(i.e. ΔE = 3–4 kcal). This slightly higher value of E_T does not appear unreasonable (e.g. it is consonant with the 430-nm onset of the phosphorescence band of Cu(prophos)BH_4[2d]), and we conclude that endoergic energy transfer from the lowest triplet of Cu(prophos)BH_4 to NBD can adequately account for the efficient, sensitized production of Q.

In the case of Cu(diphos)BH_4, the low triplet energy of 60–61 kcal results in a predicted rate constant for energy transfer to NBD of $<10^4$ M^{-1} s^{-1}. This value is sufficiently small that triplet energy transfer cannot compete successfully with the other processes, with total rate constant of $\sim 10^6$ s^{-1}, which deactivate the $^3(\sigma\text{–}a_\pi)$ excited state. Consequently, the complex is ineffective (Table I) as a sensitizer for the NBD to Q conversion.

Concluding Remarks

This investigation of the triplet-state properties of Cu(diphos)BH_4 and Cu(prophos)BH_4 has yielded information that can be used to characterize the bimolecular quenching and sensitization processes of these complexes in the presence of dienes. The key findings and their implications can be summarized as follows.

(1) Both Cu(diphos)BH_4 (E_T = 60–61 kcal) and Cu(prophos)BH_4 (E_T = 66–67 kcal) possess triplet-state energies that fall well below the average value of 76 kcal reported for a series of $Cu(PPh_3)_xCl$ and $Cu(PPh_2Me)_xCl$ (x = 1–3) complexes.[3a] By comparison, the triplet energies of all the corresponding free phosphine ligands lie in the 75–77 kcal range.[9] Thus, while coordination of a monodentate phosphine to copper produces relatively little perturbation in the energy of the lowest $^3(\sigma\text{–}a_\pi)$ state, chelation of a bis(phosphine) causes a marked energy decrease. A possible explanation for this latter behavior is provided by the observation that the energy of the l–a_π transition in arylphosphines drops upon the introduction of alkyl groups at the ortho position of the aromatic ring.[7,8,16] It is thought that steric crowding by these substituents alters the C–P–C valence angle and/or the twist angle (angle between the axis of the phosphorus l orbital and the axis of the adjacent carbon $2p_\pi$ orbital) from the characteristic value(s) in the uncoordinated phosphine and thereby affects the transition energy. In a similar fashion, steric constraints imposed by formation of the five- and six-membered chelate rings in Cu(diphos)BH_4 and Cu(prophos)BH_4 may cause changes in one or both angles with an accompanying lowering of the triplet state energy. Detailed structural and spectroscopic studies of a series of copper(I) complexes containing chelated phosphines of varying ring size are needed to test this suggestion.

(2) Both Cu(diphos)BH_4 and Cu(prophos)BH_4 undergo intersystem crossing from $^1(\sigma\text{–}a_\pi)$ to $^3(\sigma\text{–}a_\pi)$ with high quantum efficiency ($\phi_{isc} \geq 0.64$ and ≥ 0.78, respectively). Highly efficient ($\phi_{isc} \sim 1$) intersystem crossing has also been reported for the series of $Cu(PPh_2Me)_3X$ (X = Cl^-, Br^-, I^-) complexes.[3a] Interestingly, however, only the diphos and prophos complexes phosphoresce in room-temperature fluid solution (note also that the luminescence of $Cu(PPh_3)_2BH_4$ appears to be fluorescence rather than phosphorescence[2d]). This apparent disparity in phosphorescence yields cannot be attributed to significant differences in the nonradiative rate constants of the respective $^3(\sigma\text{–}a_\pi)$ states (k_6 and k_7 in Figure 6), since all of the complexes possess comparable triplet lifetimes under these conditions. Instead, it appears that the chelated phosphine complexes possess larger phosphorescence rate constants (k_5 in Figure 6) than their nonchelated counterparts; such behavior could again be indicative of differences in the twist angle about the phosphorus–phenyl bond.[17]

(3) Triplet–triplet energy transfer is the principal mechanism by which Cu(diphos)BH_4 and Cu(prophos)BH_4 sensitize the interconversion of *cis*- and *trans*-piperylene and the valence isomerization of NBD to Q. The process is exoergic for both complexes as donors and the piperylenes as acceptors. Energy transfer from Cu(prophos)BH_4 to NBD, on the other hand, is endoergic by 3–4 kcal; nonetheless, the long lifetime of the $^3(\sigma\text{–}a_\pi)$ excited state permits the complex to acquire sufficient thermal energy from the surroundings to overcome this deficit and energy transfer occurs with high quantum efficiency. In the Cu(diphos)BH_4/NBD system, the endoergicity rises to $\sim$9 kcal and energy transfer can no longer compete with the other deactivation processes of the $^3(\sigma\text{–}a_\pi)$ state.

