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A Phosphorus-31 Magnetic Resonance Study of Tertiary Phosphine Palladium(II) Compounds[1]

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Phosphorus-31 chemical shifts are reported for thirty-one compounds of the type, cis– *and* trans–L_2PdCl_2, sym–$L_2Pd_2Cl_4$ *and* trans–$L(Am)PdCl_2$, *where L is a tertiary phosphine and Am is a nitrogen ligand. Many of the compounds are previously unreported. For a particular phosphine ligand the chemical shift of the* cis *isomer is down-field from that of the* trans *isomer. Some infrared frequencies and proton nmr results are also given.*

Introduction

We recently reported the ^{31}P chemical shifts of a series of *cis* and *trans* tertiary phosphine complexes of platinum(II) of the general formula $(R_{3-n}Ph_nP)_2$-$PtCl_2$ (where R is alkyl and n = 0,1, or 2).[3] It was suggested that the chemical shifts of the *cis* isomers were further upfield than those of the corresponding *trans* isomers because of greater metal-phosphorus pi bonding in the *cis* structure. In order to test this and to continue our investigation into the factors influencing ^{31}P chemical shifts in transition metal complexes, we have prepared a further series of complexes of the above general formula but using palladium instead of platinum as the central metal atom.

Experimental Section

Phosphorus-31 nmr spectra were measured with a Varian Associates DP60 spectrometer at 24.3 MHz on concentrated dichloromethane solutions in 15mm tubes. The reference (85% phosphoric acid) was sealed in a 3 mm tube and placed concentrically into the larger sample tube through a serum stopper. The peaks were calibrated by using side band techniques. Each spectrum was recorded six times: three times in the direction of increasing field and three times in the direction of decreasing field. The six values were then averaged.

Proton nmr spectra were measured with a Varian Associates A60A spectrometer at 60 MHz on concentrated deuterochloroform solutions.

Melting points were taken with a Mel-Temp melting point apparatus (Laboratory Devices, Cambridge, Mass.). They are reported uncorrected.

Infrared spectra in the 600-250 cm^{-1} region were recorded with an evacuated Perkin-Elmer 621 spectrophotometer. Samples were examined as Nujol mulls supported on low-density polyethylene plates. The spectrophotometer was calibrated with water vapor and peaks are accurate to 2 cm^{-1}.

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

All tertiary phosphines except commercial $(C_4H_9)_3P$ were prepared by the Grignard method with PCl_3, $(C_6H_5)PCl_2$ or $(C_6H_5)_2PCl$. The amines were commercially available and were used after one distillation or recrystallization.

Melting points and analytical data for the coordination compounds are summarized in Table I. The monomers and dimers were prepared according to the method of Mann.[4,5] The amine-phosphine complexes were prepared by the method of Chatt.[6] All preparations involving tertiary phosphines were carried out in a nitrogen atmosphere.

cis- *and* trans- *Dichlorobis(dibutylphenylphoshpine) palladium(II).* To potassium tetrachloropalladate(II) (3 g, 9.2 mmole) in 50 ml of nitrogen-purged water, dibutylphenylphosphine (4.46 ml, 1.8 mmole) was added. The reaction was stirred for three hours and then extracted with 50 ml of dichloromethane. The dichloromethane layer was evaporated with a rotating evaporator to give a light yellow solid (A). The yellow solid was extracted with 10 ml portions of petroleum ether (30-60°) until the extract was no longer colored. The petroleum ether extracts were cooled to precipitate *trans*–$((C_4H_9)_2(C_6H_5)P)_2PdCl_2$. The product was recrystallized from petroleum ether (30-60°). The residue of (A), insoluble in petroleum ether, was recrystallized from methanol and washed with petroleum ether (30-60°) to give *cis*–$((C_4H_9)_2$-$(C_6H_5)P)_2PdCl_2$.

Discussion

Complexes of the type $(PdCl_2(R_nPh_{n-3}P)_2)$ (R =

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(2) Taken in part from the Ph. D. thesis of R. L. Keiter, University of Maryland, 1967.

(3) S. O. Grim, R. L. Keiter, W. McFarlane, *Inorg. Chem.* 6, 1113 (1967).

