teraction between the dihydrogen and the metal. They indeed find the potential minimum when rotating the η^2-H_2 ligand about the H_2–Fe–H axis about 20° off to one side of the equilibrium orientation determined by the crystal structure analysis. If one were to add an electronic component to this with a strong preference for an H–H orientation parallel to the P–Fe–P axis, it is not difficult to see how the potential derived in our analysis could arise. It should be added, however, that the parametrization for the rotational potential that we used in terms of sinusoidal function may not be an accurate representation of the "true" potential curve and that therefore our result has to be regarded as tentative in this sense. It is, however, consistent with all available experimental data as described.

As far as the value for the barrier height is concerned, the molecular mechanics calculation yields a value of about 1.7 kcal/mol, while our results are either 1.8 kcal/mol for the pure V_2 potential or effectively about 2.3 kcal/mol for the modulated form. If one were to add an electronic component of approximately 1–2 kcal/mol[21] to the "steric" part given by the molecular mechanics calculation, the total comes out somewhat higher than these experimental values. Nonetheless, the agreement must be viewed as remarkable, since these values for barrier heights are below what is normally considered a reliable range for these type of calculations.

In conclusion, we have obtained the first vibrational and rotational data for the dihydrogen ligand in one of the most studied molecular hydrogen complexes, *trans*-$[FeH(H_2)(PPh_2CH_2CH_2PPh_2)_2]BF_4$. We have analyzed the rotational transitions including the tunneling transition within the ground state in terms of planar rotation with one angular degree of freedom and derived a potential that appears to reflect some competition between the nonbonded interactions of the dihydrogen and the other ligands on the one hand and the direct dihydrogen–metal binding on the other. Further neutron-scattering studies on these systems are in progress with the aim of trying to separate the contributions to the rotational barrier from each other and to study the high-temperature rotational dynamics of the dihydrogen ligand.

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Solid-State Structures of $(R_3P)_2PtX_2$ Complexes As Determined by a Combination of $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR Spectroscopy

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Cross-polarization, combined with magic-angle spinning, has been employed to obtain high-resolution solid-state ^{13}C and ^{31}P NMR spectra of a series of 31 $(R_3P)_2PtX_2$ complexes. These data together with spectra obtained in solution were used to compare the solid-state structures with those in solution. It was found that most of these complexes, which have regular square-planar structures in solution, are distorted in the solid state. The extent of the solid-state distortion is a function of the bulk of the coordinated ligands and increases as the ligand size increases. The solid-state distortions appear to result from intramolecular steric effects for *cis*-$(R_3P)_2PtX_2$ and probably from intermolecular crystal packing forces for *trans*-$(R_3P)_2PtX_2$.

Introduction

The technique of cross-polarization combined with magic-angle spinning (CP/MAS) has tremendous potential for structure determination by NMR in the solid state.[2] In a recent study,[3] we showed that CP/MAS ^{13}C and ^{31}P spectroscopy were useful for elucidation of the solid-state structures of palladium(II) and platinum(II) complexes of $MePh_2P$ and Me_2PhP. Though they possess regular square-planar structures in solution, most of these complexes were distorted in the solid state. Their CP/MAS ^{31}P NMR spectra were straightforward and easy to interpret. In contrast, only the methyl region of their CP/MAS ^{13}C NMR spectra provided meaningful information. The aromatic regions of these spectra were broad unresolved envelopes. The isomeric structures of the platinum complexes (cis or trans) were easily determined from the magnitude of $^1J(PtP)$. In order to gain greater understanding of the driving force for these solid-state distortions and to further explore the utility of CP/MAS spectroscopy for solid-state structural determination, we have prepared a series of 31 $(R_3P)_2PtX_2$ complexes containing ligands of significantly different size and obtained their CP/MAS ^{13}C and ^{31}P NMR spectra. These data are compared with $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra obtained in $CDCl_3$ solutions at 300 K.

Experimental Section

A. Reagents and Physical Measurements. All chemicals used were reagent grade and were used as received or synthesized as described below. 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. Elemental analysis were performed by Galbraith Laboratories, Knoxville, TN 37921.

The solution $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 25- and 40.26-MHz respectively on a JEOL FX-100 spectrometer. Carbon chemical shifts were obtained relative to internal Me_4Si, while phosphorus chemical shifts were referenced to Ph_3P in $CDCl_3$ ($\delta = -6$ ppm) and converted to a 85% H_3PO_4 reference with positive values being downfield of the respective references. Cross-polarization magic-angle spinning (CP/MAS) $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian VXR-300 spectrometer operating at 75 and 121.4 MHz, respectively. The proton-decoupling field was 65 KHz. Carbon chemical shifts were referenced to an external sample of poly(dimethylsilane) ($\delta = 0$ ppm), while phosphorus chemical shifts were referenced to an external sample of Ph_3P ($\delta = -6$ ppm). The uncertainties in chemical shifts and coupling constants are estimated to be ±0.5 and ±20 Hz, respectively, for the CP/MAS measurements.

B. Synthesis. Most of the phosphines were obtained from either Strem Chemical or Organometallics, Inc., and were used as received. Tribenzylphosphine,[4] dibenzylphenylphosphine,[5] 1-phenyldibenzophosphole[6] (DBP), 1-phenyl-3,4-dimethylphosphole[7] (DMPP), and

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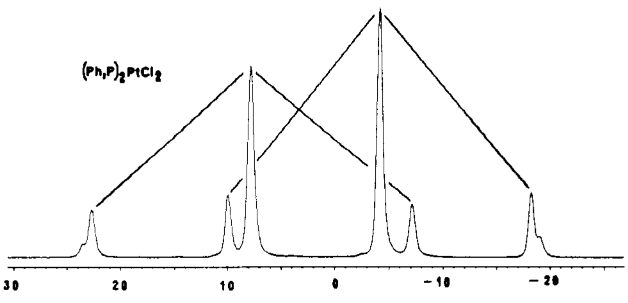

Figure 1. 121.4-MHz CP/MAS ^{31}P NMR spectrum of *cis*-$(Ph_3P)_2PtCl_2$. The ^{195}Pt satellites associated with the two ^{31}P chemical shifts are indicated by lines. $^1J(PtP)$ is the separation between the outer two lines in the approximately 1:4:1 Pseudo triplets.

