complex arises largely from the difference in the activation enthalpies for the two reactions. This enhanced lability of octahedral Co(II) complexes with respect to those of Ni(II) has been noted for many other systems[2,4,10,13,43–45] and has been discussed in terms of crystal field theory.[45,46] The ambiguities in the crystal field interpretation have been considered elsewhere,[2,44] and a more critical evaluation of the factors affecting relative solvent substitution rates does not seem warranted until the appropriate data become available for a wider variety of cations, particularly those of the nontransition elements!

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A Phosphorus-31 Nuclear Magnetic Resonance Study of Tertiary Phosphine Complexes of Platinum(II)[1]

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The phosphorus-31 nmr spectra of eleven *cis* and seven *trans* compounds of the type $(R_n(C_6H_5)_{3-n}P)_2PtCl_2$, where R = alkyl and $n = 1, 2,$ or 3, show that the platinum-195 to phosphorus-31 coupling constant is always larger for the *cis* compound than for the corresponding *trans* compound and that the phosphorus chemical shift of the *cis* compound is upfield from that of the corresponding *trans* compound. The formation of the trisphosphine complex by addition of excess tertiary phosphine to the monomer has been demonstrated by conductivity and ^{31}P nmr measurements and confirmed by isolation of the compounds $[(CH_3(C_6H_5)_2P)_3PtCl]Cl$ and $[(C_3H_7(C_6H_5)_2P)_3PtCl]B(C_6H_5)_4$. The preparation of several new chlorine-bridged dimers is also reported.

Introduction

Pidcock, Richards, and Venanzi[2] reported in a brief note a few years ago that the $^{195}Pt-^{31}P$ coupling constant in *cis*-dichlorobis(tributylphosphine)platinum(II) is significantly larger than the coupling constant in the *trans* isomer. They also reported the coupling constants in various other phosphorus–platinum compounds, although no other *cis–trans* pairs were reported and chemical shifts were not cited.

The difference in coupling constants was ascribed to the increased π bonding between phosphorus and platinum in the *cis* case, in which the platinum can use d_{xz} and d_{yz} orbitals (in addition to in-plane π bonding by the d_{xy} orbital), as opposed to the *trans* case, in which platinum can use only the d_{xz} orbital (again, in addition to in-plane π bonding) with the x axis defined as the P–Pt–P direction. If this argument is correct, one would expect the phosphorus atoms in the *cis* compound to have a higher electron density than those in the *trans* isomer because of increased back donation by the electrons of the platinum d orbitals.

Results and Discussion

We have prepared pure *cis* isomers for eleven different tertiary phosphines and seven of the corresponding *trans* isomers as described in the Experimental Section. The phosphorus-31 nmr data are shown in Table I. For convenience, the coordination chemical shifts are listed in column 4. The coordination chemical shift is defined as the chemical shift (relative to any reference in general, but for this case relative to 85% H_3PO_4) of phosphorus in the complex compound minus the chemical shift (relative to the same reference) of phosphorus in the free ligand. This concept has been used before in several papers[3–6] on phosphorus coordination compounds.

The results in Table I substantiate the original observation[2] that the *cis*-tributylphosphine compound has a significantly larger coupling constant than the *trans* compound and show that this is true for all of the seven *cis–trans* pairs measured. In addition, the chemical shift of the *cis* isomer for a particular tertiary phosphine is always upfield from that of the *trans* isomer. This agrees with the simple shielding ideas outlined above, *i.e.*, a good σ donor on coordination produces a large downfield coordination chemical shift and increased metal to ligand π bonding produces an upfield coordination chemical shift. These ideas were discussed by Meriwether and Leto[3] in the first report on ^{31}P nmr of phosphorus coordination compounds. The results of ^{31}P studies of *trans*-$(R_3P)_3RhCl_3$ compounds[4] are opposite to those expected from the simple