(4) F. G. Hann and A. F. Wells, *J. Chem. Soc.* 702 (1938).

(5) F. G. Mann and D. J. Purdie, *ibid*, 873 (1936).

(6) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 2787 (1955).

Table I. Melting Points and Analytical Data.

Compound	Mp, °C	Analytical Data, % Calcd. C	Calcd. H	Calcd. Cl	Found C	Found H	Found Cl
trans—$((C_2H_5)_3P)_2PdCl_2$	138-139 (139 [a])						
trans—$((C_3H_7)_3P)_2PdCl_2$	95-96 (96 [a])						
trans—$((C_4H_9)_3P)_2PdCl_2$	65-66 (66 [a])						
cis—$((CH_3)_2(C_6H_5)P)_2PdCl_2$	192-193 (192-194 [b])	42.36	4.90		42.39	4.93	
cis—$((C_2H_5)_2(C_6H_5)P)_2PdCl_2$	139-140	47.90	5.93	13.90	47.23	6.10	14.05
trans—$((C_4H_9)_2(C_6H_5)P)_2PdCl_2$	73-73.5	54.05	7.45	11.40	53.86	7.30	11.28
cis—$((C_4H_9)_2(C_6H_5)P)_2PdCl_2$	94-95	54.05	7.45	11.40	53.84	7.20	11.30
trans—$((CH_3)(C_6H_5)_2P)_2PdCl_2$	201-203	48.49	4.28		48.77	4.55	
trans—$((C_2H_5)(C_6H_5)_2P)_2PdCl_2$	211-213	55.51	5.00		55.80	5.20	
trans—$((C_3H_7)(C_6H_5)_2P)_2PdCl_2$	219-221	56.82	5.40	11.18	56.57	5.51	11.04
trans—$((C_4H_9)(C_6H_5)_2P)_2PdCl_2$	130-131	58.04	5.78	10.71	58.20	5.76	10.69
trans—$((C_6H_5)_3P)_2PdCl_2$	250-270 (250-270 [c])						
sym—$((C_2H_5)_3P)_2Pd_2Cl_4$	232-234 (230 [d])						
sym—$((C_3H_7)_3P)_2Pd_2Cl_4$	187-189 (189 [d])						
sym—$((C_4H_9)_3P)_2Pd_2Cl_4$	144-145 (145 [d])						
sym—$((CH_3)(C_6H_5)_2P)_2Pd_2Cl_4$	d. 216-255	41.38	3.47		41.65	3.75	
sym—$((CH_3)_2(C_6H_5)P)_2Pd_2Cl_4$	d. 216-220 (215-230 [b])						
sym—$((C_2H_5)(C_6H_5)_2P)_2Pd_2Cl_4$	d. 250-254	42.94	3.86		42.83	4.10	
sym—$((C_6H_5)_3P)_2Pd_2Cl_4$	d. 250 (slowly d. [b])						
trans—$(C_3H_7NH_2)((CH_3)(C_6H_5)_2PdCl_2$	70-77	43.98	5.08		44.00	4.98	
trans—$(C_6H_{10}NH_2)((CH_3)(C_6H_5)_2P)PdCl_2$	147-147.5	47.84	5.49		47.90	5.58	
trans—$(C_2H_5)_3N)((CH_3)(C_6H_5)_2P)PdCl_2$	112-120	47.64	5.89		47.37	5.68	
trans—$(C_5H_5N)((CH_3)(C_6H_5)_2P)PdCl_2$	183-185	47.31	3.97		47.58	4.04	
trans—$(C_6H_5NH_2)((CH_3)(C_6H_5)_2PdCl_2$	183-184	48.46	4.28		48.39	4.27	
trans—$(m{-}CH_3C_6H_4NH_2)((CH_3)(C_6H_5)_2P)PdCl_2$	141-142	49.43	4.77		49.60	4.58	
trans—$(p{-}CH_3C_6H_4NH_2)((CH_3)(C_6H_5)_2P)PdCl_2$	176-177	49.43	4.77		49.79	4.64	
trans—$(C_5H_{10}NH)(CH_3)(C_6H_5)_2P)PdCl_2$	d. 156-159	46.70	5.32		46.54	5.32	
trans—$(C_2H_5)_2NH)((CH_3)(C_6H_5)_2P)PdCl_2$	158-159	45.28	5.47		45.40	5.47	

[a] F. G. Mann and D. J. Purdie, *J. Chem. Soc.*, 1549 (1937). [b] Ref. 10. [c] Ref. 5. [d] Ref. 4.

