Table IV. Differences in Energies (kcal/mol) between Electronic Configurations of 4 and 5

| configuration	6-31G* ΔE (3N − 2N)	MP2/6-31G* ΔE (3N − 2N)
BBAT	−3.5	−10.5
6PS	−15.1	−7.2
4PBBS	−2.9	−2.1
6PT	+1.2	+2.9
4PT	+9.6	+13.5

present in **4** because of the smaller overlap integral between the AO's of the σ MO's in **5**.

Comparison of Energies of Configurations of 4 and 5. A comparison of the energies of the various electronic configurations of **4** and **5** provides a direct means of evaluating the effect of the position of the nitrogen atom on the relative stability of the carbene states. There is a very interesting trend in the relative stabilities. In the lowest energy **5BBAT** and **6PS** configurations the **2N** systems are more stable than the **3N** systems by 10.5 and 7.2 kcal per mole at the MP2/6-31G* level (see Table IV). As the energies of the states decrease, the **2N** systems become less stable relative to the **3N** systems, with a cross over at with the **6PT** configurations where the **3N** systems are now more stable than the **2N** systems.

There appears to be two dominant factors which result in the observed trend: (1) a stabilization gained by delocalization of the nonbonded nitrogen AO with the carbene carbon AO to form the MO's and (2) a destabilization due to increased electron repulsion when the antisymmetric σ MO is occupied.

One might have expected that the greatest difference in energy would be seen with the **6PS** configuration, with the **2N** system being lower in energy because of the greater overlap integral between the nonbonded pair AO on the nitrogen atom and the σ AO on the carbene carbon atom compared to that in the **3N** system. However, such delocalization would result in greater charge density and separation in the **2N** system because of this greater overlap. This can be viewed in terms of the resonance contributing structures for the **6PS** configurations of **4** and **5** in which the multiply charged form contributes relatively more in **4** than in **5** because of the greater overlap. This must result in a substantial loss of the stabilization gained by the delocalization of the nonbonded pair of nitrogen in **4**.
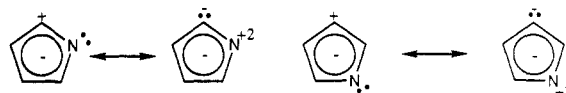
In the **5PBBAT** configurations delocalization of the nobonded nitrogen AO with the AO on the carbene carbon atom is possible and again is greater in the **2N** system than in the **3N** system because of the larger overlap integral between the AO's on the nitrogen and the carbene carbon atoms. In these cases, however, this delocalization does not result in the formation of additional charge density as is illustrated in the resonance contributing structures shown below. The addition of an electron to the antisymmetric σ MO should increase the electron repulsion in the σ MO's to a greater extent that the reduction in π-electron repulsion by loss of one electron.
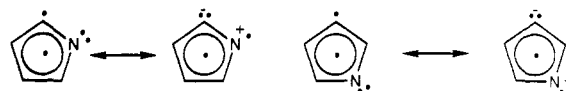
In the **4PBBS** configurations of **4** and **5** the balance of the various contributing factors appears to be very similar.

It is not obvious what all of the contributing factors are in determining the relative energies of the **6PT** and **4PT** configurations or **4** and **5**, although subtle differences in α and β electron distributions in these triplet states might play a role.

Supplementary Material Available: Tables of orbital energies and coefficients of **4** and **5** (5 pages). Ordering information is given on any current masthead page.

Polyethylene-Bound Soluble Recoverable Palladium(0) Catalysts

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The use of diphenylphosphine-terminated ethylene oligomers as ligands for palladium(0) and palladium(II) is described. With use of these polymeric ligands, it is possible to carry out homogeneous reactions characteristic of $(Ph_3P)_4Pd$ and $(Ph_3P)_2Pd(OAc)_2$ with essentially complete recovery of the Pd catalyst. The only limitation to repeated reuse of the catalyst is its immolative catalytic oxidation of the phosphine ligand by adventitious oxygen.