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TABLE I

PHOSPHORUS-31 NMR DATA OF TERTIARY PHOSPHINE–PLATINUM(II) COMPOUNDS

Compound	Chem shift, ppm, *vs.* H_3PO_4 Ligand	Complex	Coordn chem shift, ppm	Coupling const for $^{195}Pt-^{31}P$, cps
cis-$((CH_3)_2C_6H_5P)_2PtCl_2$	46.9	15.2	−31.7	3549
cis-$(CH_3(C_6H_5)_2P)_2PtCl_2$	28.1	1.2	−26.9	3616
cis-$((C_2H_5)_3P)_2PtCl_2$	20.4	−9.6	−30.0	3520
trans-$((C_2H_5)_3P)_2PtCl_2$	20.4	−12.3	−32.7	2400
cis-$((C_2H_5)_2C_6H_5P)_2PtCl_2$	17.1	−3.3	−20.4	3530
trans-$((C_2H_5)_2C_6H_5P)_2PtCl_2$	17.1	−11.3	−28.4	2482
cis-$(C_2H_5(C_6H_5)_2P)_2PtCl_2$	12.5	−9.8	−22.3	3640
cis-$((C_3H_7)_3P)_2PtCl_2$	33.0	0.2	−32.8	3530
trans-$((C_3H_7)_3P)_2PtCl_2$	33.0	−3.8	−36.8	2385
cis-$((C_3H_7)_2C_6H_5P)_2PtCl_2$	27.7	2.7	−25.0	3561
trans-$((C_3H_7)_2C_6H_5P)_2PtCl_2$	27.7	−6.3	−34.0	2463
cis-$(C_3H_7(C_6H_5)_2P)_2PtCl_2$	17.6	−6.9	−24.5	3639
cis-$((C_4H_9)_3P)_2PtCl_2$	32.3	−1.2	−33.5	3500
trans-$((C_4H_9)_3P)_2PtCl_2$	32.3	−5.1	−37.4	2392
cis-$((C_4H_9)_2C_6H_5P)_2PtCl_2$	26.2	2.3	−23.9	3551
trans-$((C_4H_9)_2C_6H_5P)_2PtCl_2$	26.2	−6.5	−32.7	2462
cis-$(C_4H_9(C_6H_5)_2P)_2PtCl_2$	17.1	−7.0	−24.1	3641
trans-$(C_4H_9(C_6H_5)_2P)_2PtCl_2$	17.1	−12.0	−29.1	2531

TABLE II

^{31}P COORDINATION CHEMICAL SHIFTS AND $^{195}Pt-^{31}P$ COUPLING CONSTANTS IN $(R_n(C_6H_5)_{3-n}P)_2PtCl_2$

		cis Compounds		
		$(C_2H_5)_3P$	$(C_3H_7)_3P$	$(C_4H_9)_3P$
Δ		−30.0	−32.8	−33.5
J		3520	3530	3500
	$(CH_3)_2C_6H_5P$	$(C_2H_5)_2C_6H_5P$	$(C_3H_7)_2C_6H_5P$	$(C_4H_9)_2C_6H_5P$
Δ	−31.7	−20.4	−25.0	−23.9
J	3549	3530	3561	3551
	$CH_3(C_6H_5)_2P$	$C_2H_5(C_6H_5)_2P$	$C_3H_7(C_6H_5)_2P$	$C_4H_9(C_6H_5)_2P$
Δ	−26.9	−22.3	−24.5	−24.1
J	3616	3640	3639	3641
		trans Compounds		
		$(C_2H_5)_3P$	$(C_3H_7)_3P$	$(C_4H_9)_3P$
Δ		−32.7	−36.8	−37.4
J		2400	2385	2392
		$(C_2H_5)_2C_6H_5P$	$(C_3H_7)_2C_6H_5P$	$(C_4H_9)_2C_6H_5P$
Δ		−28.4	−34.0	−32.7
J		2482	2463	2462
				$C_4H_9(C_6H_5)_2P$
Δ				−29.1
J				2531

shielding concepts, however, and it seems that the explanations must be more complicated.