1,3,4-trimethylphosphole[7] (TMP) were prepared by literature methods. Most $(R_3P)_2PtCl_2$ complexes were prepared by reacting 2 equiv of the phosphine or phosphole with 1 equiv of $(PhCN)_2PtCl_2$ in CH_2Cl_2 under an N_2 atmosphere.[8] When R_3P was *n*-Bu_3P, *n*-Pr_3P, or Et_3P, 2 equiv of the phosphine were reacted with 1 equiv of K_2PtCl_4.[9]

Dichlorobis(diphenylvinylphosphine)platinum(II). To 2.51 g (5.30 mmol) of $(PhCN)_2PtCl_2$ in 75 mL of $CHCl_3$ under N_2 was added 2.5 mL (10.6 mmol) of diphenylvinylphosphine via syringe. The resultant solution was stirred magnetically for 4 h at ambient temperature and filtered and the solution volume was reduced to approximately 35 mL on a rotary evaporator. Methanol was added to induce crystallization, and the pale yellow hexagonal plates that resulted were isolated by filtration, washed with cold methanol, and vacuum-dried overnight; yield 2.33 g (63.5%).

The bromide and iodide complexes were prepared by metathesis of the chloride complexes in a $CH_2Cl_2/CH_3OH/H_2O$ solvent mixture for 7 days at ambient temperature employing a 4:1 mole ratio of NaX to chloride complex. The physical properties of the $(R_3P)_2PtCl_2$ complexes (R_3P = Me_3P,[10] Et_3P,[9] *n*-Pr_3P,[11] *i*-Pr_3P,[12] *n*-Bu_3P,[9] Cy_3P,[12] Ph_3P,[13] Bzl_3P,[14] Bzl_2PhP,[14] $BzlPh_2P$,[14] and TMP[15]) agreed with the literature data. The physical properties of $(PhVy_2P)_2PtX_2$,[16] $(DMPP)_2PtX_2$,[15] all ((cyanoethyl)phosphine)$_2PtX_2$[17] and $(n\text{-}Bu_3P)_2PtX_2$ (X = Br, I)[18] agreed with the literature data. Satisfactory carbon and hydrogen analyses were obtained for all compounds except $(TMP)_2PtBr_2$ (vide infra).

Results and Discussion

I. Solution Spectra. The solution geometry of $(R_3P)_2PtX_2$ complexes can be easily deduced from a combination of $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy. Their $^{31}P\{^1H\}$ NMR spectra display singlets for either the cis or the trans isomer with platinum satellites due to the presence of ^{195}Pt ($I = {}^1/_2$; 33.8%). The magnitude of $^1J(PtP)$ is indicative of geometry.[11,19,20] For cis isomers $^1J(PtP)$ is typically greater than 3000 Hz while for trans isomers $^1J(PtP)$ is usually less than 2500 Hz. Each $^{13}C\{^1H\}$ resonance is typically a 1:2:1 triplet for the trans isomer and a doublet, a doublet of doublets, a five-line multiplet, or a non-1:2:1 triplet for the cis isomer.[21,22] The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR data in Tables I and II were used to make solution structure assignments.

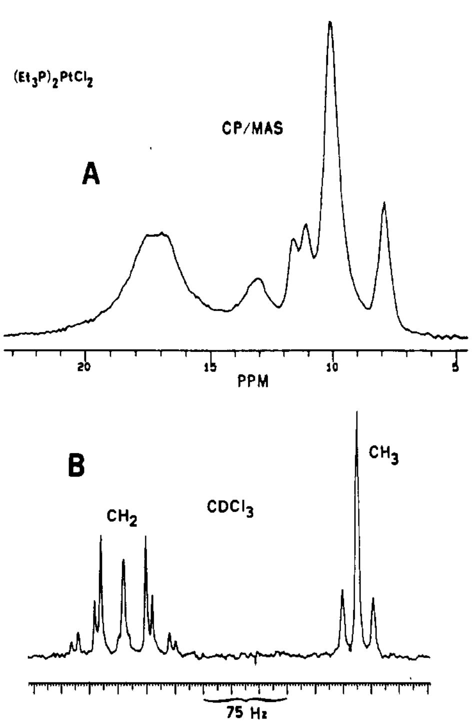

Figure 2. Comparison of (A) 75-MHz CP/MAS ^{13}C and (B) 25.0-MHz $^{13}C\{^1H\}$ (in $CDCl_3$ at 300 K) NMR spectra of *cis*-$(Et_3P)_2PtCl_2$.

II. CP/MAS Spectra. The $^{31}P\{^1H\}$ spectrum in $CDCl_3$ solution and the ^{31}P CP/MAS spectrum of *cis*-$(Me_3P)_2PtCl_2$ are very similar. Each spectrum displays a single resonance with the magnitude of $^1J(PtP)$ characteristic of the cis isomer. The ^{13}C NMR spectra in the two states are quite different. In $CDCl_3$ solution, the methyl resonance is a five-line AXX′ multiplet, while in the solid state (Table III) the methyl resonance is a broad singlet ($\Delta\nu_{1/2}$ = 75 Hz). With resolution enhancement, this broad singlet appears to consist of three closely spaced equally intense resonances (δ 19.4, 19.2, and 18.9 ppm). The crystal structure[23] of *cis*-$(Me_3P)_2PtCl_2$ shows that the two Pt–P bond lengths are not equal, differing by 0.01 Å. There are four molecules in the unit cell, and for none of them are the methyl groups symmetry equivalent. Hence, the ^{13}C CP/MAS data are consistent with the crystal structure, but the ^{31}P CP/MAS spectrum does not exhibit two chemical shifts as anticipated. The chemical shift dispersion range of ^{31}P is greater than that of ^{13}C, and ^{31}P chemical shifts usually experience a greater change with subtle environmental changes than do ^{13}C chemical shifts. The single narrow ($\Delta\nu_{1/2}$ = 40 Hz) ^{31}P CP/MAS resonance could be due to low-energy molecular librations that render the two phosphorus nuclei equivalent on the NMR time scale.