Hybrid catalysts combining the attributes of conventional homogeneous catalysts with the experimental simplicity of heterogeneous catalysts have proven to be fruitful subjects for research by both academic and industrial chemists.[1] However, while the concept of attaching a homogeneous catalyst to an insoluble polymer is both elegant and simple, there are some subtle problems associated with using insoluble polymers as supports for homogeneous catalysts. In particular, the microenvironment within a polymer and the heterogeneous nature of an insoluble polymer have led to altered or decreased activities, more difficult ligand synthesis and characterization, and undesirable diffusional limitations on reaction rates. As we and others have shown, soluble polymers are useful if largely unexplored alternatives to insoluble polymers.[2,3]

(1) Pittman, C. U., Jr. In *Comprehensive Organometallic Chemistry*; Wilkinson, G. C., Ed.; Pergamon Press: Oxford, 1982; Vol. 8, pp 553–611. Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109–148. Hartley, F. R. *Supported Metal Complexes. A New Generation of Catalysts*; D. Reidel: Netherlands, 1985.

(2) Schurig, V.; Bayer, E. *CHEMTECH* **1986**, 212–214.

Table I. Allylic Substitution of Allylic Esters by Secondary Amines Catalyzed by Tetrakis(polyethylenediphenylphosphine)palladium(0)[a]

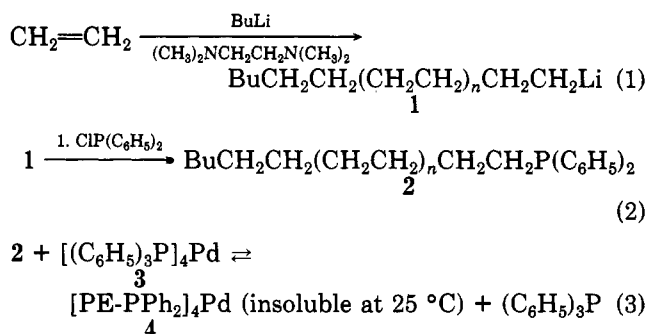| substrate	amine	products	yield,[b] %	cycles	turnovers
allyl benzoate	piperidine	$H_2C=CHCH_2NC_5H_{10}$	100	10	500
allyl benzoate	morpholine	$H_2C=CHCH_2NC_4H_8O$	100	10	500
allyl octanoate	morpholine	$H_2C=CHCH_2NC_4H_8O$	100	5	250
allyl octanoate	piperidine	$H_2C=CHCH_2NC_5H_{10}$	100	5	250
cinnamyl acetate	piperidine	$H_2C=CHCH(C_6H_5)NC_5H_{10}$	16		40
		$(E)\text{-}C_6H_5CH=CHCH_2NC_5H_{10}$	85	5	214
cinnamyl acetate	morpholine	$H_2C=CHCH(C_6H_5)NC_4H_8O$	15		26
		$(E)\text{-}C_6H_5CH=CHCH_2NC_4H_8O$	84	5	210

[a] Reactions were carried out at 100 °C in toluene solutions using a 50:1 (mol/mol) substrate/catalyst ratio and were complete within 10 min as judged by the complete consumption of starting material. [b] Yields were determined by gas chromatography using internal standards and the identity of the products was confirmed by isolation of the allylic amines and their identification by ^1H and ^{13}C NMR spectroscopy.

This paper describes the use of such polymers with palladium(0) and palladium(II) catalysts. The results described demonstrate that the concept of using linear polymers with temperature-dependent solubility is feasible with these oxygen-sensitive catalytic systems and thus further extend the applicability of these soluble polymeric ligands in homogeneous catalysis.

