These ligands combine the soft donor character of phosphines with the conformational rigidity associated with nitrogen heterocycles, while offering steric protection in the axial direction. We report here the synthesis, coordination chemistry, and preliminary ethylene carbon monoxide copolymerization activities

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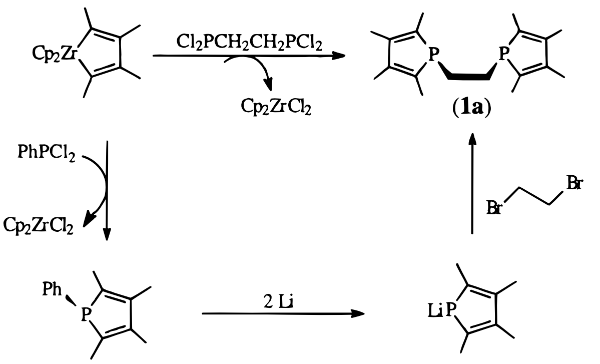
Scheme 1



for catalyst systems based on [$Pd_3(OAc)_6$], methanesulfonic acid, and bis(phosphole), which compare favorably with those obtained using bis(diphenylphosphino)propane-based catalysts under similar conditions.

The bis(phosphole) 1,2-bis(2,3,4,5-tetramethylphospholyl)ethane (**1a**) is readily prepared by treating a thf solution of a 2,3,4,5-tetramethyl zirconacycle[10] with 1,2-bis(dichlorophosphino)ethane according to Scheme 1.[11] This is the first report of electrophilic cleavage of a zirconacyclopentadiene to generate a diphosphine, a methodology that offers immense potential for the synthesis of a wide range of new bidentate phosphorus donor ligands. Alternatively, **1a** can be prepared by quenching a thf solution of (2,3,4,5-tetramethylphospholyl)lithium with 1,2-dibromoethane.[12] Similarly, 1,3-bis(2,3,4,5-tetramethylphospholyl)propane (**1b**) and 1,2-bis(2,3,4,5-tetramethylphospholyl)-*o*-xylene (**1c**) can be prepared from the reaction of (2,3,4,5-tetramethylphospholyl)lithium with 1,3-dibromopropane and α,α′-dibromo-*o*-xylene, respectively.

The reaction of **1a**−**c** with [(cycloocta-1,5-diene)$PdCl_2$] in dichloromethane for 12 h at room temperature affords [$(\{\overline{\text{C(Me)C(Me)C(Me)C(Me)P}}\}_2X)PdCl_2$] (**2a**, $X = C_2H_4$; **2b**, $X = C_3H_6$; **2c**, $X = 1,2\text{-}(CH_2)_2C_6H_4$) in yields of up to 88%.[11] For each compound the ^{31}P NMR spectrum contains a single resonance, shifted downfield relative to that of the free ligand, with **1a** exhibiting a much larger coordination chemical shift ($\Delta = 71.2$ ppm) than either **1b** ($\Delta = 15.6$) or **1c** ($\Delta = 15.8$).[13]

Single-crystals of **2c**·$CHCl_3$ suitable for X-ray analysis were grown from a chloroform solution layered with diethyl ether.[14] The molecular structure is shown in Figures 1 and 2, which clearly show that the coordination sphere around Pd(1) is close to square planar. The Pd−P bond lengths (Pd(1)−P(1) = 2.2323(13) Å, Pd(1)−P(2) = 2.2407(13) Å) are within the range expected for related palladium diphosphine complexes such as [Pd(dppe)Cl_2][15] (mean value 2.231(3) Å), [Pd(BIPHOS)Cl_2][16] (mean value 2.2287(9) Å), and [Pd(DMPP)Cl_2][17] (mean value 2.240(3) Å). The distances and angles in the phosphole rings are similar to values previously reported for related compounds, including [Pd(bidmpp)$_2$],[18] [Pd(DMPP)Cl_2],[17] and [Pd(BIPHOS)Cl_2].[18] The two phosphole rings are essentially planar and parallel, forming a dihedral angle of 18.6°, and are oriented perpendicular to the PdP_2Cl_2 plane (Figure 2).