The crystal structure[24] of *cis*-$(Ph_3P)_2PtCl_2$ shows that for this complex as well the two platinum–phosphorus bond lengths differ by 0.01 Å. The CP/MAS ^{31}P NMR spectrum (Figure 1) of this complex displays two resonances[25] that are separated by 12 ppm. Such a large chemical shift difference could be interpreted to mean that the solid is a mixture of cis and trans isomers, but for both resonances the magnitude of $^1J(PtP)$ is in the characteristic range for cis isomers. Only the cis isomer is present in solution, and the value of $^1J(PtP)$ observed in solution (3551 Hz) is within experimental uncertainty equal to the average value observed in the solid state (3523 Hz). These observations suggest that the phosphine cone angle[26] plays a larger role in determining the

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Table I. Solution and CP/MAS ^{31}P NMR Data for $(R_3P)_2PtX_2$ Complexes

		CP/MAS		$CDCl_3$	
R_3P^a	X	$\delta(^{31}P)^b$	$^1J(PtP)^c$	$\delta(^{31}P)^b$	$^1J(PtP)^c$
Me_3P	Cl	−16.3	3429	−25.1	3481
Et_3P	Cl	13.3	3412	8.6	3516
		11.8	3460		
n-Pr_3P	Cl	8.7	2358	2.7	2380
		8.5	2367		
		8.2	2369		
		7.9	2398		
		7.1	2358		
i-Pr_3P	Cl	33.9	2411	26.6	2417
n-Bu_3P	Cl	8.2	3492	0.1	3508
		7.4	3486		
n-Bu_3P	Br	8.8	2411	−1.1	2319
		6.2	2358		
		3.6	2332		
n-Bu_3P	I	−5.1	2240	−9.0	2253
		−7.5	2222		
Cy_3P	Cl	17.8	2410	15.8	2396
Ph_3P	Cl	7.9	3625	−7.8	3551
		−4.1	3421		
DBP	Cl	10.7	3269	4.5	3491
		4.0	3567		
$BzlPh_2P$	Cl	18.3	3768	9.0	3735
		16.5	3792		
		15.1	3774		
Bzl_2PhP	Cl	10.8	2484	8.4	2534
Bzl_3P	Cl	14.2	3694	4.7	3652
		5.3	2448	5.3	2462
		0.3	2387		
Bzl_3P	Br	−0.7	2375	−1.8	2397
		−7.4	2315		
Bzl_3P	I	−13.8	2322	−10.5	2341
$PhVy_2P$	Cl	8.4	3750	−4.4	3574
		4.2	3447		
$PhVy_2P$	I	2.7	3494	−7.7	3368
		0.8	3526		
		0.3	3547		
		−3.9	3325		
		−6.4	3268		
		−8.2	3101		
Ph_2VyP	Cl	15.2	3663	2.7	3633
		6.9	3661		
		−0.5	3662		
Ph_2VyP	Br	14.6	3670	2.3	3581
Ph_2VyP	I	6.1	3536	−0.3	3433
		4.7	3443	0.5	2454
		2.8	3205		
		1.8	3271		
DMPP	Cl	21.3	3384	8.1	3345
		18.1	3179		
DMPP	I	8.0	3022	5.1	3120
				4.7	2336
TMP	Cl	1.8	3112	−2.1	3291
		0.1	3323		
TMP	Br	3.5	3107	−1.8	3236
		−2.1	3239		
$(CE)Ph_2P$	I	3.8	2400	1.8	2451
$(CE)_2PhP$	Cl	0.8	3670	0.3	3560
		−4.6	3475		
$(CE)_2PhP$	Br	8.9	···	0.1	3521
		7.9	···		
		6.9	3490		
		5.4	3440		
		4.0	···		
		0.4	3490		
		−1.0	3520		
		−3.2	···		
$(CE)_2PhP$	I	−0.4	2345	−0.5	2395
$(CE)_3P$	Cl	15.7	2440	10.5	3489
				4.8	2476
$(CE)_3P$	Br	−0.5	2484	6.3	2407
$(CE)_3P$	I	3.1	2350	−0.4	2344

[a] Me = methyl; Et = ethyl; Pr = propyl; Bu = butyl; Cy = cyclohexyl; DBP = phenyldibenzophosphole; Bzl = benzyl; Vy = $-CH{=}CH_2$; DMPP = 1-phenyl-3,4-dimethylphosphole; TMP = 1,3,4-trimethylphosphole; CE = $NCCH_2CH_2-$. [b] In ppm at 300 K, relative to Ph_3P = −6 ppm. [c] In hertz.

Table II. Solution $^{13}C\{^1H\}$ NMR Data for $(R_3P)_2PtX_2$ Complexes

R_3P	X	$\delta(^{13}C)^a$ (carbon type, multiplicity),^{b} J^c
Me_3P	Cl	17.05 (CH_3, f), −1.6^g, 45.6,^{g} 15.5^d
Et_3P	Cl	8.45 (CH_3, t), 1.5,^{e} 28.0;^{f} 16.80 (CH_2, f), 1.9,^{g} 37.2,^{g} 17.9,^{d} 42^f
n-Pr_3P	Cl	22.76 (C_α, t), 32.7^e, 23;^{f} 17.21 (C_β, t), 15.6;^{e} 15.73 (CH_3, t), 14.2^e
i-Pr_3P	Cl	21.22 (CH, t), 27.4,^{e} 22.5;^{f} 19.10 (CH_o, t), 13.2^e
n-Bu_3P	Cl	26.07 (C_β, t), 16.1;^{e} 23.85 (C_α, f), 0.02,*g* 37.46^g 15.7;^{d} 23.64 ($C\gamma$, f), 14.6*e*
Bzl_3P	Cl	133.6 (C_i, s); 130.3 (C_o, s); 128.46 (C_m, s); 126.68 (C_p, s); 27.61 (CH_2, f) 28.5^e
DMPP	I	154.9 (C_β, f), 12.2;^{e} 127.8 (C_α, f), 65.9,^{e} 29.3;^{f} 18.5 (CH_3, f), 13.4^e
TMP	Cl	154.0 (C_β, f), 12.2,^{e} 35.4;^{f} 124.9 (C_α, f), 64.7,^{e} 35.4;^{f} 18.6 (3,4-CH_3, t), 13.4^e, 40.3,^{f} 12.5 (1-CH_3, f), 41.5^e
$(CE)Ph_2P$	I	133.78 (C_o, t), 10.9;^{e} 131.24 (C_p, s); 129.15; (C_i, s); 128.46 (C_m, t), 10.9;^{e} 118.32 (CN, m); 28.36 (c_α, m) 29.0;^{e} 13.50 (C_β, s)
$(CE)_2PhP$	Cl	131.9 (C_p, s); 131.1 (C_o, t), 9.8;^{e} 128.96 (Cm, t), 9.8;^{e} 125.95 (C_i, d), 63.4;^{e} 119.01 (CN, f), 0.9,^{g} 17.3,^{g} 17.1;^{d} 19.60 (C_α, m), 39.1;^{e} 12.23 (C_β, t), 29.3^e
$(CE)_2PhP$	Br	132.24 (C_p, s); 131.37 (C_o, m); 129.47 (C_m, m); 119.72 (CN, m); 21.01 (C_α, m) 39.1;^{e} 12.74 (C_β, m)
$(CE)_2PhP$	I	132.88 (C_o, t) 12.2;^{e} 131.32 (C_p, s); 129.56 (C_i, s); 128.54 (Cm, t) 13.0;^{e} 119.43 (CN, m); 23.42 (C_α, m) 35.4;^{e} 12.69 (C_β, m)
cis-$(CE)_3P$	Cl	119.40 (CN, m); 16.32 (C_α, m); 11.44 (C_β, m)
trans-$(CE)_3P$	Cl	119.74 (CN, m); 18.96 (C_α, m); 12.28 (C_β, m)
$(CE)_3P$	Br	120.01 (CN, m); 15.8;^{e} 17.96 (C_α, d) 34.2;^{e} 12.06 (C_β, t) 21.9^e
$(CE)_3P$	I	119.81 (CN, m); 21.86 ($C\alpha$, m); 12.52 (C_β, m)