Palladium is one of the richest transition metals in terms of its catalytic chemistry. Both Pd(0) in the form of its phosphine complex and Pd(II) either with or without an associated phosphine ligand are useful for a plethora of transformations.[4,5] Quite a few reports have appeared in which such catalysts are bound to various sorts of polymers.[6-9] To examine the utility of the polyethylene ligand chemistry we described earlier for Rh(I), Ni(0), and phase-transfer catalysts in palladium chemistry,[10-12] we have examined the use of phosphinated polyethylene ligands in nucleophilic substitutions of allylic acetates, rearrangements of allyl esters, and diene dimerizations. Insoluble DBV-crosslinked polystyrene containing simple and optically active phosphine ligands has been used previously to prepare a recoverable, recyclable polymer-bound analogue of $(Ph_3P)_4Pd$ and of Pd(II) diene dimerization catalysts.[13,14] While we have not explicitly compared these catalysts with the polyethylene-bound Pd catalysts described herein, our prior work has shown that the soluble polyethylene-bound catalysts are generally as reactive as their homogeneous counterparts, and thus their reactivity compares quite favorably with typical insoluble polymer-bound catalysts.

Preparation of the catalyst is straightforward. Anionic oligomerization of ethylene with butyllithium–TMEDA followed by quenching with $ClPPh_2$ leads to the phosphinated oligomer which can then be treated with $Pd(PPh_3)_4$. Equilibration of excess 1 with $Pd(PPh_3)_4$ at 100 °C in toluene followed by cooling and precipitation of the polyethylene-bound species leads to a light yellow polyethylene powder and a clear solution which by ^{31}P NMR spectroscopy contains $(C_6H_5)_3P$. Even when 1:1 molar ratios of 2 and 3 are used in eq 3, the final solution is clear, suggesting that equilibrium 3 favors 4. This could reflect the greater σ-basicity of the polyethylenediphenylphosphine ligand versus a triphenylphosphine ligand. Alternatively, interactions of the ethylene oligomers with one another or the precipitation process itself may help favor 4 in equilibrium 3.

$$CH_2=CH_2 \xrightarrow[\text{(CH}_3)_2NCH_2CH_2N(CH_3)_2]{\text{BuLi}}$$
$$BuCH_2CH_2(CH_2CH_2)_nCH_2CH_2Li \quad (1)$$
$$\mathbf{1}$$

$$\mathbf{1} \xrightarrow{\text{1. ClP(C}_6H_5)_2} BuCH_2CH_2(CH_2CH_2)_nCH_2CH_2P(C_6H_5)_2$$
$$\mathbf{2}$$
$$(2)$$

$$\mathbf{2} + [(C_6H_5)_3P]_4Pd \rightleftharpoons$$
$$\mathbf{3}$$
$$[PE\text{-}PPh_2]_4Pd \text{ (insoluble at 25 °C)} + (C_6H_5)_3P \quad (3)$$
$$\mathbf{4}$$

The molecular weight of 2 varied depending on the conditions used for the oligomerization step.[15] It was typically in the range of 1400–2000 as determined by end-group analysis with ^1H NMR spectroscopy. The degree of functionalization of 2 was such that there typically were about 0.6 mequiv of PPh_2 groups/g of oligomer. The actual molecular weight of 2 and the presence of some H-terminated oligomers along with 2 however did not affect 4's utility so long as 2 was in this molecular weight range (or larger) so that it had polyethylene-like temperature-dependent solubility.

Once formed, 4 readily dissolves on heating to 100 °C in toluene or dibutyl ether. The catalyst 4 can be quantitatively recovered from such solutions (or from reaction mixtures) by simply cooling these solutions to 25 °C based on Pd analysis of filtrates after the solid 4 has been recovered from the resultant suspension (vide infra). Solutions of 4 are stable at 100 °C so long as no oxygen is present. In the presence of oxygen, the phosphine ligands of 4 are oxidized to polyethylenediphenylphosphine oxide. In cases where oxygen was deliberately or inadvertently added to a reaction mixture, this adventitious oxidation produced a black precipitate of palladium metal. In these cases, analysis of a 110 °C toluene-d_8 solution of the catalyst by ^{31}P NMR spectroscopy showed polyethylenedi-

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(9) Kaneda, K.; Tarasawa, M.; Imanaka, T.; Teranishi, S. *J. Organomet. Chem.* 1978, *196*, 403–414.

(10) Bergbreiter, D. E.; Chandran, R. *J. Am. Chem. Soc.* 1987, *109*, 174–179.

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(12) Bergbreiter, D. E.; Blanton, J. R. *J. Org. Chem.* 1985, *50*, 5828–5833.