The coordination chemical shifts and $^{195}Pt-^{31}P$ coupling constants are listed again in Table II. Several points should be noted. The coordination chemical shifts of triethyl-, tripropyl-, and tributylphosphine decrease in that order in both the *cis* and *trans* series corresponding to an increase in σ-donor ability in the same order. The mixed alkylphenylphosphine complexes have this same trend from ethyl to propyl but the coordination chemical shifts of the butyl compounds are about the same as those of propyl or slightly higher, which indicates the expected close similarity of these compounds. Of greater significance is the fact that the coupling constant increases in every case in both the *cis* and *trans* series in going from trialkyl- to dialkylphenyl- and then to the alkyldiphenylphosphines. This corresponds to the increasing π acceptor character of the phosphines as the number of phenyls on the phosphorus increases. The coupling constant in *cis*-dichlorobis(triphenylphosphine)platinum(II) is of interest here, but the compound was not sufficiently soluble to detect the ^{31}P nmr signal.

Since separation of many of the pure isomers is tedious, the crude products of the direct reaction of potassium tetrachloroplatinate(II) and tertiary phosphine were extracted into dichloromethane and the extracts were concentrated in order to measure the ^{31}P nmr spectra directly. In general, there were two main peaks with their corresponding pairs of satellites due to the ^{195}Pt (natural abundance = 33.7%, spin = 1/2) splitting. A sample spectrum is shown in Figure 1. Because of the difference in chemical shifts of the *cis* and *trans* compounds and of the large difference in the coupling constant, the satellites can easily be unequivocally assigned as belonging to either the *cis* or *trans* isomer. This technique can therefore be used readily for equilibrium studies between *cis* and *trans* isomers.

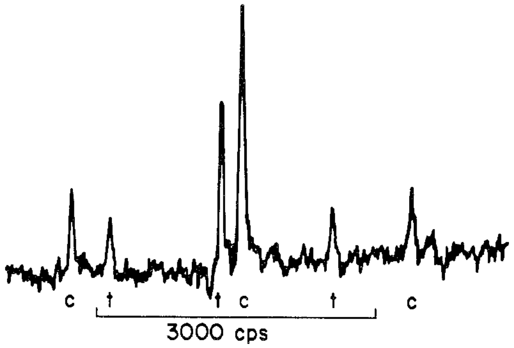

Figure 1.—The ^{31}P nmr spectrum of a solution containing *cis*- and *trans*-$(C_2H_5(C_6H_5)_2P)_2PtCl_2$.

On several occasions when measurements were made on both the crude reaction mixtures and on solutions of pure isolated isomers, it was found that the coupling constants were noticeably different (mostly smaller by about 50–200 cps) in both isomers of the mixture and that the chemical shifts were also somewhat different. At first it was thought that these differences might be due to ligand exchange between the isomers or between a given isomer and excess uncoordinated phosphine, but it is now clear that mixtures contained the tris tertiary phosphine complex, $[(R_3P)_3PtCl]^+$. This was proved as explained below. Pure *trans*-dichlorobis(phenyldipropylphosphine)platinum (δ = −6.3 ppm, *J* = 2460 cps) was placed in dichloromethane solution and the ^{31}P nmr was measured. Three drops of phenyldipropylphosphine was added and the spectrum was remeasured to give a small peak (*trans*, δ = −5.7 ppm, *J* not measurable) and a large peak (*cis*, δ = 3.2 ppm, *J* = 3550 cps; pure *cis* has δ = 2.7 ppm and *J* = 3560 cps). The small amount of excess phosphine causes equilibration with the *cis* isomer being the predominant species. The differences in chemical shifts and coupling constants are thought to be due to experimental error, but they could also be due to ligand exchange. Addition of 0.3 ml of phosphine yielded a spectrum with two main peaks, one "*trans*" (relative intensity = 2, $\delta = -6.0$ ppm, $J = 2326$ cps), and the other "*cis*" (relative intensity = 1, $\delta = 5.6$ ppm, $J = 3500$ cps). The "*trans*" peak corresponds to the mutually *trans* phosphines in the tris-phosphine complex and the "*cis*" peak corresponds to the phosphine which is *trans* to the chlorine in the complex and therefore behaves like the phosphines in the *cis* isomer. In addition, the spectrum showed a peak due to the excess phosphine and a small new peak at $\delta = -8.6$ ppm. This new peak may be due to the tetrakis complex, *i.e.*, $((C_3H_7)_2C_6H_5P)_4Pt^{2+}$, but no additional evidence on this point has been obtained.