Table II. Phosphorus-31 nmr Data of Tertiary Phosphine-Palladium(II) Compounds

Compound	Chemical Shift Ligand (ppm *vs.* H_3Po_4)	Chemical Shift Complex (ppm *vs.* H_3Po_4)	Coordination Chemical Shift (ppm)
trans—$((C_6H_5)_3P)_2PdCl_2$	7.0	insoluble	—
trans—$((CH_3)_2(C_6H_5)P_2PdCl_2$	46.9	+5.0(0.3)	−41.9
cis—$((CH_3)_2(C_6H_5)P)_2PdCl_2$	46.9	−6.4(0.2)	−53.3
cis—$((CH_3)(C_6H_5)_2P)_2PdCl_2$ [a]	28.1	−19.1(0.3)	−47.2
trans—$((CH_3)(C_6H_5)_2P)_2PdCl_2$	28.1	−7.8(0.4)	−35.9
trans—$((C_2H_5)_3P)_2PdCl_2$	20.4	−17.8(0.4)	−38.2
trans—$((C_3H_7)_3P)_2PdCl_2$	33.0	−9.2(0.4)	−42.2
trans—$((C_4H_9)_3P)_2PdCl_2$	32.3	−10.0(0.4)	−42.3
cis—$((C_2H_5)_2(C_6H_5)P)_2PdCl_2$	17.1	−25.4(0.4)	−42.5
trans—$((C_2H_5)_2(C_6H_5)P)_2PdCl_2$	17.1	−16.1(0.4)	−33.2
cis—$((C_4H_9)_2(C_6H_5)P)_2PdCl_2$	26.2	−19.8(0.4)	−46.0
trans—$((C_4H_9)_2(C_6H_5)P)_2PdCl_2$	26.2	−10.9(0.4)	−37.1
cis—$((C_2H_5)(C_6H_5)_2P)_2PdCl_2$	12.5	−30.2(0.3)	−42.7
trans—$((C_2H_5)(C_6H_5)_2P)_2PdCl_2$	12.5	−19.3(0.4)	−31.8
cis—$((C_3H_7)(C_6H_5)_2P)_2PdCl_2$	17.6	−27.4(0.2)	−45.0
trans—$((C_3H_7)(C_6H_5)_2P)_2PdCl_2$	17.6	−16.3(0.4)	−33.9
cis—$((C_4H_9)(C_6H_5)_2P)_2PdCl_2$	17.1	−27.1(0.2)	−44.2
trans—$((C_4H_9)(C_6H_5)_2P)_2PdCl_2$	17.1	−16.3(0.4)	−33.4
sym—$((C_2H_5)_3P)_2Pd_2Cl_4$	20.4	−48.8(0.5)	−69.2
sym—$((C_3H_7)_3P)_2Pd_2Cl_4$	33.0	−39.7(0.3)	−72.7
sym—$((C_4H_9)_3P)_2Pd_2Cl_4$	32.2	−40.1(0.4)	−72.3
sym—$((CH_3)_2(C_6H_5)P)_2Pd_2Cl_4$	46.9	−15.4(0.2)	−62.3
sym—$((CH_3)(C_6H_5)_2P)_2Pd_2Cl_4$	28.1	insoluble	—
sym—$((C_2H_5)(C_6H_5)_2P)_2Pd_2Cl_4$	12.5	−33.8(0.2)	−46.3
sym—$((C_6H_5)_3P)_2Pd_2Cl_4$	7.0	insoluble	—

[a] J. P. Fackler, Jr., J. A. Fetchin, J. Mayhew, W. C. Seidel, T.J. Swift and M. Weeks, *J. Am. Chem. Soc.*, *91*, 1941 (1969) report a spectrum for this compound but no chemical shift.

alkyl) were prepared by the reaction of the appropriate tertiary phoshpine with potassium tetrachloropalladate(II) in aqueous solution. It is well known that compounds of this type may exist either as « *cis* » or « *trans* » isomers and although both isomers of platinum(II) complexes usually can be obtained, the more labile palladium(II) complexes have been isolated usually in only the *trans* form.