(13) Pittman, C. U.; Wuu, S. K.; Jacobson, S. E. *J. Catal.* 1976, *44*, 87–100.

(14) Terasawa, M.; Kaneda, K.; Imanaka, T.; Teranishi, S. *Chem. Lett.* 1975, 1005–1008.

(15) Bergbreiter, D. E.; Blanton, J. R.; Chandran, R.; Hein, M. D.; Huang, K.-J.; Walker, S. A. *J. Polym. Sci.*, submitted for publication.

Table II. Decarboxylation–Allylic Substitution of Allylic Esters of β-Keto and β-Cyano Carboxylic Acids Using Tetrakis(polyethylenediphenylphosphine)palladium(0)[a]

substrate	products	yield,[b] %	cycles	turnover
$H_2C=CHCH_2O_2CCH_2COCH_3$	$H_2C=CHCH_2CH_2COCH_3$	100	10	500
$H_2C=CHCH_2O_2CCH(CH_3)COCH_3$	$H_2C=CHCH_2CH(CH_3)COCH_3$	100	10	500
$(E)\text{-}CH_3CH=CHCH_2O_2CCH_2COCH_3$	$(E)\text{-}CH_3CH=CHCH_2CH_2COCH_3$	100	5	250
(E)-2-butenyl 2-oxocyclohexanecarboxylate	2-((E)-2-butenyl)cyclohexanone	87	5	218
	2-(1-methyl-2-propenyl)cyclohexanone	13		32
1-methyl-2-propenyl 2-oxocyclohexanecarboxylate	2-((E)-2-butenyl)cyclohexanone	86	5	216
	2-(1-methyl-2-propenyl)cyclohexanone	14		34
$H_2C=CHCH_2O_2CCH_2C\equiv N$	$(H_2C=CHCH_2)_2CHC\equiv N$	100[c]	5	250

[a] Reactions were carried out at 100 °C in toluene solutions using a 50:1 (mol/mol) substrate/catalyst ratio. [b] Yields were determined by gas chromatography using internal standards, and the identity of the products was confirmed by isolation of the allylic substitution product and its identification by ^1H and ^{13}C NMR spectroscopy. [c] Acetonitrile was formed as the other C≡N containing product.

phenylphosphine oxide was present (δ 26 for polyethylenediphenylphosphine oxide versus δ −14.5 for polyethylenediphenylphosphine (relative to external H_3PO_4)).

Our initial work showed that **4** behaved in catalytic reactions like Pd(PPh₃)₄ as expected. For example, **4** was successfully used as a catalyst for substitution of allylic esters by secondary amines (eq 4). Palladium catalysis
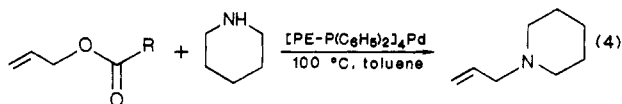

using $Pd[P(C_6H_5)_3]_4$ as a homogeneous catalyst is known to be useful in such reactions in which both carbon and heteroatom nucleophiles substitute for allylic carboxylate groups.[16] Yields and typical examples of this reaction are listed in Table I. In these reactions and in the other chemistry discussed below, **4** could be reused repeatedly so long as adventitious oxygen was excluded. Typically we recycled the catalyst **4** at least five times. However, in selected cases, the catalyst was used 10 times with no decrease in activity. Occasionally the catalytic activity of **4** would noticeably decrease from one cycle to the next. When we encountered such a situation and when we then examined the catalyst solution at 110 °C by ^{31}P NMR spectroscopy, ^{31}P NMR spectroscopy showed that oxidation of the phosphine ligand had occurred.