[a] In ppm at 300 K in $CDCl_3$, relative to TMS = 0 ppm. [b] Carbon type: CH = methine; CH_2 = methylene; CH_3 = methyl; C_i = ipso; C_o = ortho; C_m = meta; C_p = para; CN = cyano; C_α = C attached to P; C_β = second C from P; C_γ = third C from P. Multiplicity: s = singlet; d = doublet; t = triplet; f = five-line multiplet. [c] All *J*'s in hertz. [d] $^2J(PP)$. [e] $|^nJ(PC) + {}^{n+2}J(PC)|$. [f] $J(PtC)$. [g] $^1J(PC)$ or $^3J(PC)$ with $^1J(PC) > {}^3J(PC)$.

chemical shift differences observed in the solid-state ^{31}P NMR spectra than do M–P bond lengths. The cone angle for Ph_3P is 145° while that of Me_3P is only 118°. Thus, whereas *cis*-$(Me_3P)_2PtCl_2$ is perhaps mobile in the solid state, *cis*-$(Ph_3P)_2PtCl_2$ is conformationally rigid and tetrahedrally distorted.

The crystal structure[27] of *cis*-$(Et_3P)_2PtCl_2$ shows that this compound also has two different Pt–P bond lengths. For it, two CP/MAS ^{31}P resonances are observed at 13.3 and 11.8 ppm with $^1J(PtP)$ values of 3412 and 3460 Hz, respectively (cf $^1J(PtP)$ = 3516 Hz in $CDCl_3$ solution).[28] At least six resonances are present in its CP/MAS ^{13}C NMR spectrum (Figure 2), and their assignment to methyl and methylene carbons cannot be unequivocally made. The solution state $^{13}C\{^1H\}$ NMR spectrum (Figure 2) contains two resonances, a five-line multiplet with associated platinum satellites for the methylene carbons and a singlet with $^3J(PtC)$ = 28 Hz for the methyl carbons. The cone angle of Et_3P (132°) appears to be sufficiently large as to distort this molecule in the solid state just enough that chemical shift inequivalence is observed for both the phosphorus and carbon atoms.

A resolution-enhanced CP/MAS ^{31}P NMR spectrum of *trans*-(*n*-$Pr_3P)_2PtCl_2$ displays five resonances, spanning a range of 1.6 ppm, all with $^1J(PtP)$'s characteristic of trans isomers. Only the trans isomer is present in $CDCl_3$ solution. Its CP/MAS ^{13}C NMR spectrum contains three broad envelopes. The α-CH_2 resonances lie between 22 and 26 ppm, the β-CH_2 resonances lie

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Table III. GP/MAS ^{13}C NMR Data for $(R_3P)_2PtX_2$ Complexes

R_3P	X	$\delta(^{13}C)$ (carbon type)[a]
Me_3P	Cl	19.2 (CH_3)
Et_3P	Cl	17.0,[b] 13.0 (CH_2); 11.7, 11.1 ((C?); 10.1, 7.9 (CH_3)
n-Pr_3P	Cl	24.0[b] (C_α); 19.4, 18.8, 17.8, 17.3, 16.7, 16.2, (C_β, C_γ)
i-Pr_3P	Cl	24.1, 20.7 (CH); 22.2, 21.7, 20.1, 19.6, 19.3 (CH_3)
n-Bu_3P	Cl	29.1, 28.4, 26.6, 25.9, 25.4 (CH_2); 18.1, 16.9, 15.7, 15.0 (CH_3)
n-Bu_3P	Br	28.5, 27.7, 27.3, 25.8, 25.3, 20.4 (CH_2); 15.4, 15.0 (CH_3)
n-Bu_3P	I	28.3, 27.1, 25.8, 23.5, (CH_2); 16.5, 16.3, 15.5, 15.0 (CH_3)
Bzl_3P	Cl	126–135 (Ph); 32.9, 30.4, 28.6, 27.4, 25.5 (CH_2)
Bzl_3P	Br	124–135 (Ph); 33.7, 31.0[b] (CH_2)
Bzl_3P	I	125–136 (Ph); 38.1, 35.6, 33.8, 32.3 (CH_2)
DMPP	I	157.3, 155.2, 154.1, 152.0, 150.2 (C_β); 121–136 (C_α, Ph); 21.8, 20.6, 19.8, 19.2, 18.7 (CH_3)
TMP	Cl	154.3, 149.7 (C_β); 125.4, 124.4, 123.1 (C_α); 21.2, 17.7, 16.5, 13.0 (CH_3)
$(CE)Ph_2P$	I	121–134 (Ph, CN); 30.1 (C_α); 15.4 (C_β)
$(CE)_2PhP$	Cl	117–121 (CN); 121–139 (Ph); 24.0 (C_α); 10–22 (C_α, C_β)
$(CE)_2PhP$	Br	116–123 (CN); 123–137 (Ph); 26.5, 23.9 (C_α); 11–21 (C_α, C_β)
$(CE)_2PhP$	I	118–122 (CN); 127–136 (Ph); 28.6 (C_α); 18.8, 15.3 (C_β)
$(CE)_3P$	Cl	123.9, 121.6, 118.6 (CN); 24.3, 19.4 (C_α); 15.5, 14.5 (C_β)
$(CE)_3P$	Br	116–124 (CN); 25.0, 21.0, 19.9 (C_α); 13.3,[b] (C_β)
$(CE)_3P$	I	122.2, 119.4 (CN); 23.0, 21.9, 19.9 (C_α); 17.7 (C?); 16.3, 14.7 (C_β)