A similar experiment was performed beginning with pure *cis*-dichlorobis(dibutylphenylphosphine)platinum ($\delta = 2.6$ ppm, $J = 3540$ cps). Addition of 3 drops of the phosphine gave equilibration of *cis* ($\delta = 2.5$ ppm, $J = 3540$ cps) and *trans* ($\delta = -6.1$ ppm, J not measurable; pure *trans* has $\delta = -6.5$ ppm and $J = 2460$ cps). Addition of excess (0.6 ml) phosphine gave the tris-substituted product with its corresponding spectrum with three peaks, one "*trans*" (relative intensity = 2, $\delta = -6.2$ ppm, $J = 2305$ cps), one "*cis*" (relative intensity = 1, $\delta = 5.7$ ppm, $J = 3490$), and one uncomplexed peak.

A conductivity study was carried out with pure *cis*-dichlorobis(diphenylpropylphosphine) platinum and diphenylpropylphosphine in dichloromethane. The conductivity increases steadily to about a 1:1 molar ratio and then slowly increases (Figure 2). In a blank experiment, diphenylpropylphosphine in dichloromethane conducted only slightly. The results would yield a horizontal line from the origin if plotted on the same scale as used in Figure 2. Ionic species are known for nitrogen[7] and arsenic[8] compounds of platinum, but none of the tris(phosphine)platinum variety has previously been isolated. Chlorotris(diphenylpropylphosphine)-platinum(II) tetraphenylborate was prepared by metathetical reaction from the solution used for conductivity measurements. Chlorotris(methyldiphenylphosphine)platinum(II) chloride was prepared as described in the Experimental Section.

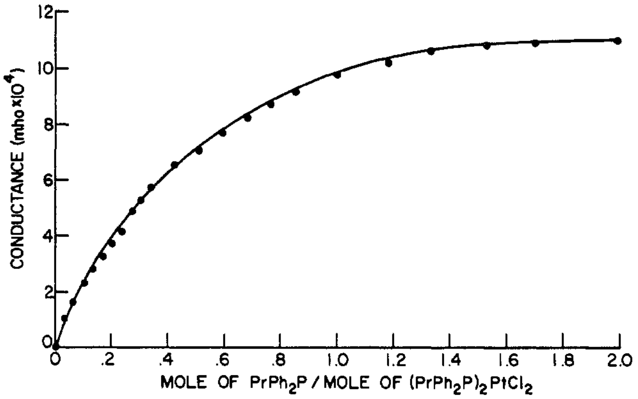

Figure 2.—The conductivity of solutions of $C_3H_7(C_6H_5)_2P$ and *cis*-$(C_3H_7(C_6H_5)_2P)_2PtCl_2$ in CH_2Cl_2.

Experimental Section

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Dr. Franz Kasler, University of Maryland.

Phosphorus-31 nmr spectra were measured with a Varian Associates DP-60 spectrometer at 24.3 Mcps on concentrated dichloromethane solutions in 15-mm tubes. The reference (85% H_3PO_4) was sealed in a 3-mm tube and placed concentrically into the large sample tube through a serum stopper. The peaks were calibrated by side-band techniques. Generally, each spectrum was recorded six times: three times with the field sweeping in each direction, *i.e.*, increase and decrease. The six values were then averaged. The main peaks are thought to be accurate to ±0.4 ppm and the coupling constants, to about ±20 cps. Proton nmr spectra were measured with a Varian Associates A-60A spectrometer.

All tertiary phosphines except commercial $(C_4H_9)_3P$ were prepared by the Grignard method with PCl_3, $C_6H_5PCl_2$, or $(C_6H_5)_2PCl$.

Melting points and analytical data for the coordination compounds are summarized in Table III. The monomers were prepared by the methods of Jensen[9] and by those of Chatt[10,11] and Wilkins.[11] The dimers were prepared by the method of Goodfellow and Venanzi.[12] All preparations involving tertiary phosphines were carried out in a nitrogen atmosphere.