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Registry No. Cu(diphos)BH_4, 19681-25-5; Cu(prophos)BH_4, 81432-70-4; *cis*-piperylene, 1574-41-0; *trans*-piperylene, 2004-70-8.

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Palladium(II) Complexes of Diphenylvinyl- and Phenyldivinylphosphine

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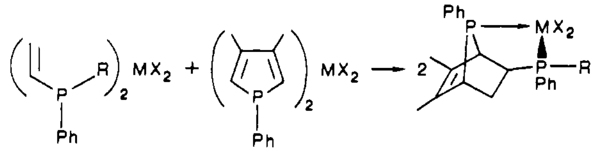
Palladium(II) complexes of the ligands L = $Ph_2PCH{=}CH_2$ and $PhP(CH{=}CH_2)_2$ have been prepared and characterized by elemental analysis, infrared spectroscopy, and ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^1H/^{13}C$ HETCOR nuclear magnetic resonance spectroscopy. These complexes exist as temperature-dependent equilibrium mixtures of cis and trans isomers in solution. Equilibrium thermodynamics for the isomerization process *cis*-$L_2PdX_2 \rightleftharpoons$ *trans*-L_2PdX_2, determined by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy, demonstrate that the cis isomers are in general thermodynamically more stable than the trans isomers. However, the relative isomer stabilities are anion dependent with the trans isomer becoming more stable in the order Cl < Br < I. Coordination of a vinylphosphine to palladium(II) strongly polarizes the C=C double bond as evidenced by ^{13}C NMR data.

Introduction

We have recently reported[1] the synthesis of novel rigid asymmetric bidentate phosphines by intramolecular Diels–Alder cycloaddition reactions of metal phosphole complexes with metal vinylphosphine complexes. For M = Pd and Pt reaction 1 occurs. The rates of these reactions are a function of the metal, the halide,



(1)

M = Pt, Pd; R = $CH{=}CH_2$, Ph; X = Cl, Br, I

and the phosphine. In order to gain greater understanding regarding the factors that influence these reactions we have com-

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Table I. Physical Data for the L_2PdX_2 Complexes

L	X	color and shape	% yield	mp, °C	$\nu_{C=C}$, cm^{-1}	ν_{Pd-X}, cm^{-1}
$Ph_2PCH{=}CH_2$	Cl	yellow-orange plates	89.9	204–207	1598	365, 310
$Ph_2PCH{=}CH_2$	Br	yellow plates	99.5	208–209	1597	278
$Ph_2PCH{=}CH_2$	I	dark red needles	98.7	200–206	1592	214
$PhP(CH{=}CH_2)_2$	Cl	pale yellow needles	63.0	200–202	1600	308, 290
$PhP(CH{=}CH_2)_2$	Br	orange plates	81.0	160–164	1596	242
$PhP(CH{=}CH_2)_2$	I	dark red needles	97.1	250–260	1594	200

pletely characterized the palladium vinylphosphine complexes and report the results herein.

Experimental Section

(A) Reagents and Physical Measurements. All chemicals used were reagent grade and used as received or synthesized as described below. Diphenylvinylphosphine and phenyldivinylphosphine were obtained from Strem Chemical and used as received. All solvents, when necessary, were dried by standard procedures and stored over Linde 4-Å molecular sieves. All reactions involving phosphines were conducted under an N_2 atmosphere. Melting points were determined on a Mel-Temp apparatus and are uncorrected.

Infrared spectra were obtained on a Perkin Elmer 599 spectrophotometer as CsI pellets. Far-infrared spectra were recorded on a Perkin-Elmer 1800 FT infrared spectrophotometer as polyethylene pellets. The $^{31}P\{^1H\}$ spectra were recorded at 40.26 MHz on a JEOL FX-100 spectrometer in the FT mode. ^1H, $^1H\{^{31}P\}$, and $^{13}C\{^1H\}$ spectra were recorded at 300, 300, and 75 MHz, respectively, on an IBM NR-300 AF spectrometer. Heteronuclear chemical-shift-correlated (HETCOR) spectra were obtained at 9.4 T by using the following pulse sequence: delay–$(\pi/2, {}^1H)$–$(t_{1/2})$–Δ_1–$(\pi/2, {}^1H; \pi/2, {}^{13}C)$–$\Delta_2$–acquisition with decoupling. All pulses were phase cycled according to ref 2. A 2.0 s recycling delay was used, and the delay times $\Delta_1 = {}^1/_2J$ and $\Delta_2 = {}^1/_4J$ were calculated from a compromise value of $^1J_{CH} = 120$ Hz. The $\pi/2$ ^1H pulse was 11.0 μs and the $\pi/2$, ^{13}C pulse was 10.0 μs. The spectral width in the F_2 (carbon) domain was 601 Hz, and that in the F_1 (proton) domain was 1000 Hz; 2048 points were used in both F_1 and F_2 domains, and the data were pseudoecho processed in both domains. Proton and carbon chemical shifts are relative to internal Me_4Si, while phosphorus chemical shifts are relative to external 85% H_3PO_4, with a positive value being downfield of the respective reference. Spin simulations were performed on a JEOL JEC 980B computer using the program FASN03-760812 supplied by the JEOL Co. Equilibrium thermodynamics for the cis–trans isomerization of the L_2PdX_2 complexes were determined in $CDCl_3$ as previously reported.[3]

