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Solid-State Distortions of Nominally Square-Planar Palladium and Platinum $(R_3P)_2MX_2$ Complexes As Determined by a Combination of $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR Spectroscopy

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Phosphorus-31 and carbon-13 NMR spectra have been obtained for a series of 20 $(R_3P)_2MX_2$ complexes (R_3P = $MePh_2P$ and Me_2PhP; M = Pd, Pt; X = Cl, Br, I, CN, N_3) in the solid state by cross-polarization and magic-angle-spinning (CP/MAS) techniques. Comparison of these data with spectral data obtained at 300 K in $CDCl_3$ solutions was made in order to investigate the influence of local symmetry on ^{31}P and ^{13}C chemical shifts in the solid state. It was found that most of these compounds, which have regular square-planar geometries in solution, are distorted in the solid state. The solid-state distortions are evidenced by additional ^{31}P and ^{13}C resonances in the CP/MAS spectra as compared to the solution spectra. The nature and degree of these distortions are discussed.

Introduction

For years chemists have used NMR spectral measurements on compounds in isotropic solutions together with infrared and other spectral measurements on solid samples of the same materials to predict solid-state structures. This has been done with the full realization that the structures in solution and in the solid state may not be and often are not the same. With the advent of high-resolution solid-state NMR techniques,[2] a direct probe of solid-state structures is now available. In a recent report[3] of the cross-polarization maggic-angle-spinning (CP/MAS) ^{31}P NMR spectra of six $(R_3P)_2MX_2$ complexes, we have shown that the solution and solid-state NMR data for these complexes are quite different. In general, the CP/MAS ^{31}P NMR spectra displayed more resonances than were observed in solution due to solid-state distortions of the nominally square-planar geometry. In solution these distortions are averaged out by low-energy molecular motions. Because the CP/MAS techniques has tremendous potential for the structural determination of noncrystalline solids such as organic and inorganic polymers,[2] polymer-supported transition-metal complexes,[4] and biological materials,[2] we have commenced studies to obtain CP/MAS ^{13}C and ^{31}P NMR parameters for simple crystalline molecular solids to provide a data base for future work. In this paper we present the results for a series of 20 nominally square-planar $(R_3P)_2MX_2$ complexes, where R_3P = $MePh_2P$ and Me_2PhP, M = Pd and Pt, and X = Cl, Br, I, CN, and N_3. These compounds were chosen for several reasons. First, d^8 complexes of metals with large *Dq* values such as Pd and Pt have a large crystal field stabilization energy in the square-planar environment. Hence, solid-state distortions might be expected to be moderately high-energy processes. Second, these are exceedingly well-studied species in solution, and they are prototypical square-planar complexes. Third, due to the geometry dependence of ^1J(PtP), the isomeric structure (cis or trans) may be readily ascertained for the platinum complexes. Fourth, the methyl phosphines give rise to simple ^{13}C NMR spectra that are easily and unambiguously assigned. Fifth, the platinum complexes are robust, and as a consequence, their solution and solid-state geometries should be the same. In contrast, the palladium complexes are labile and exist as temperature- and solvent-dependent equilibrium mixtures of the cis and trans isomers in solution.[5] As a result, their solution and solid-state structures may not be the same.

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.

Table I. Solid- and Solution-State ^{31}P NMR Data for $(MePh_2P)_2MX_2$ Complexes

		$\delta(^{31}P^a)$ $(^1J_{Pt-P})^b$	
M	X	CPMAS	$CDCl_3{}^c$
Pd	Cl	26.3, 28.9, 17.2	18.0, 6.9
Pd	Br	8.8, 6.2	5.9, 4.2
Pd	I	−1.1	−5.7
Pd	CN	8.1, 5.7 ($^2J_{PP}$ = 420 Hz)	6.8
Pd	N_3	27.0, 24.8	16.0, 7.3
Pt[d]	Cl	10.2 (3828), 7.7 (3682)	−1.7 (3623)
Pt	Br	8.6 (3633)	−2.1 (3572)
Pt	I	6.4 (3614), 3.5 (3573), −1.3 (2422)	−4.8 (3423), −7.4 (2395)
Pt	CN	2.7 (2246)	*e*
Pt	N_3	6.1 (3710), 2.6 (3750)	−3.6 (3440)

[a] In ppm, relative to Ph_3P = −6.0. [b] In hertz. [c] At 300 K. [d] See ref 25. [e] Ligand exchange occurs in solution.