***cis*-Dichlorobis(tributylphosphine)platinum(II).**—A solution of K_2PtCl_4 (4.1 g, 0.010 mole) in 50 ml of N_2-purged H_2O was stirred vigorously with $(C_4H_9)_3P$ (5.0 ml, 4.1 g, 0.020 mole) for 3 hr. The resulting salmon-colored precipitate was removed by filtration, washed with water, and dried for 12 hr at 60° (3 torr). The solid was extracted with six 10-ml portions of cold petroleum ether (bp 30–60°). The insoluble residue was dissolved by dropwise addition of 95% C_2H_5OH to the residue in 50 ml of boiling petroleum ether. The solution was cooled to 0° and the resultng white crystals were collected by filtration and recrystallized in the same manner to yield 1.8 g of the white *cis* isomer. *cis*-Dichlorobis(dimethylphenylphosphine)platinum(II) was also prepared in this manner, but the crude dried product was recrystallized twice from *i*-C_3H_7OH. Proton nmr: $J_{PtPCH} = 35.1$ cps (lit.,[13] 35 cps); $J_{PCH} = 11.3$ cps (lit.,[13] 11 cps).

***trans*-Dichlorobis(tributylphosphine)platinum(II).**—The petroleum ether extracts of the previous preparation were evaporated under reduced pressure to give a yellow solid which was twice recrystallized from C_2H_5OH to give 1.1 g of the yellow *trans* isomer.

***cis*- and *trans*-Dichlorobis(tripropylphosphine)platinum(II).**—A solution of K_2PtCl_4 (4.1 g, 0.010 mole) in 50 ml of H_2O was stirred with $(C_3H_7)_3P$ (3.2 g, 0.020 mole) for 3 hr. The red-brown precipitate of $[((C_3H_7)_3P)_4Pt]PtCl_4$ was not isolated, but the mixture was converted to the *cis* and *trans* mixture by heating on the steam bath for 1 hr. Drying, extraction, and purification were the same as for the $(C_4H_9)_3P$ complexes. Also prepared in this manner were *cis*- and *trans*-dichlorobis(triethylphosphine)platinum(II).

Di-μ-chloro-dichlorobis(dimethylphenylphosphine)diplatinum(II).—An intimate mixture of *cis*-$((CH_3)_2C_6H_5P)_2PtCl_2$ (3.0 g, 5.5 mmoles), $PtCl_2$ (1.5 g, 5.7 mmoles), and naphthalene (10 g) was heated slowly to about 200° in an oil bath and held at that temperature for 5 min. The heat was then removed and the mixture was allowed to cool slowly to room temperature. The naphthal-