[a] In ppm relative to PDMS = 0 ppm; CH_2 = methylene; CH_3 = methyl; Ph = phenyl; CN = cyano; C_α = carbon attached to P; C_β = second carbon from P; C_γ = third carbon from P; C? = assignment uncertain. [b] Broad.

between 17 and 20 ppm, and the CH_3 resonances come between 15 and 17 ppm and are comparable to the chemical shifts observed in $CDCl_3$ solution (Table II). A crystal structure analysis has not been done on this complex, but the CP/MAS data suggest that there are slight conformational differences of the propyl groups leading to slightly different environments for both the phosphorus and carbon atoms in the solid state. This notion could be tested by variable-temperature CP/MAS spectroscopy.

The solution $^{13}C\{^1H\}$ NMR spectrum of *cis*-$(n\text{-}Bu_3P)_2PtCl_2$ displays four resonances, with the α-, β-, and γ-methylene carbon resonances appearing as a five-line multiplet (23.85 ppm), a triplet (26.07 ppm), and a five-line multiplet (23.64 ppm), respectively. The methyl resonance is a singlet at 13.23 ppm. The CP/MAS ^{13}C NMR spectrum contains a broad envelope from 25 to 29.1 ppm that can be assigned to all three methylene resonances. Even in solution, there was considerable overlap of these resonances. Upfield of this envelope are four well-resolved narrow singlets at 18.1, 16.9, 15.7 and 15.0 ppm in a 1:1:2:2 intensity ratio attributable to the CH_3 groups. Two resonances are observed in its CP/MAS ^{31}P NMR spectrum at 8.2 and 7.4 ppm. The magnitudes of $^1J(PtP)$ indicate that this compound is the cis isomer both in solution and in the solid state. The small (0.8 ppm) difference in these two ^{31}P resonances suggests that the extent of molecular distortion in the solid state is small. The solid-state structure is rigid and possesses fixed conformations of the phosphines.

The analogous bromide complex, $(n\text{-}Bu_3P)_2PtBr_2$, is trans in the solid state and in solution and exhibits three CP/MAS ^{31}P resonances. Its CP/MAS ^{13}C spectrum is very similar to that of *cis*-$(n\text{-}Bu_3P)_2PtCl_2$, displaying a broad envelope of resonances between 20 and 29 ppm, but in this case, only two broad methyl resonances appear at 15.0 and 15.4 ppm. The CP/MAS ^{31}P NMR spectrum of $(n\text{-}Bu_3P)_2PtI_2$ (Figure 3) shows a well-resolved AB multiplet. The magnitudes of $^1J(PtP)$ and $^2J(PP)^{29}$ = 440 Hz are both consistent with the trans geometry. Only the trans isomer is present in solution. The two phosphines in several of the previously discussed complexes were also inequivalent, but in these cases, P–P coupling was not observed because coupling between cis phosphines is generally[29] less than 50 Hz, which is smaller than the typical line width of CP/MAS ^{31}P spectra. The CP/MAS ^{13}C NMR spectrum of *trans*-$(n\text{-}Bu_3P)_2PtI_2$ parallels those of the chloride and bromide analogues.

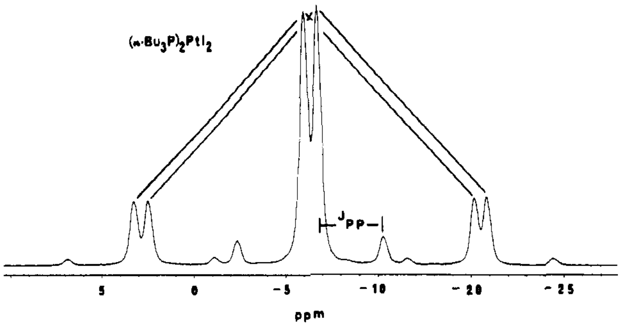

Figure 3. 121.4-MHz CP/MAS ^{31}P NMR spectrum of *trans*-$(n\text{-}Bu_3P)_2PtI_2$ (AB spin system).

Since all the compounds thus far considered except *cis*-$(Me_3P)_2PtCl_2$ display two or more CP/MAS ^{31}P resonances because of solid-state distortions, one may expect that the solid-state distortion would increase with increasing bulk of the ligands. However, in the case of *trans*-$(Cy_3P)_2PtCl_2$, only one narrow ($\Delta\nu_{1/2}$ = 64 Hz) CP/MAS ^{31}P resonance is observed, even though Cy_3P has a very large cone angle (182°). This suggests that *trans*-$(Cy_3P)_2PtCl_2$, like *cis*-$(Me_3P)_2PtCl_2$, may be conformationally mobile in the solid state.

The CP/MAS ^{31}P NMR spectrum of *trans*-$(i\text{-}Pr_3P)_2PtCl_2$ also displays only one resonance in spite of the steric bulk of i-Pr_3P (cone angle 160°). Its CP/MAS ^{13}C NMR spectrum is compared with the solution $^{13}C\{^1H\}$ spectrum in Figure 4. As one can see, the two different carbon resonances are readily distinguished in the latter but not in the former. Even resolution enhancement does not aid in the assignment of the CH and CH_3 CP/MAS resonances. Assignments can, however, be made by way of an interrupted decoupling experiment[30] (Figure 5). This interrupted decoupling experiment indicates that five of the seven resonances are due to CH_3 carbons and two are due to the CH carbons. The crystal structure[31] of *trans*-$(i\text{-}Pr_3P)_2PtCl_2$ shows that the two equivalent molecules in the unit cell are related by an inversion center and each possesses inversion symmetry. This predicts a single CP/MAS ^{31}P resonance. A single fixed conformation of the phosphine is consistent with the number of observed CP/MAS ^{13}C resonances with one pair of methyl groups being accidentally chemical shift equivalent.