(B) Synthesis. Dichlorobis(diphenylvinylphosphine)palladium(II). To 3.84 g (10.0 mmol) of dichlorobis(benzonitrile)palladium(II) in 100 mL of CH_2Cl_2 under N_2 was added 4.7 mL (20.0 mmol) of diphenylvinylphosphine via syringe. The resulting solution was stirred magnetically for 4 h at ambient temperature, filtered, and solvent reduced to approximately 30 mL. Methanol was added to induce crystallization, and the yellow-orange plates that resulted were isolated by filtration, washed with cold methanol, and vacuum-dried overnight; yield 5.41 g (89.9%).

Dichlorobis(phenyldivinylphosphine)palladium(II). To 3.84 g (10.0 mmol) of dichlorobis(benzonitrile)palladium(II) in 100 mL of benzene under N_2 was added 3.3 mL (20.0 mmol) of phenyldivinylphosphine via syringe. Upon addition of the phosphine, a light yellow precipitate formed. This solution was stirred magnetically for 4 h at ambient temperature, and the solvent was removed via rotary evaporation. The yellow material that remained was dissolved in CH_2Cl_2 and filtered. Methanol was added to induce crystallization and the pale yellow needles that resulted were isolated by filtration and vacuum-dried overnight; yield 3.16 g (63.0%).

The bromide and iodide complexes were prepared by metathesis of the chloride complexes in $CH_2Cl_2/CH_3OH/H_2O$ for 24 h with a 4:1 molar ratio of NaX to chloride complex. The physical properties of the complexes are listed in Table I. Satisfactory carbon and hydrogen analysis were obtained for all compounds (Galbraith Laboratories, Knoxville, TN 37921).

Results

Reaction of $(PhCN)_2PdCl_2$, in the appropriate solvent, with 2 equiv of phosphine gives the corresponding L_2PdCl_2 complexes, where L is $Ph_2PCH{=}CH_2$ or $PhP(CH{=}CH_2)_2$. Addition of a CH_3OH/H_2O solution of NaBr or NaI to a CH_2Cl_2 solution of L_2PdCl_2 gives the corresponding halide complexes. The physical properties and $^{31}P\{^1H\}$ NMR, equilibrium thermodynamics, ^1H NMR, and $^{13}C\{^1H\}$ NMR data are given in Tables I–VI, respectively.

Table II. $^{31}P\{^1H\}$ Spectral Data for L_2PdX_2 Complexes

L	X	$\delta(^{31}P)^a$	$\Delta\delta(^{31}P)^b$	geometry	% in soln^c
$Ph_2PCH{=}CH_2$	free ligand	−11.4			
	Cl	22.4	33.8	cis	32.7
	Cl	14.1	25.5	trans	67.3
	Br	19.9	31.4	cis	6.7
	Br	12.1	23.4	trans	93.3
	I	4.7	16.1	trans	100.0
$PhP(CH{=}CH_2)_2$	free ligand	−17.0			
	Cl	14.6	31.5	cis	69.3
	Cl	7.2	24.1	trans	30.7
	Br	12.0	28.9	cis	13.7
	Br	4.6	21.5	trans	86.3
	I	−2.9	14.1	trans	100.0

[a] Relative to 85% H_3PO_4; in ppm. [b] $\Delta\delta(^{31}P) = \delta(^{31}P_{complex}) - \delta(^{31}P_{ligand})$. [c] At 300 K.

Table III. Equilibrium Thermodynamics for the Isomerization *cis*-$L_2PdX_2 \rightleftharpoons$ *trans*-L_2PdX_2 in $CDCl_3$ ($\mu = 1.01$ D)

L	X	ΔS, eu	ΔH, kJ/mol	ΔG_{300}, kJ/mol	$r^{2\,a}$
$Ph_2PCH{=}CH_2$	Cl	88.5	24.5	−2.08	0.9820
$Ph_2PCH{=}CH_2$	Br	39.5	5.30	−6.55	0.9830
$PhP(CH{=}CH)_2$	Cl	104.3	33.2	1.89	0.9823
$PhP(CH{=}CH)_2$	Br	36.2	6.32	−4.54	0.9795
Ph_2PCH_3[9]	Cl	79.9	22.2	−1.80	
$PhP(CH_3)_2$[9]	Cl	37.7	13.0	1.67	

[a] Correlation coefficient for the least-squares regression analysis of the linear relation of $\ln K_{eq}$ with T^{-1}; since $\Delta G = -RT \ln K_{eq} = \Delta H - T\Delta S$ then $\ln K_{eq} = \Delta S/R - \Delta H/(RT)$.