Catalyst recovery was essentially quantitative. Analysis of filtrates from the first cycle of an allylic substitution reaction of ICP (inductively coupled plasma) analysis showed no detectable Pd in comparison to a blank. In these analyses, amounts of Pd as small as 1 ppm could have been detected. The loss of palladium to solution is thus less than 0.001% of the charged palladium catalyst. The ability to recovery the ligand and palladium thus paralleled our experience with rhodium(I) and nickel(0) catalysts.[10,11]

We used cinnamyl acetate to examine the regioselectivity of this reaction and to compare it to the homogeneous catalyst $Pd[P(C_6H_5)_3]_4$. Small differences in regioselectivity were seen. In the case of $Pd[P(C_6H_5)_3]_4$ a 70:30 mixture of primary to secondary amine formed as compared to an 85:15 ratio for **4**. However, we believe these small differences are not due to the polymeric nature of **4**. Rather, we believe that this slight difference is due to the use of an alkyldiphenylphosphine as a ligand for these reactions. This assumption is based in part on the results of our earlier work with polyethylene-bound catalysts. In these studies we did note some electronic effects because

of our use of an alkyldiphenylphosphine ligand in place of triphenylphosphine. However, when the oligomeric and low molecular weight ligands were electronically equivalent, our prior studies comparing polyethylene-bound and homogeneous Ni(0) and Rh(I) catalysts showed that the polymeric ligand had no effect on catalyst activity or selectivity so long as the catalyst was in solution, i.e. at 100 °C.

The decarboxylative rearrangement of allyl esters of β-keto carboxylates occurs thermally at high temperatures (170–200 °C) and can be catalyzed by $Pd[P(C_6H_5)_3]_4$ at lower temperatures.[18] We observed similar rearrangements using **4** as a catalyst (eq 5). For example, addition
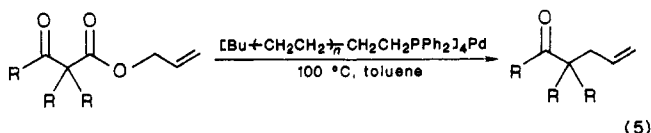
of allyl acetoacetate to a toluene solution of **4** at 100 °C (50:1 molar ratio of ester to **4**) resulted in high yields of 1-hexen-5-one in 5 min or less. Cooling the solution and filtration recovered the catalyst **4** which was recycled as noted in Table II. As noted in the table, this reaction proved to be general for a variety of allylic esters of β-keto carboxylates. We were also able to extend this reaction further. Under our conditions, mixtures of allyl alcohol and a simple ester of a β-keto carboxylate also yielded products in which C–C bond formation occurred with a recyclable catalyst. This reaction, which has precedence in (Ph₃P)₄Pd chemistry,[19] works equally well with this oligomerically ligated catalyst. For example, at 100 °C, ethyl acetoacetate was allowed to react with allyl alcohol for 6 h to yield a 70:30 mixture of mono- and disubstituted products (eq 6). As in the reactions described above,
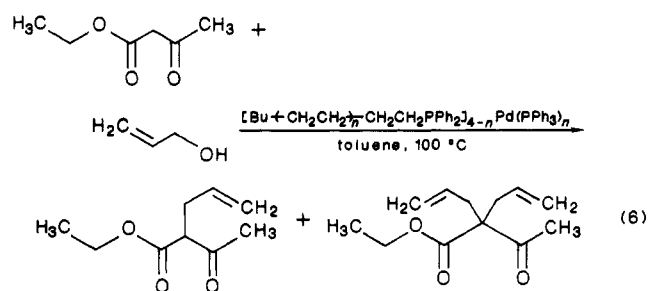
recycling the Pd(0) catalyst was quite successful here. In this example the catalyst was recycled 10 times with >95% conversion of ethyl acetoacetate to allylated product (total

(16) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 418–419.

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(18) Tsuji, J.; Yamada, T.; Minami, I.; Yuhara, M.; Nisar, M.; Shimizu, I. *J. Org. Chem.* **1987**, *52*, 2988–2995.

(19) Bergbreiter, D. E.; Weatherford, D. A. *J. Chem. Soc., Chem. Commun.*, in press.

turnover number of >450 mmol product/mmol of catalyst).