A series of benzylphosphine complexes was examined to further explore steric effects. For *cis*-$(BzlPh_2P)_2PtCl_2$, *trans*-$(Bzl_2PhP)_2PtCl_2$, and $(Bzl_3P)_2PtCl_2$ the number of CP/MAS ^{31}P resonances were three, one, and three respectively. The observation of a single resonance for *trans*-$(Bzl_2PhP)_2PtCl_2$ suggests that a symmetry element (probably *i*) is present that relates the phosphines. The crystal structure[31] shows that for the cis isomer, in which intramolecular steric interactions are likely more pronounced than for the trans isomer, a C_2 axis relates the two phosphines.

Solid-state ^{13}C spectra of $(Bzl_3P)_2PtX_2$ (X = Cl, Br, I) show that, as for the palladium and platinum complexes[3] of $MePh_2P$ and Me_2PhP, the phenyl carbon resonances appear as broad envelopes between 120 and 140 ppm. Their methylene carbon resonances were also broad envelopes between 25 and 33 ppm (X = Cl), 25 and 34 ppm (X = Br), and 31 and 39 ppm (X = I). The CP/MAS ^{31}P spectrum of $(Bzl_3P)_2PtCl_2$ displays three

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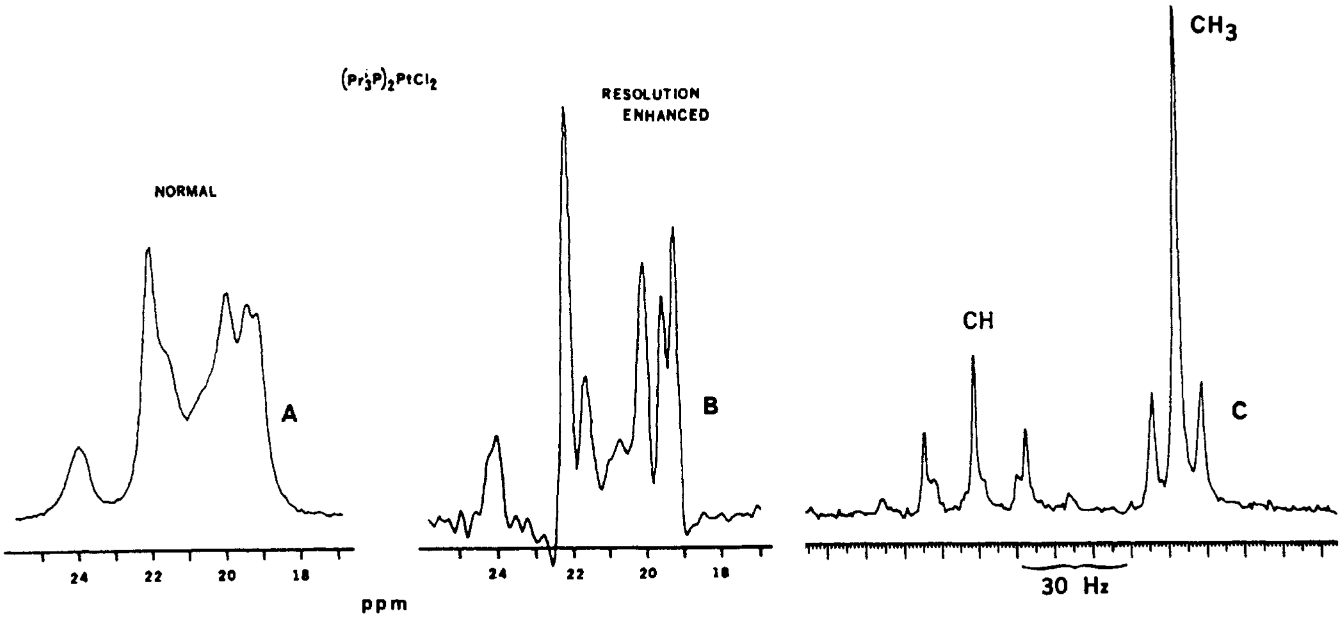

Figure 4. Comparison of (A) normal 75-MHz CP/MAS, (B) resolution-enhanced 75-MHz CP/MAS, and (C) 25-MHz $^{13}C\{^1H\}$ (in $CDCl_3$ at 300 K) NMR spectra of *trans*-$(i\text{-}Pr_3P)_2PtCl_2$.

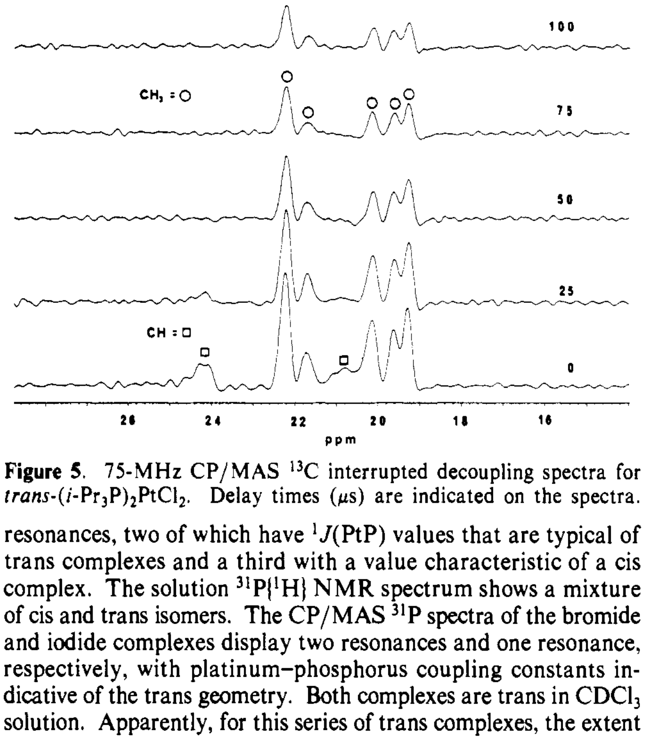

Figure 5. 75-MHz CP/MAS ^{13}C interrupted decoupling spectra for *trans*-$(i\text{-}Pr_3P)_2PtCl_2$. Delay times (μs) are indicated on the spectra.

resonances, two of which have $^1J(PtP)$ values that are typical of trans complexes and a third with a value characteristic of a cis complex. The solution $^{31}P\{^1H\}$ NMR spectrum shows a mixture of cis and trans isomers. The CP/MAS ^{31}P spectra of the bromide and iodide complexes display two resonances and one resonance, respectively, with platinum–phosphorus coupling constants indicative of the trans geometry. Both complexes are trans in $CDCl_3$ solution. Apparently, for this series of trans complexes, the extent of the solid-state distortion decreases with increasing halide size. This suggests that part of the distortion is induced by intermolecular packing effects.