Discussion

Phosphorus NMR and Infrared Spectroscopy. The geometries of the L_2PdX_2 complexes (X = Cl, Br, I) were determined by a combination of ^{31}P NMR (Table II) and infrared spectroscopy[4-8] (Table I). Infrared spectroscopy shows that the L_2PdCl_2 complexes are both primarily cis in the solid state as indicated by the presence of two bands for ν_{Pd-Cl}. The presence of only one ν_{Pd-X} band for the bromide and iodide complexes suggests that they are trans in the solid state.

All of the L_2PdX_2 complexes display singlets in their ^{31}P NMR spectra for each isomer present in solution. The L_2PdCl_2 and L_2PdBr_2 complexes exist as temperature-dependent equilibrium mixtures of cis and trans isomers in $CDCl_3$ solution, whereas the L_2PdI_2 complexes display only one resonance, which can be assigned to the trans isomer. Coordination chemical shifts, $\Delta\delta(^{31}P)$, defined by the equation $\Delta\delta(^{31}P) = \delta(^{31}P_{complex}) - \delta(^{31}P_{ligand})$

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Table IV. 300-MHz ^1H NMR Data for Diphenylvinylphosphine and Its Palladium Halide Complexes L_2PdX_2

X	position	$\delta(^1H)$	J, Hz: $^3J_{ab}$	$^3J_{ac}$	$^2J_{bc}$	$^nJ_{PH}$
free ligand	H_a	6.64	12.44	18.06		11.47
	H_b	5.89	12.44		2.20	31.74
	H_c	5.61		18.06	2.20	14.16
	H_{omp}	7.35				
cis Cl	H_a	6.42	11.89	18.15		23.48
	H_b	5.80	11.89		1.50	40.69
	H_c	5.15		18.15	1.50	20.35
	H_m	7.58				
	H_{op}	7.30				
trans Cl	H_a	7.20	12.52	18.78		24.73[a]
	H_b	6.14	12.52		1.57	38.19[a]
	H_c	5.40		18.78	1.57	18.76[a]
	H_m	7.68				
	H_{op}	7.40				
cis Br	H_a	6.45	11.65	17.71		29.12
	H_b	5.77	11.65		1.52	40.04
	H_c	5.20		17.71	1.52	18.00
	H_m	7.67				
	H_{op}	7.40				
trans Br	H_a	7.19	11.65	18.20		25.48[a]
	H_b	6.17	11.65		1.82	38.22[a]
	H_c	5.33		18.20	1.82	18.19[a]
	H_m	7.67				
	H_{op}	7.40				
trans I	H_a	7.47	12.00	18.00		24.80[a]
	H_b	5.94	12.00		2.00	42.80[a]
	H_c	5.23		18.00	2.00	18.00[a]
	H_m	7.62				
	H_{op}	7.40				

[a] $|^nJ_{PH} + {}^{n+2}J_{P'H}|$.

Table V. 300-MHz ^1H NMR Data for Phenyldivinylphosphine and Its Palladium Halide Complexes L_2PdX_2

X	position	$\delta(^1H)$	J, Hz: $^3J_{ab}$	$^3J_{ac}$	$^2J_{bc}$	$^nJ_{PH}$
free ligand	H_a	6.47	11.70	17.90		11.70
	H_b	5.88	11.70		2.30	31.30
	H_c	5.71		17.90	2.30	14.70
	H_{omp}	7.42				
cis Cl	H_a	6.43	11.77	18.19		23.57
	H_b	5.97	11.77		1.07	41.79
	H_c	5.51		18.19	1.07	21.42
	H_m	7.66				
	H_{op}	7.40				
trans Cl	H_a	6.67	11.77	18.83		24.64[a]
	H_b	6.16	11.77		1.71	38.57[a]
	H_c	5.69		18.83	1.71	18.20[a]
	H_m	7.80				
	H_{op}	7.47				
cis Br	H_a	6.47	12.00	17.52		23.90
	H_b	5.95	12.00		1.20	41.46
	H_c	5.47		17.52	1.20	21.95
	H_m	7.72				
	H_{op}	7.40				
trans Br	H_a	6.80	12.00	18.00		25.61[a]
	H_b	6.10	12.00		1.92	39.02[a]
	H_c	5.57		18.00	1.92	18.25[a]
	H_m	7.72				
	H_{op}	7.40				
trans I	H_a	7.00	12.64	18.96		25.26[a]
	H_b	5.96	12.64		1.58	38.57[a]
	H_c	5.40		18.96	1.58	17.37[a]
	H_m	7.66				
	H_{op}	7.40				

[a] $|^nJ_{PH} + {}^{n+2}J_{P'H}|$.

correlate linearly[9-11] with the free ligand chemical shifts for a number of complexes. Correlation equations, for cis and trans L_2PdX_2 complexes, of the form $\Delta\delta(^{31}P) = A\delta(^{31}P_{ligand}) + B$ have found utility in determining the geometry[9,11] and in evaluating the donor ability of phosphorus ligands. A values reflect phosphorus substituent effects and polarizability, and B values reflect average coordination chemical shifts.