The solution $^{31}P\{^1H\}$ NMR spectra were recorded at 40.26 MHz on a JEOL FX-100 spectrometer in the FT mode. Solution $^{13}C\{^1H\}$ NMR spectra were recorded at 25 or 75 MHz on JEOL FX-100 or General Electric GN-300 spectrometers respectively. Carbon chemical shifts are relative to internal Me_4Si, while phosphorus chemical shifts were referenced to Ph_3P in $CDCl_3$ (δ = −6 ppm) and converted to 85% H_3PO_4 with a positive value being downfield of the respective reference. Cross-polarization magic-angle-spinning (CP/MAS) $^{31}P\{^1H\}$ NMR spectra were obtained on a Chemagnetics CMC-300 medium-bore (70-mm) spectrometer operating at 7.05 T (^{31}P at 121 MHz) and using either a 20- or 40-kHz sweep width, a recycle delay time of 3 s, and a proton-decoupling field of 10 G. The CP/MAS $^{13}C\{^1H\}$ NMR spectra were obtained on a Chemagnetics CMC 200 medium-bore (70-mm) spectrometer operating at 4.7 T (^{13}C at 50 MHz) and using a 20-kHz sweep width, a recycle time of 7 s, and a proton-decoupling field of 10 G. Between 200 and 300 mg of compound was spun at 3–4 kHz in Delrin or Kel-F rotors for ^{31}P measurements and at 4–7.5 kHz in alumina rotors for ^{13}C measurements. Carbon chemical shifts were referenced to an external sample of polydimethylsilane (δ = 0 ppm) while phosphorus chemical shifts were referenced to an external sample of Ph_3P (δ = −6 ppm). The uncertainties in chemical shifts and coupling constants are estimated to be ±0.5 ppm and ±20 Hz, respectively, for the CP/MAS measurements.

Infrared spectra in the 4000–400-cm^{-1} region were obtained on a Perkin-Elmer 599 infrared spectrophotometer as Nujol mulls between KBr windows and in the 400–50-cm^{-1} region on a Perkin-Elmer 1800 FT infrared spectrophotometer as polyethylene pellets.

(B) Synthesis. Dimethylphenylphosphine and methyldiphenylphosphine were synthesized by standard Grignard techniques.[6] All $(R_3P)_2MCl_2$ complexes were prepared by reacting 2 equiv of the phosphine with 1 equiv of the appropriate $(PhCN)_2MCl_2$ complex in CH_2Cl_2 under an N_2 atmosphere as previously reported.[7] The bromide, iodide,

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Table II. Solid- and Solution-State ^{13}C NMR Data in the Methyl Region for $(MePh_2P)_2MX_2$ Complexes

		CPMAS	CDCl$_3$				
M	X	$\delta(^{13}C)^a$	geometry	$\delta(^{13}C)^a$	multiplicity	$J_{PC}{}^c$	$^2J_{PP}{}^c$
Pd[d]	Cl	22.7	cis	17.7	doublet	37.1*	
		15.9	trans	12.0	triplet	33.2*	
		11.6					
Pd	Br	16.0	trans	15.2	triplet	34.2*	
		13.5	cis	13.5	triplet	32.2*	
Pd	I	20.7	trans	21.5	triplet	35.1*	
Pd	CN	19.9	trans	17.2	singlet		
		16.0					
Pd	N_3	19.3	cis	14.2	triplet	37.1*	
		11.1	trans	10.9	triplet	30.3*	
Pt	Cl	20.3	cis	16.9	5 line	47.2	14.9
		11.4				−0.2	
Pt	Br	21.9	cis	18.5	5 line	45.3	14.7
		11.6				1.6	
Pt	I	27.3	cis	20.7	5 line	59.0, −10.4	31.6
		19.0	trans	19.3	triplet	42.0*	
Pt	CN[e]	17.6					
Pt	N_3	19.2	cis	14.4	5 line	40.7	27.0
		11.2				2.2	

[a] In ppm, relative to DDS or TMS at 0 ppm, at 300 K. [b] In hertz where $J_{PC}{}^* = |{}^nJ_{PC} + {}^{n+2}J_{PC}|$. [c] In hertz. [d] See ref 21. [e] Ligand exchange occurs in solution.