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TABLE III

MELTING POINTS AND ANALYTICAL DATA

		Analytical data, %					
		Calcd			Found		
Compound	Mp, °C	C	H	Cl	C	H	Cl
cis-$((CH_3)_2C_6H_5P)_2PtCl_2$	200–201 (199–200[13])	35.44	4.08		35.58	4.20	
cis-$(CH_3(C_6H_5)_2P)_2PtCl_2$	253–268	46.85	3.93	10.64	46.77	4.06	10.75
cis-$((C_2H_5)_3P)_2PtCl_2$	192–194 (191–192[9])						
trans-$((C_2H_5)_3P)_2PtCl_2$	142–144 (142–143[9])						
cis-$((C_2H_5)_2C_6H_5P)_2PtCl_2$	205–206 (202–203[9])	40.14	5.05	11.85	40.40	5.23	11.81
trans-$((C_2H_5)_2C_6H_5P)_2PtCl_2$	123–124 (122.5–123.5[9])						
cis-$(C_2H_5(C_6H_5)_2P)_2PtCl_2$	232–236	48.42	4.35	10.21	48.57	4.30	10.11
cis-$((C_3H_7)_3P)_2PtCl_2$	149–150 (149–150,[9] 150–151[10])						
trans-$((C_3H_7)_3P)_2PtCl_2$	82–83 (82–82.5,[9] 85–86[10])						
cis-$((C_3H_7)_2C_6H_5P)_2PtCl_2$	208–209	44.04	5.85	10.83	43.99	5.78	10.65
trans-$((C_3H_7)_2C_6H_5P)_2PtCl_2$	111–112	44.04	5.85		43.92	5.74	
cis-$(C_3H_7(C_6H_5)_2P)_2PtCl_2$	207–209	49.87	4.98	9.81	49.85	5.08	9.93
cis-$((C_4H_9)_3P)_2PtCl_2$	141–143 (144[9])						
trans-$((C_4H_9)_3P)_2PtCl_2$	63–65 (65–66[9])						
cis-$((C_4H_9)_2C_6H_5P)_2PtCl_2$	139–140	47.33	6.52	9.98	47.38	6.67	10.20
trans-$((C_4H_9)_2C_6H_5P)_2PtCl_2$	65–66	47.33	6.52		47.42	6.47	
cis-$(C_4H_9(C_6H_5)_2P)_2PtCl_2$	187–189	51.26	5.10	9.45	51.07	5.04	9.26
trans-$(C_4H_9(C_6H_5)_2P)_2PtCl_2$	150–151	51.26	5.10	9.45	51.19	5.16	9.28
$((CH_3)_2C_6H_5P)_2Pt_2Cl_4$	223–232 dec (215–230[13] dec)	23.77	2.74	17.54	23.91	2.76	17.67
$(CH_3(C_6H_5)_2P)_2Pt_2Cl_4$	263–266 dec	33.49	2.81	15.21	33.53	2.97	15.25
$((C_2H_5)_2C_6H_5P)_2Pt_2Cl_4$	163–164	27.79	3.50	16.41	28.03	3.39	16.70
$((C_3H_7)_2C_6H_5P)_2Pt_2Cl_4$	199–201	31.31	4.16	15.40	31.18	4.20	15.55
$((C_4H_9)_2C_6H_5P)_2Pt_2Cl_4$	176–177	34.44	4.75		34.22	4.75	
$(C_2H_5(C_6H_5)_2P)_2Pt_2Cl_4$	236–241 dec	35.01	3.15	14.76	34.93	3.39	14.98
$(C_3H_7(C_6H_5)_2P)_2Pt_2Cl_4$	240–245 dec	36.45	3.46	14.35	36.55	3.41	14.57
$(C_4H_9(C_6H_5)_2P)_2Pt_2Cl_4$	205–220 dec	37.58	4.33	13.87	37.46	4.13	13.80
$[(CH_3(C_6H_5)_2P)_3PtCl]Cl$	215–220	54.43	4.50	8.24	54.20	4.62	8.51
$[(C_3H_7(C_6H_5)_2P)_3PtCl]B(C_6H_5)_4$[a]	85–100 dec	67.12	5.95	2.87	67.20 67.20	5.91 5.93	2.68

[a] *Anal.* Calcd: P, 7.53. Found: P, 7.48.

ene was extracted with petroleum ether and CH_2Cl_2 was added to the residue. Unreacted $PtCl_2$ was removed by filtration. The filtrate was concentrated to about 50 ml, and petroleum ether was added slowly until the solution just became cloudy. Cooling in an ice bath caused precipitation of bright yellow crystals of the chlorine-bridged dimer. Two recrystallizations by the same procedure produced 1.3 g of product. All of the dimers listed in Table III were prepared by this method. It is important to heat the reaction mixture in these preparations just slightly higher than the melting point; otherwise extensive decomposition occurs.

***cis*-Dichlorobis(methyldiphenylphosphine)platinum(II).**—The use of C_2H_5OH–H_2O as a solvent system was found to give cleaner products than when only H_2O was used as a solvent, and this method was adoped in the following preparations. A mixture of K_2PtCl_4 (4.1 g, 0.010 mole), $CH_3(C_6H_5)_2P$ (3.7 ml, 4.0 g, 0.020 mole), 50 ml of C_2H_5OH, and 30 ml of H_2O was stirred for 16 hr and filtered. The residue was washed with water, dried, and dissolved in CH_2Cl_2–CH_3OH. White crystals of the *cis* compound formed as the solution evaporated. Attempts to prepare the *trans* isomer were not successful.