While Pd(0) is a useful and effective catalyst for many reactions including the allylic substrates discussed above, Pd(II) is also of interest in homogeneous catalysis. Since Pd(II) phosphine complexes are useful in reactions like dimerizations and oligomerizations which produce higher molecular weight products that cannot readily be separated from a homogeneous catalyst by simple distillation,[18] we have explored the applicability of polyethylenediphenyl-phosphine ligands in this chemistry. We have found that 5 is indeed an effective catalyst for dimerization like that shown in eq 7. Comparison of the yields of products noted
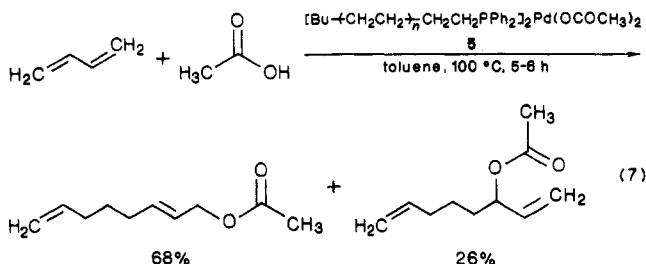
in eq 7 for the polyethylene-bound palladium(II) catalyst and [(C6H5)3P)2Pd(OAc)2] show that these two catalysts are quite similar. As was true for the Pd(0) chemistry discussed above, ICP analysis of the filtrates from the first cycle of eq 6 showed that no detectable Pd(II) was lost to solution. We have only conducted limited studies on the recyclability of 5. However, we have found that 5 is re-cyclable for at least four cycles. As was true for the chemistry of 4, adventitious oxygen contamination appears to be the most serious problem with recycling the catalyst.

In summary, polyethylenediphenylphosphine is a prac-tical ligand for recycling and separating homogeneous palladium(0) and palladium(II) catalysts from solutions of reaction products. Although oxidation by adventitious oxygen at elevated temperatures is a problem which can lead to catalyst decomposition, careful exclusion of oxygen allows this polymeric ligand which has useful temperature dependent solubility to be reused many times without either loss of catalyst to solution or diminution in catalyst activity. Catalyst activity is comparable to that of a close homogeneous analogue Pd[P(C6H5)3]4.

Experimental Section

General Methods. Butadiene was obtained from Matheson Co. Ethylene was purchased from Air Products. Inorganic chemicals were obtained from Alfa Chemical Co. and used without further purification. Organic substrates used were obtained from Aldrich Chemical Co. Hydrocarbon and ethereal solvents were distilled under nitrogen from sodium benzophenone ketyl im-mediately prior to use. Other solvents used were reagent grade and were generally not further purified. Tetramethylethylene-diamine was distilled from potassium metal and stored under nitrogen until use. Nitrogen was purified by passage through a calcium chloride drying tower. Butadiene was purified by suc-cessively passing it through two columns containing calcium sulfate (Drierite) and 4A molecular sieves respectively. The ethylene used in the oligomerization reaction was reagent grade and used without further purification. All glassware was dried in an oven at 130 °C overnight prior to use. Magnetic stirring or shaking on a wrist-action shaker was generally used for agitation of reactions. Syringes and stainless steel cannulae were utilized to transfer water- and air-sensitive solvents and reagents, and standard inert techniques were used in carrying out all reactions of water- and air-sensitive reagents.[20] GC analyses were carried out using an HP Model 5730A chromatograph containing a DB5 30-m fused-

silica capillary column. Mass spectra were obtained with an HP 5790 GC coupled to mass selective detector. Infrared spectra of products were taken using thin films on NaCl disks and were recorded on an IBM Model 32 FT-IR spectrometer. ^{1}H NMR and ^{31}P NMR spectra were obtained with a Varian FT-80, XL-200, or XL-400 or a GEMINI 200 Model NMR spectrometer. ^{1}H and ^{31}P NMR spectra of oligomers were obtained in toluene-d_8 at 110 °C so that the oligomer was in solution. Quantitative end group analysis of the polymeric ligand was accomplished with ^{1}H NMR spectroscopy with hexamethyldisiloxane as an internal standard (typical sample sizes of 0.015 g of oligomer and 0.01 g of HMDS). [1]H and ^{13}C chemical shifts are reported relative to TMS.