Table III. Solid- and Solution-State ^{31}P NMR Data for $(Me_2PhP)_2MX_2$ Complexes

		$\delta(^{31}P)^a\ (^1J_{Pt-P})^b$	
M	X	CPMAS	CDCl$_3{}^c$
Pd	Cl	16.1, 4.8	5.0, −6.0
Pd	Br	−7.7, −10.2	−7.6, −10.1
Pd	I	−19.5	−20.4
Pd	CN	−1.6, −6.7 ($^2J_{PP}$ = 418 Hz)	−5.8
Pd	N_3	11.8, 10.3	3.8, −3.8
Pt	Cl	−1590 (3415), −16.0 (3677)	−16.0 (3547)
Pt	Br	−14.5 (3638), −15.8 (3251)	−16.0 (3500)
Pt	I	−16.3 (3129), −25.2 (2094)	−18.1 (3364), −23.3 (2316)
Pt	CN	−14.7 (2009)	−13.8 (2190)
Pt	N_3	−12.5 (3400)	−16.9 (3370)

[a] In ppm, relative to Ph_3P = −6.0. [b] In hertz. [c] At 300 K.

cyanide, and azide complexes were prepared by metathesis of the chloride complexes in a $CH_2Cl_2/CH_3OH/H_2O$ solvent mixture for 1–7 days for the palladium and platinum complexes, respectively. Except for the cyanide complexes, a 4:1 molar ratio of NaX to chloride complex was employed. For the cyanide complexes a 2:1 molar ratio of NaCN to chloride complex was used. The physical properties of all complexes agreed with the literature data.[5,8-14] The CP/MAS and solution $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data are given in Tables I–IV.

Results and Discussion

I. Solution Spectra. The solution geometry of the $(R_3P)_2MX_2$ complexes can be easily deduced from a combination of $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectra of $(R_3P)_2PtX_2$ complexes display singlets for either the cis or the trans isomer with platinum satellites due to the presence of ^{195}Pt (33.8%, $I = {}^1/_2$). The magnitude of $^1J(PtP)$ is indicative of the geometry.[11,15,16] For cis isomers, $^1J(PtP)$ is typically greater than 3000 Hz and for the trans isomers $^1J(PtP)$ is usually less than 2500 Hz. The $^{31}P\{^1H\}$ NMR spectra of $(R_3P)_2PdX_2$ complexes usually show two resonances (one for each isomer) due to the existence of a temperature- and solvent-dependent cis–trans equilibrium in solution,[5] with the resonance for the cis isomer lying downfield of that for the trans isomer. Often, particularly for the azide complexes, the resonance for the cis isomer is broader than that for the trans isomer. For both the $(R_3P)_2PtX_2$ and $(R_3P)_2PdX_2$ complexes, 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.[17] This is because the ^{13}C forms part of a second-order AXX′ (A = ^{13}C; X, X′ = ^{31}P) spin system.[17] The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data in Tables I–IV were used to make the structural assignments given in Table V.

II. CP/MAS Spectra. A. Platinum Complexes. The isomeric structures of the platinum complexes were deduced from the magnitudes of $^1J(PtP)$ (Tables I and III). Because platinum complexes are inert, one anticipates that their solution and solid-state structures would be similar, and the conclusions in Table V bear this out. Complexes that are only cis or trans in solution are also only cis or trans in the solid state. Similarly, complexes that exist as cis–trans isomeric mixtures in solution are also cis–trans isomeric mixtures in the solid state. Most of the complexes are distorted in the solid state, and considering the number of ^{13}C methyl resonances together with the number of phosphorus resonances, some conclusions regarding the nature of these distortions may be made.