Chlorotris(methyldiphenylphosphine)platinum(II) Chloride.—Excess $CH_3(C_6H_5)_2P$ added to *cis*-$(CH_3(C_6H_5)_2P)_2PtCl_2$ (2 g) caused the white crystals to become yellow. Petroleum ether (10 ml) was added to the mixture which was stirred for 30 min and filtered. The residue was washed several times with $(C_2H_5)_2O$ and dried at 40° (3 torr) for 14 hr to give $[(CH_3(C_6H_5)_2P)_3PtCl]Cl$. Phosphorus nmr: "*cis*," relative intensity = 1, δ = 5 ppm, J = 3673 cps; "*trans*," relative intensity = 2, δ = -9.4 ppm, J = 2374 cps. Attempts to recrystallize the tris product gave only the *cis* isomer.

***cis*-Dichlorobis(diethylphenylphosphine)platinum(II).**—A mixture of K_2PtCl_4 (3.0 g, 7.2 mmoles), $(C_2H_5)_2C_6H_5P$ (2.6 ml, 2.5 g, 15 mmoles), 80 ml of C_2H_5OH, and 50 ml of H_2O was stirred for 18 hr and then filtered. The filtrate was evaporated and the resulting residue was recrystallized from *i*-C_3H_7OH to give the *cis* isomer. The *cis* isomers of $(C_3H_7)_2C_6H_5P$ and $(C_4H_9)_2C_6H_5P$ were also prepared in this manner. The *cis* isomers of $C_2H_5(C_6H_5)_2P$, $C_3H_7(C_6H_5)_2P$, and $C_4H_9(C_6H_5)_2P$ were prepared in the same manner, but they were recrystallized from C_2H_5OH.

***trans*-Dichlorobis(dibutylphenylphosphine)platinum(II).**—To a sample of *cis*-$((C_4H_9)_2C_6H_5P)_2PtCl_2$ (2 g, 2.8 mmoles) suspended in 50 ml of C_6H_6 was added 0.2 ml of $(C_4H_9)_2C_6H_5P$. After equilibration had occurred excess of the chlorine-bridged dimer, $((C_4H_9)_2C_6H_5P)_2Pt_2Cl_4$ (5 g, 5.1 mmoles), was added. The solution was evaporated to dryness and the residue was extracted with $(C_2H_5)_2O$. The extracts were evaporated to give the yellow *trans* compound, which was recrystallized three times from C_2H_5OH.

***trans*-Dichlorobis(butyldiphenylphosphine)platinum(II).**—To a solution of $(C_4H_9(C_6H_5)_2P)_2Pt_2Cl_4$ (2.0 g, 2.0 mmoles) in 200 ml of boiling C_6H_6 was added $C_4H_9(C_6H_5)_2P$ (0.6 ml, 0.6 g, 2.5 mmoles). The solution was boiled for 5 min and then evaporated at reduced pressure. The solids were extracted with $(C_2H_5)_2O$, and the extracts were evaporated to give the yellow *trans* isomer, which was recrystallized twice from C_2H_5OH. Also prepared by this method were the *trans* isomers of $(C_2H_5)_2C_6H_5P$ and $(C_3H_7)_2C_6H_5P$.

Conductivity of $[(C_3H_7(C_6H_5)_2P)_3PtCl]Cl$.—The conductivity experiment was performed with an International Instrument Co. conductivity bridge, Model RC16B2, and a Jones-Bollinger cell (cell constant = 0.529 cm^{-1}) in modified pipet form. Dichloromethane was used as a solvent. It was purified by shaking with aqueous K_2CO_3, followed by drying over $CaCl_2$ and distillation. A solution (20 ml) of *cis*-$(C_3H_7(C_6H_5)_2P)_2PtCl_2$ (0.79 g, 1.1 mmoles) was titrated with a solution of $C_3H_7(C_6H_5)_2P$ (1.0 g, 4.4 mmoles) in 25 ml of CH_2Cl_2. The results are shown in Figure 2.

Chlorotris(diphenylpropylphosphine)platinum(II) Tetraphenylborate.—The solution from the conductivity experiment was poured into 100 ml of C_2H_5OH and the CH_2Cl_2 was evaporated. An excess of $NaB(C_6H_5)_4$ in C_2H_5OH (50 ml) was then added with the immediate formation of cloudiness. An oil formed after addition of 10 ml of H_2O to the cloudy solution. The solution was decanted from the oil, to which petroleum ether was added. Persistent scratching caused formation of a white powder of $[(C_3H_7(C_6H_5)_2P)_3PtCl]B(C_6H_5)_4$, which was isolated by filtration, washed with petroleum ether, and dried at 30° (3 torr) for 10 hr.