A group of (cyanoethyl)phosphine complexes was also studied to determine the effects of halide and phenyl substitution. Of the three trans iodide complexes, only the $(NCCH_2CH_2)_3P$ complex shows two CP/MAS ^{31}P resonances, indicating that it is more distorted than the other two complexes. This is evidenced in their CP/MAS ^{13}C NMR spectra as well. Six resonances were observed for the CH_2 carbons of *trans*-$[(NCCH_2CH_2)_3P]_2PtI_2$, suggesting that there are no symmetry elements within this molecule in the solid state. The CP/MAS ^{13}C NMR spectrum of *trans*-$[(NCCH_2CH_2)Ph_2P]_2PtI_2$ displays two CH_2 resonances at 31.0 and 15.4 ppm. The upfield resonance corresponds to the CH_2 group attached to the CN moiety. The observation of one phosphorus and only two methylene resonances shows that for this complex there is very little solid-state distortion. For *trans*-$[(NCCH_2CH_2)_2PhP]_2PtI_2$ three CH_2 resonances and one ^{31}P resonance were observed. Therefore, its solid-state structure possesses a symmetry element that relates the two phosphorus atoms but not the CH_2 carbons.

The CP/MAS ^{31}P NMR spectra of *trans*-$[(NCCH_2CH_2)_3P]_2PtX_2$ (X = Cl, Br, I) display one, one, and two resonances, respectively. Their CP/MAS ^{13}C NMR spectra display five CH_2 and three CN resonances (X = Cl), one broad CH_2 resonance and one broad CN envelope (X = Br), and six CH_2 and two CN resonances (X = I). Their CP/MAS NMR data suggest that for this series of complexes the amount of solid-state distortion increases as the size of the halide increases. Thus, with flexible alkyl chains as in *n*-Pr_3P, *n*-Bu_3P, and $(NCCH_2CH_2)_3P$, hindered rotation about the M–P bond leads to conformationally rigid complexes and distortions in the solid state.

The CP/MAS ^{31}P NMR spectra of the $[(NCCH_2CH_2)_2PhP]_2PtX_2$ complexes differ markedly from each other. In solution the chloride and bromide are cis and the iodide trans. The CP/MAS ^{31}P NMR spectra of the iodide and chloride complexes display one and two resonances, respectively, with $^1J(PtP)$ values that parallel those observed in solution. The CP/MAS ^{31}P NMR spectrum of the bromide is quite complex, containing at least eight resonances over a 12 ppm range, all with $^1J(PtP)$ indicative of the cis geometry. In their CP/MAS ^{13}C spectra, only the methylene carbon resonances can be assigned with certainty as the cyano carbon and phenyl resonances overlap. The CP/MAS data for these three complexes indicate that solid-state distortions are slight for the trans iodide and greater for the cis chloride and bromide complexes with the bromide complex possibly existing as a polymorphic mixture in the solid state.

The CP/MAS ^{31}P NMR spectra of the *cis*-$(Ph_2VyP)_2PtX_2$ complexes (X = Cl, Br, I) are all quite different from one another. One (X = Br), three (X = Cl) and four (X = I) ^{31}P resonances were observed, and on the basis of the magnitudes of $^1J(PtP)$, all three complexes are cis in the solid state. It should be noted that the line width of the single ^{31}P resonance observed for the bromide complex was quite broad ($\Delta\nu_{1/2}$ = 430 Hz) compared to the resonances observed for the analogous chloride and iodide complexes ($\Delta\nu_{1/2}$ = 100–130 Hz). This suggests that the bromide complex may be distorted in the solid state, but low-energy librations cause line broadening, obscuring the expectedly small chemical shift differences. The presence of narrower multiple resonances for the chloride and iodide complexes suggests that these two complexes are conformationally more rigid.

The CP/MAS ^{31}P NMR spectrum of $(PhVy_2P)_2PtI_2$ shows six resonances with $^1J(PtP)$ characteristic of the cis geometry. In solution, this complex exists as a temperature- and solvent-dependent mixture of cis and trans isomers,[16] yet it crystallizes as

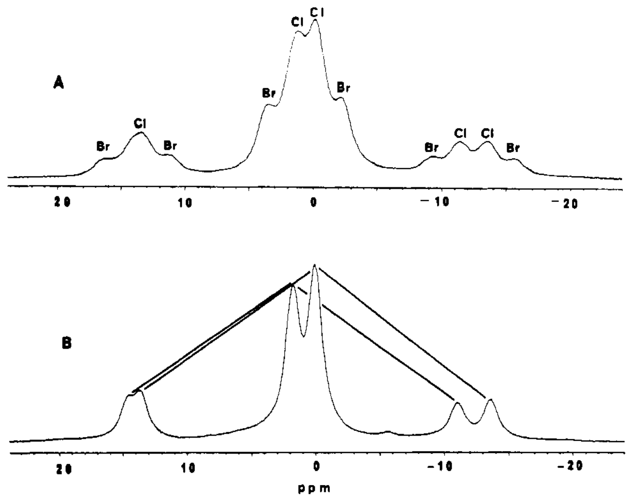

Figure 6. 121.4-MHz CP/MAS ^{31}P NMR spectra of (A) a solid-state mixture of *cis*-$(TMP)_2PtX_2$ (X = Cl, Br) and (B) *cis*-$(TMP)_2PtCl_2$.

the cis isomer. The CP/MAS ^{31}P NMR spectrum of the chloride analogue displays only two resonances, suggesting less molecular distortion and rigidity than for the iodide complex. The crystal structure[16] of *cis*-$(PhVy_2P)_2PtCl_2$ shows that neither a mirror plane nor a C_2 axis relates the two phenyldivinylphosphine ligands, consistent with the observation of two ^{31}P resonances.

The CP/MAS NMR data obtained for *cis*-$(DMPP)_2PtI_2$ suggest that a pseudo mirror plane exists, relating the two phosphorus nuclei but not the phosphole planes. Its resolution-enhanced CP/MAS ^{13}C NMR spectrum displays five methyl resonances that span a 3.1 ppm range. In addition to these methyl resonances, a group of five resonances between 150 and 157 ppm may be assigned to C_β on the basis of the chemical shifts of these carbon resonances in solution.[15] The CP/MAS ^{31}P NMR spectrum of the chloride analogue contains two resonances consistent with its crystal structure[16] in which there is no symmetry element relating the two DMPP ligands.