Three platinum complexes [viz. $(MePh_2P)_2PtI_2$, $(Me_2PhP)_2PtI_2$, and $(MePh_2P)_2Pt(CN)_2$] all with the trans geometry, display little or no distortion. The CP/MAS ^{31}P and ^{13}C NMR spectra of the two iodide complexes each contain only one phosphorus and one methyl carbon resonance. Hence, these two complexes possess at least C_{2v} symmetry in the solid state. The ^{31}P NMR spectrum of the cyanide complex also exhibits only one resonance, but the methyl resonance in the ^{13}C NMR spectrum is broad, which could be due to an unresolved overlap of two methyl resonances. It should be noted that the two iodide complexes exist as mixtures with their corresponding cis isomers and that $(MePh_2P)_2PtI_2$ is the only complex for which more phosphorus than methyl carbon resonances were observed. For all other complexes, the number of methyl carbon resonances was equal to or greater than the number of phosphorus resonances.

For four of the platinum complexes, *cis*-$(MePh_2P)_2PtBr_2$, *cis*-$(Me_2PhP)_2PtI_2$, *trans*-$(Me_2PhP)_2Pt(CN)_2$, and *cis*-

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Table IV. Solid- and Solution-State ^{13}C NMR Data in the Methyl Region for $(Me_2PhP)_2MX_2$ Complexes

		CPMAS	CDCl$_3$				
M	X	$\delta(^{13}C)^a$	geometry	$\delta(^{13}C)^a$	multiplicity	$J_{PC}{}^b$	$J_{PP}{}^c$
Pd^d	Cl	27.1	cis	15.75	doublet	37.4*	
		20.0	trans	11.66	triplet	32.2*	
		14.3					
Pd	Br	16.5	cis	13.02	triplet	32.2*	
		13.0	trans	14.50	triplet	33.2*	
Pd	I	28.3	trans	20.46	triplet	35.2	
		20.0					
Pd	CN	24.8	trans	15.90	triplet	27.4*	
		22.9					
		18.6					
		16.5					
Pd	N$_3$	21.0	cis	13.41	5-line	33.25, 1.91	37.4
		18.4	trans	10.99	triplet	30.7*	
		13.0					
Pt	Cl	23.6	cis	15.12	5-line	43.9	19.3
		21.2				1.0	
		16.5					
Pt	Br	24.8	cis	16.78	5-line	44.8	14.1
		20.0				0.2	
Pt	I	30.6	cis	18.40	triplet	37.1*	
		26.2	trans	18.52	triplet	41.0*	
		17.7					
Pt	CN	18.3	trans	15.47	triplet	41.0*	
		14.7					
Pt	N$_3$	20.0	cis	13.49	triplet	42.0*	
		16.5					
		11.8					

[a] In ppm, relative to poly(dimethylsilane) or TMS at 0 ppm, at 300 K. [b] In hertz where $J_{PC}{}^* = |{}^nJ_{PC} + {}^{n+2}J_{P'C}|$. [c] In hertz. [d] See ref 21.

Table V. Structural Conclusions for $(R_3P)_2MX_2$ Complexes

R$_3$P	M	X	CDCl$_3$ soln (300 K)	solid
MePh$_2$P	Pt	Cl	cis	cis, no symmetry planes
		Br	cis	cis, T_d distortion
		I	63% cis; 37% trans	cis, T_d distortion trans, C_{2v} symmetry
		CN	trans	trans, some distortion
		N$_3$	cis	cis, no symmetry planes
	Pd	Cl	34% cis; 66% trans	cis, T_d distortion trans, C_{2v} symmetry
		Br	30% cis; 70% trans	cis, C_{2v} symmetry trans, C_{2v} symmetry
		I	trans	trans, C_{2v} symmetry
		CN	trans	trans, no symmetry
		N$_3$	64% cis; 36% trans	cis, no symmetry
Me$_2$PhP	Pt	Cl	cis	cis, no symmetry
		Br	cis	cis, C_s symmetry
		I	43% cis; 57% trans	cis, C_s symmetry trans, C_{2v} symmetry
		CN	trans	trans, C_s symmetry
		N$_3$	cis	cis, C_s symmetry
	Pd	Cl	86% cis; 14% trans	cis, C_s symmetry trans, C_{2v} symmetry
		Br	15% cis; 85% trans	cis, C_{2v} symmetry trans, C_{2v} symmetry
		I	trans	trans, C_s symmetry
		CN	trans	trans, no symmetry
		N$_3$	88% cis; 12% trans	cis, no symmetry