The coordination chemical shifts for the vinylphosphine complexes calculated by using coordination chemical shift equations for L_2PdX_2 complexes,[11] where L is either a phosphole or a phosphine, suggest that the vinylphosphines behave more like phospholes than like typical phosphines. The presence of the electronegative vinyl group on the vinylphosphines results in a larger polarization of the phosphorus atom as compared to trialkylphosphines. This polarization increases the π-back-bonding between palladium and the vinylphosphine ligands and decreases the coordination chemical shift.

Coordination chemical shift equations also demonstrate that in general $\Delta\delta(^{31}P)$ for trans L_2PdX_2 complexes are less than $\Delta\delta(^{31}P)$ for the corresponding cis complexes. This is consistent with trans-influence theories[12] because the trans influence of phosphines is greater than that of halides. From the above generalization the downfield resonance in the ^{31}P NMR spectra of the L_2PdCl_2 and L_2PdBr_2 complexes can be assigned to the cis isomer and the upfield resonance to the trans isomer. In the case of the L_2PdI_2 complexes where only one resonance is present, the small $\Delta\delta(^{31}P)$ values(Table II) indicate that this resonance is due to the trans isomer. Also as the bulk of the halide increases (i.e. chloride to bromide) in the L_2PdX_2 complexes, the trans isomer percentage increases significantly as shown in Table II. Therefore, in going to the bulkier iodide, the trans geometry should predominate.

Equilibrium Thermodynamics. Equilibrium thermodynamic values for the *cis*-L_2PdX_2 $\rightleftharpoons$ *trans*-L_2PdX_2 isomerization were obtained by variable-temperature ^{31}P NMR spectroscopy (Table III). For the L_2PdBr_2 complexes only three temperatures could be used because at 219 K the complexes precipitated out of solution. When L and X are both small as in the case of $[PhP(CH{=}CH_2)_2]_2PdCl_2$, ΔG_{300} is positive, indicating that the cis species is more stable in solution at this temperature than the trans. A positive ΔG_{300} value for the cis–trans isomerization of the analogous $[PhP(CH_3)_2]_2PdCl_2$ complex[13] also suggests that a small ligand and halide together will favor the cis geometry. When the ligand size or cone angle is increased as is the case with $(Ph_2PCH{=}CH_2)_2PdCl_2$, ΔG_{300} becomes negative, indicating that the trans geometry is favored over the cis at this temperature in solution. A negative ΔG_{300} value is also seen[13] for the similar $(Ph_2PCH_3)_2PdCl_2$ complex. An increase in halide size also shifts the equilibrium to favor the trans geometry, further supporting the suggestion that steric considerations are the primary driving force in geometry determination in solution for $(R_3P)_2PdX_2$ complexes.

Proton and Carbon NMR Spectroscopy. Additional information regarding the structure and bonding within these complexes may be obtained from their $^{13}C\{^1H\}$ and ^1H NMR spectra. At 300 MHz it was possible to assign all proton resonances for the iodide complexes. For the chloride and bromide complexes, phosphorus decoupling was carried out in order to distinguish and assign the resonances due to the cis and trans isomers. As an illustrative example, the 300-MHz ^1H and $^1H\{^{31}P\}$ spectra in the vinyl region of $[PhP(CH{=}CH_2)_2]_2PdCl_2$ are shown in Figure 1. The data obtained, together with assignments, are given in Tables IV and V.

Assignments were made by comparing chemical shifts and coupling constants of the complexes with those of the free ligand and similar unsaturated phosphines.[14-17] The vinyl group reso-

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Table VI. 75-MHz ^{13}C NMR Data for L_2PdX_2 Complexes