Preparation of Polyethylenediphenylphosphine. Oligom-erization of ethylene and electrophilic quenching of the resulting living oligomer with ClPPh2 was accomplished according to published procedures.[10,15] Ligands were normally prepared on a 15–20-g scale and were analyzed by ^{31}P NMR spectroscopy prior to use to insure that minimal amounts of the phosphine oxide (δ 26 versus δ −14.5 for the phosphine oxide versus the phosphine) were present. The amount of PPh2 groups on the oligomer and the oligomer's molecular weight were determined by ^{1}H NMR spectroscopy by integrating the protons due to the phenyl groups of the PPh2 groups, the terminal CH3 group, and an internal standard (1,1,2,2-tetrachloroethane or hexamethyldisiloxane). Typical loadings were 0.6 mequiv of PPh2/g of oligomer. End group analysis showed that ca. 70% of the oligomers were functionalized with PPh2 groups.

Preparation of Tetrakis(polyethylenediphenyl-phosphine)palladium(0) (4). A Schlenk flask (200 mL) was equipped with a magnetic stirring bar, and Pd[P(C6H5)3]4 (0.02 mmol) and polyethylenediphenylphosphine (1.25 g, 0.6 mmol/g, 0.75 mmol) were added. The flask was then purged with argon. Toluene (20 mL) was added, and the suspension was heated to 100 °C. At this point the solution was a light gold color. Cooling to room temperature precipitated the polyethylene oligomer as a light yellow powder. The remaining solution was clear and colorless. Analysis of the filtrate by ^{31}P NMR spectroscopy showed the presence of free triphenylphosphine. The suspension of 4 so formed was then centrifuged, and the supernatant was removed by forced siphon under argon. This process was repeated twice with fresh portions of toluene, and the product 4 was then dried in vacuum. The product solid was somewhat air-sensitive and was therefore stored under argon prior to use.

General Procedure for Catalytic Reactions Using 4. The catalyst 4 prepared as described above was added to a flask, and the flask was purged three times with an argon/vacuum cycle. Toluene was added by syringe, followed by the reactant mixture. The flask was again purged three times. The solution was heated to 100 °C and stirred until it was visibly homogeneous. The reactions were then continued for the indicated time (see dis-cussion) until the substrate had been consumed. After the reaction was complete as judged by gas chromatographic analysis of ali-quots, the solution was cooled. The catalyst 4 precipitated, and the products remained in solution. The flask was then sealed, disconnected from the gas line, and transferred to a centrifuge. After isolation of 4 by centrifugation, the product mixture was removed from the flask by forced siphon using a cannula. The catalyst was washed twice with 30-mL portions of degassed toluene to insure that reaction products were not carried over into the next reaction. The catalyst 4 was then recycled by repeating this process. In cases where an abrupt or gradual color change of 4 from yellow to brown was seen there was a loss in catalytic activity. In some cases, ^{31}P NMR of such discolored catalysts was used to show that this loss of catalyst activity was accompanied by substantial formation of polyethylenediphenylphosphine oxide.

Dimerization and Acetoxylation of Butadiene. The pro-cedure used was a modification of Pittman's.[13] Into a dry 150-mL Fischer–Porter pressure bottle were placed Pd(OAc)2 (0.03 g, 0.134 mmol), diphenylphosphine-terminated ethylene oligomer (0.86 g, 0.54 mequiv of phosphine), and a magnetic stirring bar. The pressure bottle was then attached to a high-pressure apparatus equipped with two pressure valves and a pressure gauge. One valve was equipped with a septum so that injections could be made. The other valve was connected to the butadiene line. The apparatus was purged with argon and evacuated three times, and 20 mL of degassed toluene was added. Acetic acid (3 g, 50 mmol)

(20) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*; Wiley-Interscience: New York, 1986.