$(Me_2PhP)_2Pt(N_3)_2$, one ^{31}P resonance and two or more ^{13}C methyl resonances are observed. This indicates that, within the resolution of the experiment, the phosphorus atoms in these complexes are related by a symmetry element but no symmetry element relates the methyl groups. The ^{13}C NMR spectrum of *cis*-$(Me_2PhP)_2Pt(N_3)_2$ displays three methyl resonances with a 1:1:2 intensity ratio, indicating that two of the four methyl groups are chemical shift equivalent while the other two are chemical shift inequivalent. Similarly, for *cis*-$(Me_2PhP)_2PtCl_2$, three methyl resonances with a 1:1:2 intensity ratio are observed, but for this complex, two ^{31}P resonances are observed. Thus, this complex possesses no symmetry, and for it two of the methyl groups are accidentally chemical shift equivalent.

The spectra of the remaining platinum complexes exhibit two phosphorus and two methyl carbon resonances. The complexes of $MePh_2P$ have no symmetry elements that relate either the phosphorus atoms or the methyl groups. The complex *cis*-$(MePh_2P)_2PtCl_2$ crystallizes[18] in two allotropic forms, one symmetric and one asymmetric. In the asymmetric form the Pt–P bond lengths are significantly different (2.295 (16), 2.2480 (17) Å), while in the symmetric form they are only slightly different (2.246 (1), 2.2446 (6) Å). The sample that we investigated is then probably the asymmetric form. The observation of only two methyl carbon resonances for *cis*-$(Me_2PhP)_2PtBr_2$ together with two phosphorus resonances suggests that the two methyl groups on an individual phosphine are equivalent. For the platinum complexes, the amount of the solid-state distortion from an ideal square-planar geometry seems to increase as the steric bulk of the ligands increases. The $MePh_2P$ complexes are more distorted than the analogues Me_2PhP complexes, and for both phosphines, the distortion seems to increase in the order $Cl < Br < I < N_3$. These conclusions follow from a general increase in the ^{31}P chemical shift differences within a molecule in this same order. We believe that the solid-state distortions may be due to intramolecular steric interactions for the cis isomers and to intermolecular crystal packing effects for the trans isomers.

B. Palladium Complexes. Since the palladium complexes are labile and exist as temperature- and solvent-dependent cis–trans isomeric mixtures in solution, their structures in the solid state and in solution may not be the same. Moreover, the solid-state structure may depend upon how the substance was isolated. As an example, single crystals of $(Me_2PhP)_2PdCl_2$ isolated from CH_2Cl_2/CH_3OH solution are cis,[19] but isolation from hot benzene by addition of 100–120 °C petroleum ether produces the trans isomer as a solid.[20]

The solid-state structures of the palladium complexes were deduced by comparing the data obtained for the palladium and platinum complexes. The palladium azide complexes exist as

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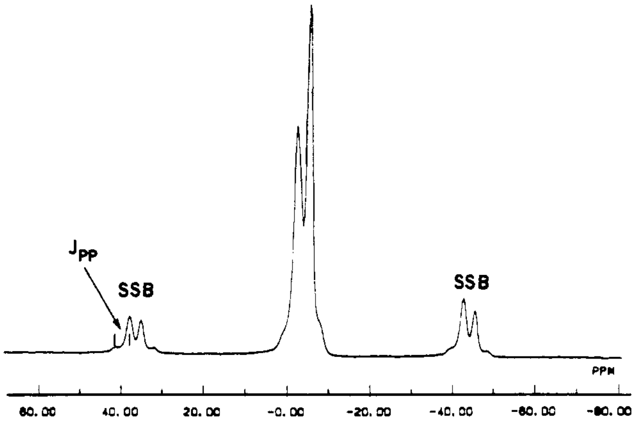

Figure 1. 121.19-MHz CP/MAS ^{31}P NMR spectrum of *trans*-$(Me_2PhP)_2Pd(CN)_2$. SSB = spinning side bands.