The two methods most often employed to determine the configuration of a particular isomer have been dipole moment measurements and far infrared spectroscopy. Jensen measured the dipole moments of $((C_4H_9)_3P)_2PdCl_2$, $((C_3H_7)_3P)_2PdCl_2$, and $((C_2H_5)_3P)_2PdCl_2$ and established that these isomers have a *trans* configuration.[7] In the far infrared spectra, one ν(M–Cl) is found in the spectrum of a *trans* isomer and two in the spectrum of a *cis* isomer.[8,9] More recently Shaw and Jenkins[10] have used proton nmr to distinguish between *cis* and *trans* isomers of $((CH_3)_2(C_6H_5)P)_2PdCl_2$.

In this study, we have examined complexes of triethyl-, tripropyl-, tributyl-, dimethylphenyl-, diethylphenyl-, dibutylphenyl-, methyldiphenyl-, ethyldiphenyl, propyldiphenyl-, and butyldiphenylphosphine with ^{31}P nmr and where useful, ^1H nmr. The ^{31}P chemical shifts are shown in Table II.

The ^{31}P spectrum of a bis tertiary phosphine complex of palladium(II) consists of a single observed peak because all naturally occuring isotopes of palladium have a spin other than 1/2 and phosphorus proton couplings are too small to be resolved. The triethyl-, tripropyl-, and tributylphosphine complexes gave only one ^{31}P resonance peak and in accordance with Jensen's dipole moment studies these peaks were attributed to the *trans* isomer. Addition of free ligand to solutions of these complexes produced spectra which were not altered in any way from spectra of solutions containing only pure complex, except that an additional peak appeared which was assigned to the free ligand. Furthermore, the same chemical shifts were recorded in benzene, methanol, and dichloromethane. Therefore, it appears that ligand exchange between the isomers or between a given isomer and excess uncoordinated trialkylphosphine is slow.

All of the dialkylphenyl-, and alkyldiphenylphosphine complexes isomerize spontaneously in dichloromethane solution, *i.e.*, free ligand is not needed to initiate an equilibrium between *cis* and *trans* isomers. Two ^{31}P resonance peaks, corresponding to the *cis* and *trans* isomers, *were* observed for each of these complexes. The assignment of peaks is supported by proton nmr in the case of $((CH_3)_2(C_6H_5)P)_2PdCl_2$, and by the isolation of both isomers in the case of $((C_4H_9)_2(C_6H_5)P)_2PdCl_2$. The proton nmr spectrum of $((CH_3)_2(C_6H_5)P)_2PdCl_2$ in dichloromethane consists of a triplet ($\tau = 7.85$, $^2J_{P-H} = 3.7$) and a doublet ($\tau = 8.06$, $^2J_{P-H} = 11.3$), corresponding to the *trans* and *cis* isomers respectively. Integration of the proton spectrum shows the equilibrium mixture to consist of 67% *cis* isomer. On this basis, the more intense ^{31}P resonance peak was assigned to the *cis* isomer, and the less intense signal was assigned to the *trans* isomer. The *cis* resonance peak was downfield from that of the *trans*. The isolation of the *cis* and *trans*–$((C_4H_9)_2(C_6H_5)P)_2PdCl_2$ is described in the experimental section. The only other previously isolated *cis-trans* pair of tertiary phosphine complexes of palladium is $(CH_3)_3P)_2PdCl_2$.[11] Each of the pure $((C_4H_9)_2(C_6H_5)P)_2PdCl_2$ isomers isomerizes rapidly in dichloromethane to give a mixture of both isomers, with ^{31}P resonance signals at −10.9 and −19.8 ppm. However, only one resonance peak is observed for each isomer in methanol. The product which is soluble in petroleum ether is assumed to be *trans* and gives a ^{31}P resonance peak at −11.0 ppm in methanol. The product which is insoluble in petroleum ether (assigned *cis*) gives a peak at −20.8 ppm in methanol. Thus, the *cis* isomer again was observed to be downfield from that of the *trans*. On the basis of these experiments it is quite likely that the *cis* isomer in all the *cis-trans* mixtures gives rise to the downfield peak. The ratios of peak heights for *cis* and *trans* isomers are recorded in Table III. With one exception the percentage of *cis* isomer decreases as bulkier groups are substituted or phosphorus, which suggests the importance of steric factors. Unfortunately, integration of the peaks was not possible and these ratios are only approximate.