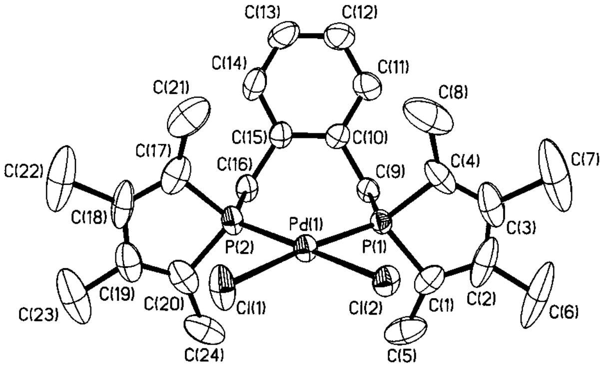


Figure 1. Molecular structure of **2c**·$CHCl_3$. Ellipsoids are at 50% probability.

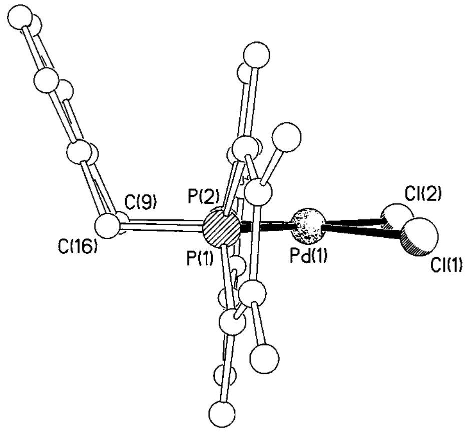


Figure 2. Molecular structure of **2c**·$CHCl_3$ viewed through the $P_2P_2Cl_2$ plane, illustrating the orientation of the phosphole rings.

Preliminary studies on the carbonylation of ethylene have shown that catalyst systems based on **1b** and **1c** are active for the copolymerization of ethylene with carbon monoxide, and polymer properties are summarized in Table 1.[20] Methanol solutions of [{bis(2,3,4,5-tetramethylphospholyl)propane}Pd$(OAc)_2$] (**3b**) or [{bis-(2,3,4,5-tetramethylphospholyl)-*o*-xylene}Pd$(OAc)_2$] (**3c**)[21] and methanesulfonic acid are active for the copolymer-

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[11] Full experimental details are given in the Supporting Information.

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[20] **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$(OAc)_2$].[22] In a typical procedure, 0.150 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, prior to GPC analysis (1,3-cresol with antioxidant, 1 mL min^{-1} at 120 °C using polystyrene standard for calibration). All GPC runs were carried out in triplicate. GPC traces for the polymers listed in Table 1 are given in the Supporting Information.

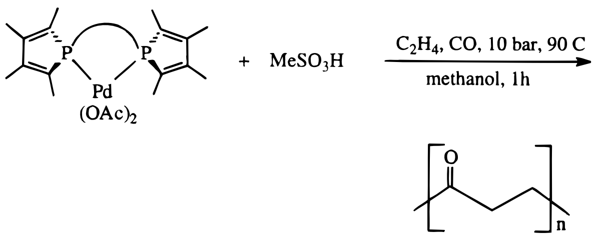
[21] Experimental details are given in the Supporting Information.

Table 1. Summary of Ethylene/Carbon Monoxide Copolymerization Results Using Ligands 1a–c

entry no.	ligand	mass of polymer[a]	activity/g of polyketone (mol of cat.)$^{-1}$ h^{-1}	M_w	M_n	M_w/M_n
1	**1a**	0.0	0			
2	**1b**	0.91	5 100	11 200	7000	1.6
3	**1c**	7.6	46 300	14 400	8530	1.7
4	dppp	5.2	33 100	14 300	8200	1.7

[a] Average mass of polymer obtained over three runs.