isomeric mixtures in solution with the cis isomer, the predominate species in $CDCl_3$ at 300 K, but only the cis isomer is present in the solid state. This conclusion was made on the basis of ^{31}P NMR data and the fact that the isomer populations in solution are time dependent.[10] The amount of the trans isomer in solution is initially quite small and increases with time, and several minutes are required for equilibrium to be established. The chemical shift difference of the two ^{31}P resonances observed for *cis*- and *trans*-$(MePh_2P)_2Pd(N_3)_2$ in solution is 8.7 ppm and for *cis*- and *trans*-$(Me_2PhP)_2Pd(N_3)_2$ is 7.6 ppm. If both the cis and trans isomers of these two compounds were present in the solid state, we would expect to see comparable chemical shift differences in the ^{31}P resonances. However, the observed ^{31}P chemical shift differences are 2.2 and 1.5 ppm respectively. The differences are similar to those observed for the analogous platinum complexes (3.5 and 0 ppm, respectively). For the platinum complexes, the magnitude of $^1J(PtP)$ allows assignment of the cis geometry in both cases. Since the energy barrier to tetrahedral distortion for palladium complexes should be less than that for platinum complexes, one might expect the palladium complexes to be more distorted, leading to a greater difference in ^{31}P chemical shifts. The ^{13}C CP/MAS spectrum of $(MePh_2P)_2Pd(N_3)_2$ shows two methyl resonances with a 1:1 intensity ratio and that of $(Me_2PhP)_2Pd(N_3)_2$ shows three methyl resonances in a 1:1:2 intensity ratio. These results, together with the ^{31}P NMR data, are consistent with the presence of distorted cis isomers in the solid state for both complexes.

The ^{31}P CP/MAS spectrum of $(MePh_2P)_2PdCl_2$ shows a major resonance at 17.2 ppm and two minor equal intensity resonances at 26.3 and 28.9 ppm. The previously reported[3] spectrum of a different sample showed only the resonance at 17.2 ppm. For the present sample, three ^{13}C methyl resonances were observed in its ^{13}C CP/MAS spectrum, and in a previous report,[21] two methyl resonances were observed. We conclude that the two samples investigated previously were trans in the solid state and that the present sample is a cis–trans mixture with the trans isomer being the dominant species.

The crystal structure[19] of *cis*-$(Me_2PhP)_2PdCl_2$ shows that this molecule is tetrahedrally distorted with a dihedral angle between the P_2Pd and Cl_2Pd planes of 171.3 ± 0.1°. Only average Pd–P bond lengths (2.260 ± 0.002 Å) were reported. This structure is consistent with the observation of two CP/MAS ^{31}P resonances and three CP/MAS ^{13}C methyl resonances in a 1:1:2 ratio as discussed previously for the analogous *cis*-$(Me_2PhP)_2Pd(N_3)_2$ complex.

trans-$(Me_2PhP)_2PdI_2$ crystallizes[23] as a red isomer with different PdP bond lengths (2.638 (3), 2.619 (3) Å) and a yellow isomer with equivalent PdP bond lengths (2.592 (3) Å). Both isomers are trans. Our CP/MAS data on the yellow isomer shows one ^{31}P and two ^{13}C (methyl) resonances, consistent with the crystal structure.

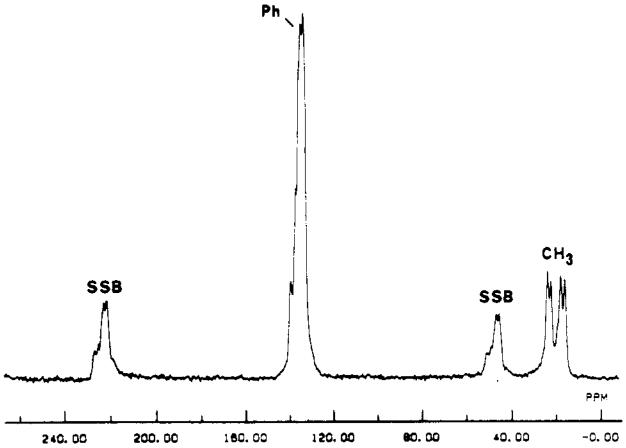

Figure 2. 50.18-MHz CP/MAS ^{13}C NMR spectrum of *trans*-$(Me_2PhP)_2Pd(CN)_2$. SSB = spinning side bands.