				Cl						Br						I		
	free ligand			cis			trans			cis			trans			trans		
position	$\delta(^{13}C)$	J, Hz	M[b]	$\delta(^{13}C)$	"J",[a] Hz	M[b]	$\delta(^{13}C)$	"J",[a] Hz	M[b]	$\delta(^{13}C)$	"J",[a] Hz	M[b]	$\delta(^{13}C)$	"J",[a] Hz	M[b]	$\delta(^{13}C)$	"J",[a] Hz	M[b]
$L = Ph_2PCH{=}CH_2$																		
α	136.65	13.70	d	130.86	50.26	d	132.19	0	s	130.67	54.50	d	132.15	0	s	126.38	46.56	t
β	129.39	24.40	d	132.88	0	s	128.95	44.38	t	132.83	0	s	131.27	45.36	t	132.21	0	s
i (ipso)	137.48	9.80	d	127.61	58.60	d	127.88	50.87	t	128.09	50.31	d	128.83	51.24	t	131.26	56.57	t
o (ortho)	133.03	19.50	d	134.35	11.92	d	134.51	12.98	t	134.38	11.77	d	134.63	12.45	t	134.68	12.15	t
m (meta)	128.34	7.80	d	128.44	11.32	d	128.30	10.64	t	128.39	11.18	d	128.16	10.72	t	127.91	10.72	t
p (para)	128.54	0	s	131.41	0	s	130.74	0	s	131.83	0	s	130.67	0	s	130.54	0	s
$L = PhP(CH{=}CH_2)_2$																		
α	136.95	13.91	d	128.40	53.13	d	127.41	45.51	t	129.65	49.58	m	129.34	46.33	t	133.76	47.47	t
β	128.10	23.16	d	133.65	0	s	132.80	0	s	133.27	0	s	132.48	0	s	132.02	0	s
i	137.31	9.17	d	127.00	62.64	d	not obsd			127.78	50.31	d	127.97	52.41	t	130.08	54.34	t
o	132.32	18.70	d	133.96	11.40	d	134.24	13.13	t	133.96	11.92	d	134.31	13.20	t	134.16	12.83	t
m	128.48	6.74	d	128.68	11.24	d	128.47	11.17	t	128.60	12.00	d	128.35	10.94	t	128.15	11.17	t
p	128.56	0.48	d	131.78	2.11	d	130.96	0	s	131.64	0	s	130.89	0	s	130.76	0	s

[a] "J" = $|^nJ_{PC} + {}^{n+2}J_{P'C}|$. [b] M = multiplicity: s = singlet; d = doublet; t = triplet; m = multiplet.

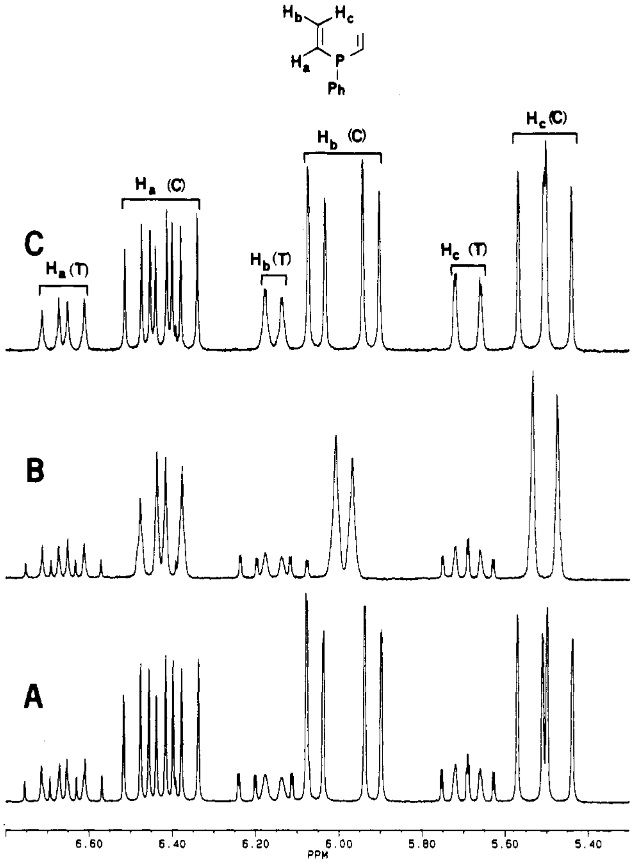

Figure 1. (A) 300-MHz ^1H NMR spectrum (vinyl region) in $CDCl_3$ at 297 K of a cis (C)/trans (T) mixture of $[PhP(CH{=}CH_2)_2]_2PdCl_2$. (B) Spectrum with decoupling of the cis downfield phosphorus resonance. (C) Spectrum with decoupling of the trans upfield phosphorus resonance.

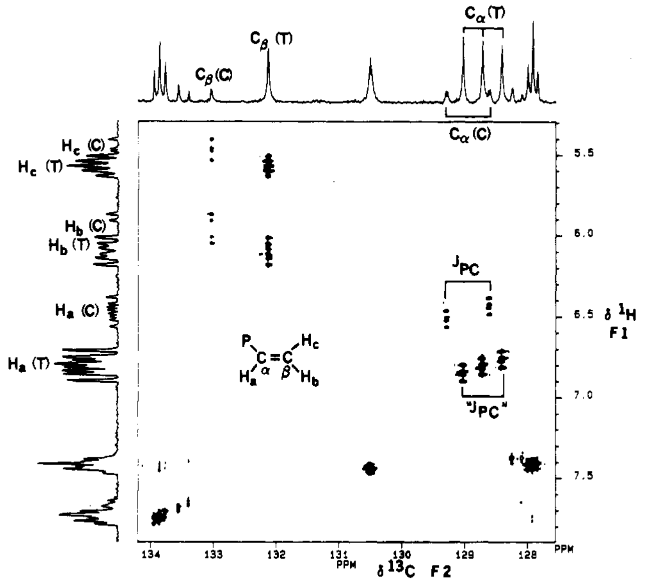

Figure 2. Heteronuclear 2D $^1H/^{13}C$ chemical shift correlation for $[PhP(CH{=}CH_2)_2]_2PdBr_2$ in $CDCl_3$ at 75.0 MHz (^{13}C). PC couplings are responsible for the splittings in F_2, while both PH and HH couplings are responsible for the splittings along F_1.