ization of ethylene and carbon monoxide, generating high-molecular-weight polymers with narrow molecular weight distributions (eq 1).[20,21] The polyketone isolated using the catalyst system based on **1c** is off-white, while that generated from **1b** is noticeably darker in color, and this is taken as evidence of catalyst decay, suggesting that the active species is not stable under these conditions. In the case of catalysts based on **1c** and dppp, large quantities of polymer precipitated from solution, which may be responsible for the near-identical molecular weights in entries 3 and 4. Interestingly, the nature of the chelate ring has a marked effect on polymer productivity,[4b] the catalyst based on [{bis(2,3,4,5-tetramethylphospholyl)ethane}Pd(OAc)$_2$] (**3a**) showing no activity and the *o*-xylene-bridged bis(phosphole)-based catalyst generating substantially more polyketone than its propane-bridged counterpart (Table 1). In a comparative experiment the copolymerization of ethylene and carbon monoxide using catalyst precursors based on [{bis(2,3,4,5-tetramethylphospholyl)-*o*-xylene}Pd(OAc)$_2$] and [{bis(diphenylphosphino)propane}-Pd(OAc)$_2$] were found to have comparable activities, the former producing, on average over three runs, 7.6 g of polyketone and the latter 5.2 g, after heating at 90 °C for 1 h under 10 bar pressure of equimolar ethylene and carbon monoxide. Since catalysts formed by combining palladium acetate, bis(diphenylphosphino)propane, and Brønsted acid have been reported to have copolymerization activities as high as 6000 g of polymer (g of Pd)$^{-1}$ h^{-1},[4b] evaluation of the new phosphole-based catalyst systems, using single-component versions, under optimum conditions is necessary and should prove informative. The ^{13}C NMR spectrum of copolymer generated using [{bis(2,3,4,5-tetramethylphospholyl)-*o*-xylene}Pd(OAc)$_2$] was recorded in hexafluoroisopropyl alcohol and found to contain resonances at δ 217.0 ($CH_3CH_2\mathit{C}O$), 176.4 ($MeO\mathit{C}O$), 6.5 ($\mathit{C}H_3CH_2$), 52.0 ($CH_2O\mathit{C}H_3$), and 27.5 ($\mathit{C}H_2{-}C(O)OMe$) which correspond to keto-ester end group polymer, i.e. the principal chain-termination step involves alcoholysis with no evidence for termination via β-elimination.[4b]



(1)

The selectivity of catalysts based on **1b**,**c** is perhaps not unexpected, since the constrained geometry at phosphorus closely resembles the planar-at-nitrogen environment provided by ligands such as 1,10-phenanthroline and bipyridine used by Brookhart; i.e., they all provide limited effective shielding of the active site. Figure 2 clearly shows the open coordination environment at palladium and highlights the perpendicular orientation of the phosphole rings with respect to the $PdCl_2P_2$ plane.

Workers at ICI have recently reported that a catalyst based on bis(di-*tert*-butylphosphino)-*o*-xylene, $Pd_3(OAc)_6$, and methanesulfonic acid is selective for the production of methyl propionate and that this catalyst is considerably more active (40 000 g of product (g of Pd)$^{-1}$ h^{-1}) than its propane-bridged derivative.[3d] We too have found that in the case of CO/ethylene copolymerization the bis(2,3,4,5-tetramethylphospholyl)propane-based catalyst is significantly less active than its xylyl-bridged counterpart (Table 1). In addition, the catalyst based on **1c** appears to be considerably more stable than its propane-bridged derivative, a trend also observed by workers at ICI for bis(di-*tert*-butylphosphino)propane and bis(di-*tert*-butylphosphino)-*o*-xylene-based alkoxycarbonylation catalysts.[22]

In conclusion, several novel C$_2$-, C$_3$-, and C$_4$-bridged bis(phospholes) and their palladium dichloride complexes have been prepared and characterized. Catalyst systems based on these bis(phospholes) are active for the copolymerization of ethylene and carbon monoxide, polymer productivity depending markedly on the nature of the bis(phosphole) tether. Notably, under similar conditions catalyst systems based on bis(2,3,4,5-tetramethylphospholyl)-*o*-xylene have a markedly higher productivity than that using bis(diphenylphosphino)propane. These are preliminary results, and clearly further studies are required to investigate fully the origin of selectivity in these catalyst systems and to optimize polymerization conditions. In particular, the influence of ligand modification on polyketone versus alkoxycarbonylation selectivity, the ability of these catalyst systems to copolymerize α-olefins and functional monomers, and the development of chiral bis(phospholes) to control polymer stereoregularity are currently underway.

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Supporting Information Available: Text giving experimental details for compounds **1a**–**c**, **2a**–**c**, and **3a**–**c**, variable-temperature ^{1}H NMR spectra of **2c** and GPC traces for polyketone, and text and tables giving details of the structure determination for **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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