Table VI. Infrared Data for $(R_3P)_2MX_2$ Complexes

R_3P	M	X	ν_{MX}, ν_{CN}, or ν_{N_3}[a]
$MePh_2P$	Pd	Cl	310, 286
	Pd	Br	286, 212, 200
	Pd	I	194
	Pd	CN	2130
	Pd	N_3	2025, 2000
Me_2PhP	Pd	Cl	302, 282
	Pd	Br	282, 202, 196
	Pd	I	204, 190
	Pd	CN	2136
	Pd	N_3	2040, 2012
$MePh_2P$	Pt	Cl	316, 292
	Pt	Br	204, 184
	Pt	I	148
	Pt	CN	2134
	Pt	N_3	2066, 2043
Me_2PhP	Pt	Cl	308, 288
	Pt	Br	196, 184
	Pt	I	166
	Pt	CN	2131
	Pt	N_3	2068, 2044

[a] In cm^{-1}.

The ^{31}P CP/MAS spectra of $(Me_2PhP)_2Pd(CN)_2$ (Figure 1) and $(MePh_2P)_2Pd(CN)_2$ both show AB quartets. The magnitudes of $^2J(PP)$ (418 and 420 Hz, respectively) are indicative of the trans geometry.[10,17,22] We have not observed $^2J(PP)$ for any of the cis complexes because it is smaller[22] (generally less than 50 Hz) than the line width (≈130 Hz). The ^{13}C CP/MAS spectrum of $(Me_2PhP)_2Pd(CN)_2$ (Figure 2) shows four narrow methyl resonances of equal intensity while that of $(MePh_2P)_2Pd(CN)_2$ shows two narrow equal-intensity methyl resonances. Thus, both of these complexes are distorted trans isomers in the solid state. Similar considerations were used to assign the solid-state structures (Table V) of the remaining complexes. A reviewer has suggested that the inequivalence of the ^{31}P and ^{13}C nuclei could arise from different rotamers, that is different substituent configurations about phosphorus co-crystallized or present as independent molecules in asymmetric units. While this is a possible explanation for some of our observations, for each of the complexes in this study where the crystal structures have been obtained, only one molecule type is present in the unit cells, rendering this explanation unlikely. We will show however, in a subsequent paper[24] on $(R_3P)_2PtX_2$ complexes that this phenomenon does occur.

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III. Infrared Spectroscopy. Infrared spectra were obtained (Table VI) in order to further assess the value of the CP/MAS technique for solid-state structure determination. The observation of single ν_{CN} vibrations is consistent with the conclusion based upon NMR data that all the cyanide complexes are trans in the solid state. The infrared spectra of all the azide complexes showed two bands corresponding to the symmetric and asymmetric ν_{N_3} stretching modes expected for cis isomers. However, the infrared data for the halide complexes are not as informative. Three of the iodides show single ν_{MI} vibrations in the observed region whereas the NMR data show the presence of both the cis and trans isomer in the solid state for two of these complexes. Similarly, for all the chlorides, only two ν_{MCl} vibrations could be identified, and for the palladium complexes, three are expected. The expected number of ν_{MBr} vibrations is observed in each case. As a consequence, the infrared data are sometimes ambiguous.

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A New Yttrium Sesquichloride Nitride, β-Y_2Cl_3N, That Is Isostructural with the Binary Yttrium Sesquichloride