The CP/MAS ^{31}P NMR spectrum for $(TMP)_2PtBr_2$ (Figure 6) was initially difficult to interpret. The central lines of this spectrum appeared to be an AB multiplet, but the magnitudes of $^1J(PtP)$ indicated a cis geometry. Its ^{13}C NMR spectrum did not aid in the assignment. These spectra became readily interpretable when the CP/MAS ^{31}P (Figure 6) and ^{13}C NMR spectra for *cis*-$(TMP)_2PtCl_2$ were obtained. As one can see, the CP/MAS ^{31}P NMR spectrum of the chloride complex displays two resonances that closely match the center two resonances (except for small environmentally induced chemical shift differences) for the bromide complex. Apparently, the putative $(TMP)_2PtBr_2$ sample was a mixture[15] of the *cis*-$(TMP)_2PtCl_2$ and *cis*-$(TMP)_2PtBr_2$ complexes. The dominant species present in solution is the mixed-halide species *cis*-$(TMP)_2PtBrCl$, which is in equilibrium with *cis*-$(TMP)_2PtCl_2$ and *cis*-$(TMP)_2PtBr_2$.[33] It is of interest in this regard that in solution the mixed-halide species, which was formed by incomplete[15] metathesis of the *cis*-$(TMP)_2PtCl_2$ complex with NaBr, is thermodynamically more stable than the two symmetric species. But in the solid state, only *cis*-$(TMP)_2PtCl_2$ and *cis*-$(TMP)_2PtBr_2$ are present. We have previously observed similar behavior[34,35] for $(R_3P)(R'_3P)PdCl_2$ complexes.

All CP/MAS ^{13}C resonances may be assigned for *cis*-$(TMP)_2PtCl_2$ by comparison with its solution $^{13}C\{^1H\}$ NMR data.[15] The two most downfield resonances correspond to the β-carbons of the phosphole ring. The α-carbons give rise to three resonances around 124 ppm, and the methyl carbons show four resonances between 13 and 21 ppm. The CP/MAS data suggest that there is no symmetry in this molecule in the solid state.

The CP/MAS ^{31}P chemical shift differences observed for the *cis*-$(R_3P)_2PtX_2$ complexes generally increase with increasing size of the coordinated ligands. This suggests that intramolecular steric effects lead to the solid-state distortions for the cis isomers. When these intramolecular steric interactions reach a threshold, the trans isomer becomes thermodynamically more stable than the cis isomer. For the *trans*-$(R_3P)_2PtX_2$ complexes, the solid-state distortions are generally more pronounced for the smaller of the coordinated ligands. This suggest that closely approaching neighboring molecules by way of intermolecular crystal packing effects induce the solid-state distortions for the trans isomers.

Phosphorus chemical shifts are extremely dependent upon environment, with significant solvent and temperature effects commonplace.[36,37] For the 31 compounds investigated herein, we find that the chemical shifts in the two states are linearly related [$\delta(^{31}P_{CP/MAS}) = 1.02\delta(^{31}P_{CDCl_3}) + 4.48$; (correlation coefficient $r^2 = 0.91$)]. Hence, the CP/MAS chemical shifts are about 4.5 ppm downfield of those observed in solution.

These $(R_3P)_2PtX_2$ compounds are frequently distorted in the solid state though they possess time-averaged regular square-planar geometries in solution. The magnitude of $^1J(PtP)$ depends upon the structure of the compound. We find that $^1J(PtP)_{CP/MAS} = 0.98\,^1J(PtP)_{CDCl_3} + 42$ ($r^2 = 0.96$). Within the uncertainty of the data, the environment has essentially no effect on the magnitude of $^1J(PtP)$.

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Registry No. *cis*-$(Me_3P)_2PtCl_2$, 15630-86-1; *cis*-$(Et_3P)_2PtCl_2$, 15692-07-6; *trans*-$(n\text{-}Pr_3P)_2PtCl_2$, 59967-54-3; *trans*-$(i\text{-}Pr_3P)_2PtCl_2$, 15977-22-7; *cis*-$(n\text{-}Bu_3P)_2PtCl_2$, 15390-92-8; *trans*-$(n\text{-}Bu_3P)_2PtBr_2$, 15391-02-3; *trans*-$(n\text{-}Bu_3P)_2PtI_2$, 15390-89-3; *trans*-$(Cy_3P)_2PtCl_2$, 60158-99-8; *cis*-$(Ph_3P)_2PtCl_2$, 15604-36-1; *cis*-$(DBP)_2PtCl_2$, 124511-92-8; *cis*-$(BzlPh_2P)_2PtCl_2$, 61586-06-9; *trans*-$(Bzl_2PhP)_2PtCl_2$, 63848-36-2; $(Bzl_3P)_2PtCl_2$, 50701-20-7; *trans*-$(Bzl_3P)_2PtBr_2$, 122109-34-6; *trans*-$(Bzl_3P)_2PtI_2$, 109131-35-3; *cis*-$(PhVy_2P)_2PtCl_2$, 102628-77-3; *cis*-$(PhVy_2P)_2PtI_2$, 102628-78-4; *cis*-$(Ph_2VyP)_2PtCl_2$, 114030-80-7; *cis*-$(Ph_2VyP)_2PtBr_2$, 118207-85-5; *cis*-$(Ph_2VyP)_2PtI_2$, 118207-86-6; *cis*-$(DMPP)_2PtCl_2$, 81011-54-3; *cis*-$(DMPP)_2PtI_2$, 81011-63-4; *cis*-$(TMP)_2PtCl_2$, 81011-50-9; *cis*-$(TMP)_2PtBr_2$, 81011-55-4; *trans*-$((CE)Ph_2P)_2PtI_2$, 101166-38-5; *cis*-$((CE)_2PhP)_2PtCl_2$, 101166-33-0; *cis*-$((CE)_2PhP)_2PtBr_2$, 101166-34-1; *trans*-$((CE)_2PhP)_2PtI_2$, 101166-35-2; *trans*-$((CE)_3P)_2PtCl_2$, 20699-88-1; *trans*-$((CE)_3P)_2PtBr_2$, 101166-31-8; *trans*-$((CE)_3P)_2PtI_2$, 101166-32-9; *cis*-$(TMP)_2PtBrCl$, 81011-64-5.

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