nances for the *cis*-L_2PdX_2 complexes were analyzed as ABCX subspectra of the complete $[ABCX]_2$ spin system: A, B, C = ^1H; X = ^{31}P. This approximation was proven valid by computer simulations of the spectra[18] for the *cis*-$[PhP(CH{=}CH_2)_2]_2PtX_2$ complexes and indicates that $^2J_{PP}$ is essentially zero for the cis complexes of both palladium and platinum.

The ^1H NMR spectra of the *trans*-L_2PdX_2 complexes could not be analyzed in this way because they were clearly second order. The proton–proton couplings for the L_2PdX_2 complexes were determined from 300-MHz $^1H\{^{31}P\}$ spectra and $|^nJ_{PH} + {}^{n+2}J_{P'H}|$ for the *trans*-L_2PdX_2 complexes were determined by comparing the phosphorus-coupled and -decoupled spectra.

There is little change in the proton spectrum of $PhP(CH{=}CH_2)_2$ upon coordination. Only a slight upfield shift in $\delta(H_c)$, a slight downfield shift in $\delta(H_b)$ and essentially no change in $\delta(H_a)$ for the *cis*-$[PhP(CH{=}CH_2)_2]_2PdX_2$ (X = Cl, Br) complexes were noted. For the trans complexes a 0.2–0.5 ppm downfield shift for $\delta(H_a)$ was noted. There is also little change in the proton spectrum of $Ph_2PCH{=}CH_2$ upon coordination except for a 0.6–0.8 ppm downfield shift in $\delta(H_a)$ for the *trans*-$(Ph_2PCH{=}CH_2)_2PdX_2$ complexes. A slight upfield shift is observed in $\delta(H_a)$ for the cis complexes. A 0.2–0.4 ppm upfield shift for $\delta(H_c)$ and small upfield and downfield shifts for $\delta(H_b)$ were noted for the cis and trans complexes, respectively.

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The 75-MHz $^{13}C\{^1H\}$ NMR data are presented in Table VI. Assignments were made consistent with earlier data of Bundesgaard and Jakobsen,[19] and with the aid of $^1H/^{13}C$ heteronuclear chemical shift correlated (HETCOR) NMR experiments. Figure 2 shows the HETCOR spectrum of $[PhP(CH{=}CH_2)_2]_2PdBr_2$. The correlations for the H_a–C_α nuclei in the HETCOR spectra indicate that $^2J_{PH}$ and $^1J_{PC_\alpha}$ are of like sign.[20] Several trends in the data are notable. Upon coordination, the phenyl ortho and para carbon resonances of both ligands, $Ph_2PCH{=}CH_2$ and $PhP(CH{=}CH_2)_2$, shift downfield and the meta carbon resonances remain essentially unchanged. The phenyl ipso carbon resonances for the L_2PdCl_2 and L_2PdBr_2 complexes experience a large upfield shift of 9–10 ppm upon coordination, and a 6–7 ppm upfield shift is noted for the L_2PdI_2 complexes. The large upfield shift may be attributed to π-back-bonding between palladium and the vinylphosphines with the phenyl group acting as an electron sink.

Upon coordination the resonances for the α-carbons of the vinyl group shift upfield, while the β-carbon resonances shift downfield, except for a slight upfield shift for the β-carbon in *trans*-$(Ph_2PCH{=}CH_2)_2PdCl_2$. This polarization of the C=C double bond is also likely a result of π-back-bonding. For alkylphosphines,[21] coordination induces an upfield shift in both the α- and β-carbon resonances. The downfield shift noted for the β-carbon resonances in the $(Ph_2PCH{=}CH_2)_2PdX_2$ and $[PhP(CH{=}CH_2)_2]_2PdX_2$ complexes was also observed for the platinum analogues[18,22] as well as for platinum[23] and palladium[24] phosphole complexes. This anomalous downfield shift for the resonance of the β-carbons of the phosphole complexes has been attributed[23] to a (2p–3d) interaction between the phosphole ring butadiene moiety and phosphorus. This explanation has been extended to explain the small coordination chemical shifts for phosphines having unsaturated groups that may conjugate with phosphorus in similar ways.[25-27]

Ligand Polarization and Diels–Alder Reactivity. With the characterization of the palladium vinylphosphine and phosphole[24] complexes complete it becomes evident that significant polarization of the C=C double bond occurs for both the vinylphosphine and phosphole ligands upon coordination. It appears that polarization of both the vinyl group of the phosphine and the phosphole are necessary for the intramolecular Diels–Alder [4 + 2] cycloaddition reactions[1] of Pd and Pt vinylphosphine and phosphole complexes to occur. This information should aid in better understanding the mechanism for these [4 + 2] cycloaddition reactions, which will be discussed in a future publication.