was then added, and the mixture was further degassed by three freeze–thaw cycles. After the reaction mixture was cooled in a dry ice/acetone bath to –78 °C, butadiene (6 g, 110 mmol) was condensed into the pressure bottle and the apparatus was sealed. After the reaction mixture was heated to 100 °C with stirring for 8 h, the reaction mixture was cooled and the resulting suspension was transferred by forced siphon with a cannula into a 30-mL centrifuge tube. Centrifugation was then used to separate 5 from the solution of products. During the entire process, 5 was continuously kept under an inert atmosphere. After centrifugation, the supernatant containing the product acetoxylated butadiene dimer was separated from the solid 5 by forced siphon. The recovered catalyst 5 was washed twice with 20-mL aliquots of degassed toluene and finally transferred back into the pressure bottle as a toluene suspension with an additional 30 mL of degassed toluene. The identity of the products and their relative amounts were found to be the same as those produced by the use of $Pd(OAc)_2(PPh_3)_2$ (generated in situ) based on GC analysis. The products' identities were confirmed by GCMS; (E)-1-acetoxy-2,7-octadiene (68%) (M^+ = 168, major fragments at m/e 126 and 108), 3-acetoxy-1,7-octadiene (26%) (M^+ = 168, major fragments at m/e 126 and 99), 1-acetoxy-2-butene (3%) (M^+ = 114), 3-acetoxy-1-butene (3%) (M^+ = 114).

Palladium Analysis. The procedure used was a modification of Shanina's.[21] The filtrate from a reaction between morpholine and allyl benzoate was concentrated and transferred to a 20-mL quartz crucible. After evaporation to dryness, 4 mL of concen-

trated H_2SO_4 was added, and the mixture was gently heated on a hot plate until the sample was completely homogeneous. Then, 10 mL of concentrated HNO_3 was added dropwise followed by further heating on the hot plate for an additional 24 h with occasional shaking. After this solution was cooled to 25 °C, the solution was diluted with distilled water in a 25-mL volumetric flask and analyzed for palladium content by ICP analysis by the Agricultural Analytical Services Laboratory at Texas A&M University. A blank palladium analysis using the same amount of reagents excluding the filtrate residue was also carried out along with a Pd sample of known concentration. The standardized solution of Pd containing 31 μg of Pd/mL analyzed correctly as having 30 μg of Pd/mL. These analyses of the residue of the filtrate from a reaction showed that there was <1 μg of Pd/mL present. Analysis of a blank solution that supposedly did not contain palladium similarly analyzed as having <1 μg of Pd/mL. Thus, the amount of Pd left in the residue from the filtrate of the first cycle of a catalytic reaction was too small to measure and corresponded to less than 0.001% of the charged catalyst. Similar analyses were also performed on a sample of oligomer 4. In this case, the same procedure described above was followed except that solid 4 was used in place of the filtrate residue. The result showed that a 0.07-g sample of oligomer 4 contained 1.07 × 10^{-3} mmol of Pd which was 95.5% of that calculated for a complete exchange of palladium as shown in eq 3.

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Permanganate Ion Oxidations. 19. Hexadecyltrimethylammonium Permanganate Oxidation of Cycloalkenes[1]

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The kinetics of hexadecyltrimethylammonium permanganate (cetyltrimethylammonium permanganate, CTAP) oxidation of cycloalkenes in dichloromethane have been studied. The relative rates of oxidation versus ^{13}C NMR chemical shifts, vertical ionization potentials, and strain energies are discussed. A comparison of the relative rate of permanganate ion oxidation with the relative rates of addition of other reagents to carbon–carbon double bonds suggests that it may act as a 1,3-dipole.

Although no unequivocable evidence has been reported, several cyclic structures, including oxametallocyclobutane 1 and manganate(V) diester 2, have been proposed as intermediates during the permanganate ion oxidation of carbon–carbon double bonds.[1-19] The philicity (ambi-

philic, electrophilic, nucleophilic) of permanganate ion during the oxidation of alkenes is also of interest. Moreover, the relative rates of alkenes and cycloalkenes (e.g., cyclopentene, cyclohexene, bicyclo[2.2.1]hept-2-ene (norbornene), 7,7-dimethylbicyclo[2.2.1]hept-2-ene) in electrophilic addition reactions have been suggested as possible criteria to distinguish between mechanisms involving acyclic and cyclic activated complexes and for determining the sizes of cyclic activated complexes.[20-26] Thus, we

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