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Isohypophosphate: Kinetics of the Hydrolysis and Potentiometric and Nuclear Magnetic Resonance Studies on the Acidity and Complexing

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The kinetics of the hydrolysis of isohypophosphate was studied in strong acid, strong base, and several buffered mixtures at 25.0, 40.0, and 60.0° in 0.5 *M* sodium chloride. The reaction is catalyzed by all Brønsted acids and by nucleophiles. The detailed rate law is written in terms of the protonated forms of isohypophosphate undergoing hydrolysis. For acid catalysis each protonated form hydrolyzes faster than any of the less protonated forms. An enhancing effect of added metal ion on the rate of base-catalyzed hydrolysis was also observed. The heats of activation for the catalysis of the $H_2P_2O_6^{2-}$ anion by H_3O^+, acetic acid, glycolic acid, and water are 26.1, 18.3, 19.0, and 24.9 kcal/mole, respectively. The pK^0 values and formation constants for 1:1 complexes of Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} were determined at 25.0° in tetramethylammonium chloride and compared with the complexing properties of pyrophosphite and pyrophosphate. Nuclear magnetic resonance studies indicate that the least acidic hydrogen atom is most strongly associated with the PO_4 group. Also, evidence for the order of deprotonation of the two strongly acidic protons is given. Analysis of the ^{31}P nmr chemical shifts for the P(III) and P(V) atoms at various metal ion concentrations suggests that the anion probably acts as a bidentate ligand.

Introduction

The kinetics of hydrolysis and metal ion complexing of condensed phosphates[1-4] and pyrophosphite[5,6] have been shown to be greatly different. Condensed phosphates undergo specific acid catalysis and are not subject to attack by nucleophiles, whereas pyrophosphite is both general acid and base catalyzed. Moreover, condensed phosphates[1,4] have been shown to undergo hydrolysis more rapidly in the presence of alkali metal ions, where no effect has been observed for pyrophosphite.[5] Grant and Payne[6] have shown that the pyrophosphite ion forms weaker metal ion complexes than condensed phosphates. Isohypophosphate,[7,8] which has the formula $H_nHP_2O_6^{(3-n)-}$, contains a P–O–P linkage involving P(III) and P(V) atoms. Hence, it is of particular interest in understanding the properties of condensed phosphorus compounds since it combines the properties of the condensed phosphates and the properties of lower oxidation states.

Also, since isohypophosphate contains phosphorus atoms in the +3 and +5 oxidation states, a ^{31}P nmr study on this compound could be of great value in defining the deprotonation steps and yielding information on the structure of its complexes with metal ions.

Experimental Section

Chemicals.—Trisodium isohypophosphate was prepared and purified by the method of Blaser and Worms[9] using phosphorus trichloride and sodium hydrogen phosphate as starting materials. Also, trisodium isohypophosphate was prepared by allowing sodium pyrophosphite to react in an aqueous solution with a large excess of sodium hydrogen phosphate and purifying as before.[9] Assay of the purified material by iodine titration and ^{31}P nmr indicated over 96% of the phosphorus was in the form of isohypophosphate. Tetramethylammonium isohypophosphate was prepared by ion exchange of the sodium salt through a Dowex 50 W-X2 resin in the tetramethylammonium form. This material, after removal of most of the water by evaporation, was stored at −10° until used. All other materials were of reagent grade quality.

Kinetics Measurements.—The analytical procedure and the techniques for rate measurements for reactions run in NaCl are essentially identical with those described previously,[5] with the exception that a phosphate buffer was employed rather than the maleate buffer for quenching the reaction mixture. The same procedure was used for reactions run in tetramethylammonium chloride except that the tetramethylammonium ion was removed by ion exchange before analysis. This was necessary since tetramethylammonium ions precipitate in the presence of triiodide.

The kinetics experiments were conducted at 25, 40, and 60° in a thermostated bath controlled at these temperatures to ±0.1°.

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