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Reactions of YCl_3, YN, and Y metal in sealed Nb containers over a range of temperatures and compositions afford β-Y_2Cl_3N, whereas only α-Y_2Cl_3N in the (α-)Gd_2Cl_3N structure is obtained in the absence of metal. β-Gd_2Cl_3N is synthesized similarly. The β-Y_2Cl_3N (β-Gd_2Cl_3N) gives a powder pattern that is indistinguishable from that of the infinite cluster chain phase Y_2Cl_3 (Gd_2Cl_3) except for small increases in lattice parameters corresponding to a 2% (1%) increase in cell volume. (α-Y_2Cl_3N: a = 12.761 (1) Å, b = 6.676 (2) Å, c = 6.1000 (7) Å (*Pbcn*). β-Y_2Cl_3N: a = 15.248 (2) Å, b = 3.8520 (4) Å, c = 10.157 (2) Å, β = 118.41° ($C2/m$, Z = 4). β-Gd_2Cl_3N: α = 15.290 (5) Å, b = 3.912 (1) Å, c = 10.209 (3) Å, β = 117.79 (3)°.) A single-crystal X-ray study of β-Y_2Cl_3N (R = 3.9%, R_w = 4.8%) demonstrates that the nitrogen atoms are positioned in tetrahedral metal sites above and below the shared metal edges of the infinite chain of octahedra found in Y_2Cl_3. The need for metal in the syntheses, the black color of the fibrous crystals, and the refined occupancy of nitrogen (81 (2)%) in the yttrium phase all suggest a small nitrogen deficiency in β-$(Y,Gd)_2Cl_3N$. The close correspondence of distances in the binary vs the ternary (β) sesquichlorides, particularly the small (0.024 Å) increase in the shared Y–Y edge, is discussed.

Introduction

The first window on a new chemistry of metal-rich halides was the discovery of gadolinium sesquichloride[2] and the demonstration that its remarkable structure contained infinite chains constructed of metal octahedra, as could be generated by condensing Gd_6Cl_8-type clusters through sharing of trans edges.[3] Since then, several isostructural sesquihalides have been described (Y_2Cl_3, Gd_2Br_3, Tb_2Cl_3),[4,5] and Gd_2Cl_3 has been shown to be a semiconductor.[6] All of these phases appear to be true binary compounds free of essential interstitial atoms.

More recently, a much larger array of ternary halides has been discovered that require an interstitial atom within each metal octahedron for stability. The employment of carbon with the gadolinium halides provides a variety of such compounds[7] but with compositions and structure types other than that of Gd_2Cl_3. For reduced yttrium chloride systems, only the layered Y_2Cl_2C[8] and Y_3Cl_3C[9] are known to contain carbon atoms within condensed Y_6 octahedra.

In contrast, the utilization of a nitrogen source in syntheses generally does not yield compounds comparable to those observed with carbon. Related to the above sesquihalide structure are the cluster chains found in Sc_4Cl_6N[10] and Sc_5Cl_8N[11] in which nitrogen-centered Sc_6Cl_{12}-type clusters also share trans metal edges. On the other hand, scandium products are usually different from those formed by any other rare-earth element, and analogues are not known elsewhere. Another nitride structure type is found in Gd_2Cl_3N[12] in which nitrogen-containing gadolinium *tetrahedra* are linked via shared opposite edges to again form infinite chains. But the result is now a gadolinium(III) compound with empty gadolinium d bands[13] and therefore negligible metal–metal bonding. More recently, the nitrogen-poorer analogue Gd_3Cl_6N has been synthesized and shown to contain isolated pairs of Gd_4N tetrahedra that share a common edge.[14]

Our exploration of the role of nitrogen in reduced yttrium chlorides has yielded not only the known Y_2Cl_3 and α-Y_2Cl_3N isostructural with the above (α-)Gd_2Cl_3N but also a good yield of a new phase with a powder pattern in which both the line positions and their intensities correspond very well to those of a slightly expanded Y_2Cl_3 structure. X-ray studies reported here show that this β-Y_2Cl_3N is isostructural with the binary phase Y_2Cl_3 save for introduction of nitrogen atoms in tetrahedral metal sites, not in the cluster-centered octahedral positions. Questions regarding the presence of metal–metal bonding and the compound's valence character, already discussed for (α-)Gd_2Cl_3N, arise again for the new β-Y_2Cl_3N.

Experimental Section

Synthesis. High-purity, sublimed yttrium metal (Johnson Matthey, 99.997%) was cut into small pieces (~3 × 3 mm) prior to use. Yttrium trichloride was prepared from the reaction of Y_2O_3 (Ames Laboratory) with NH_4Cl.[15] The resulting $(NH_4)_3YCl_6$ was decomposed to YCl_3 at 400 °C under vacuum, and the product was sublimed twice at 870 °C and ~10^{-5} Torr in a tantalum tube within a silica jacket. YN was synthesized[16] by first hydriding the metal in a molybdenum boat at 560

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