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Registry No. *cis*-$(Ph_2PCH{=}CH_2)_2PdCl_2$, 113214-83-8; *trans*-$(Ph_2PCH{=}CH_2)_2PdCl_2$, 98717-39-6; *cis*-$(Ph_2PCH{=}CH_2)_2PdBr_2$, 113109-73-2; *trans*-$(Ph_2PCH{=}CH_2)_2PdBr_2$, 113214-84-9; *trans*-$(Ph_2PCH{=}CH_2)_2PdI_2$, 113109-74-3; *cis*-$[PhP(CH{=}CH_2)_2]_2PdCl_2$, 98651-93-5; *trans*-$[PhP(CH{=}CH_2)_2]_2PdCl_2$, 98717-40-9; *cis*-$[PhP(CH{=}CH_2)_2]_2PdBr_2$, 113109-75-4; *trans*-$[PhP(CH{=}CH_2)_2]_2PdBr_2$, 113214-85-0; *trans*-$[PhP(CH{=}CH_2)_2]_2PdI_2$, 113109-76-5; $(PhCN)_2PdCl_2$, 14220-64-5; $Ph_2PCH{=}CH_2$, 2155-96-6; $PhP(CH{=}CH_2)_2$, 26681-88-9.

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Interconversion of Dinuclear and Oxo-Centered Trinuclear Cobaltic Acetates

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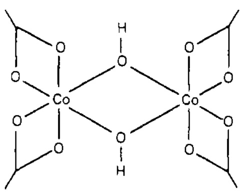
Reaction of the oxo-centered cobalt cluster $[(py)_3Co_3O(OAc)_5OH]^+$, $[\mathbf{5}]^+$, with water in acetic acid produces a dinuclear cluster, $[(py)_4Co_2(OAc)_3(OH)_2]^+$, $[\mathbf{3}]^+$, and a new oxo-centered cluster, $[(py)_5Co_3O(OAc)_3(OH)_2]^{2+}$, $[\mathbf{4}]^{2+}$, as an equilibrium mixture. The clusters $[\mathbf{3}]^+$ and $[\mathbf{4}]^{2+}$ were also synthesized by the oxidation of cobaltous acetate with peracetic acid in the presence of pyridine in aqueous acetic acid. Treatment of $[\mathbf{3}]^+$ and $[\mathbf{4}]^{2+}$ with glacial acetic acid gives a mixture of $[\mathbf{5}]^+$ and $[(py)_3Co_3O(OAc)_6]^+$, $[\mathbf{6}]^+$. $[\mathbf{3}][PF_6]$ and $[\mathbf{4}][PF_6]_2$ were characterized by X-ray crystallographic techniques. At 20 ± 1 °C, crystals of both compounds are monoclinic, with $a = 12.478$ (2) Å, $b = 14.223$ (3) Å, $c = 23.278$ (4) Å, $\beta = 103.92$ (1)°, $V = 4010$ (1) Å^3, $Z = 4$ [μ_a(Mo Kα) = 1.21 mm^{-1}], and space group $P2_1/c$-C_{2h} for $[\mathbf{3}][PF_6]$, and with $a = 16.500$ (3) Å, $b = 17.128$ (4) Å, $c = 17.357$ (4) Å, $\beta = 105.64$ (2)°, $V = 4724$ (2) Å^3, $Z = 4$ [μ_a(Mo Kα) = 1.32 mm^{-1}], and space group $P2_1/n$ for $[\mathbf{4}][PF_6]_2$.

Recently, there has been a renewed interest in transition-metal-catalyzed autoxidation reactions. In these reactions, the transition-metal is believed to be responsible for chain initiation and the decomposition of various peroxides formed during the reaction.[1] Perhaps the most studied autoxidation system over the last 20 years is the cobalt-catalyzed oxidation of aromatic hydrocarbons;[2] however, the active form of cobalt in this system is still unknown although several structures have been proposed. For example, Koubek and Edwards[3] proposed the neutral, dinuclear structure [**1**] for a green, amorphous solid obtained by the oxidation of cobaltous acetate with peracetic acid. The same structure was proposed by Kochi[4] for cobaltic acetate obtained



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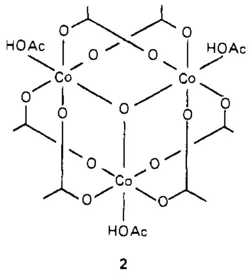

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