Table III. Peak Height Ratios of *Cis* to *Trans* Complexes of Palladium(II)

Compound	Ratio
$((C_2H_5)_3P)_2PdCl_2$	0/100
$((C_3H_7)_3P)_2PdCl_2$	0/100
$((C_4H_9)_3P)_2PdCl_2$	0/100
$((CH_3)_2(C_6H_5)P)_2PdCl_2$	67/33
$((C_2H_5)_2(C_6H_5)P)_2PdCl_2$	44/56
$((C_4H_9)_2(C_6H_5)P)_2PdCl_2$	40/60
$((CH_3)(C_6H_5)_2P)_2PdCl_2$	55/45
$((C_2H_5)(C_6H_5)_2P)_2PdCl_2$	25/75
$((C_3H_7)(C_6H_5)_2P)_2PdCl_2$	39/61
$((C_4H_9)(C_6H_5)_2P)_2PdCl_2$	20/80

It is of interest that the ^{31}P chemical shifts of the dialkylphenyl- and alkyldiphenylphosphine complexes vary with the solvent. For example, *trans*–$((C_4H_9)_2(C_6H_5)P)_2PdCl_2$ produced a resonance signal at −10.1 ppm in methanol and at −10.9 ppm in dichloromethane. In addition, *trans*–$((C_2H_5)_2(C_6H_5)P)_2PdCl_2$ produced a resonance signal at −16.1 ppm in dichloromethane and −14.9 ppm in benzene. This phenomenon was not investigated further.

The dialkylphenyl- and alkyldiphenylphosphine complexes undergo exchange in the presence of free ligand. This is illustrated as follows: pure $((CH_3)_2(C_6H_5)P)_2PdCl_2$ equilibrates in dichloromethane to form a mixture of *cis* and *trans* isomers (δ, *cis*, −6.4 ppm; δ, *trans*, 5.0 ppm). When free phosphine ligand (0.5 ml) was added, the solution became deep red and a spectrum resulted which consisted of one resonance peak (δ, 2.7 ppm). The magnitude of the shift varied with concentration of free ligand. The formation of a red color was also noted when free ligand was added to the other dialkylphenyl- and alkyldiphenylphosphine complexes. The colored species may be a five coordinate complex which is often observed with palladium(II)[12] or a trisionic product such as

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(10) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (A) 1771 (1966).

(11) P. J. D. Park and P. J. Hendra, *Spectochim. Acta*, *25A*, 909 (1969).

(12) G. Booth, « Advances In Inorganic and Radiochemistry », Vol. 6, H. J. Emeleus and A. G. Sharpe, Eds., Academic Press, New York, New York, 1964, p. 37.

Table IV. Infrared Data for Tertiary Phosphine Complexes of Palladium(II) (600-250 cm^{-1})

Compound	ν [a]					ν(Pd—Cl) [a]	
trans—$(C_6H_5)_3P)_2PdCl_2$	522(58)	509(54)	501(52)	456(20)	442(15)	357(26)	
	422(4)						
cis—$((CH_3)_2(C_6H_5)P)_2PdCl_2$	490(50)	450(31)	427(10)	351(27)	264(33)	306(38)	284(46)
trans—$(C_4H_9)_3P)_2PdCl_2$	449(10)	389(4)				354(15)	
trans—$(C_3H_7)_3P)_2PdCl_2$	444(5)	421(7)				352(25)	
trans—$(C_2H_5)_3P)_2PdCl_2$ [b]	433(8)	413(10)	376(7)	330(12)		355(37)	
trans—$(C_4H_9)_2(C_6H_5)P)_2PdCl_2$	497(56)	457(40)	421(23)	332(37)		357(40)	
cis—$(C_4H_9)_2(C_6H_5)P)_2PdCl_2$	494(41)	473(35)	465(33)	429(22)	417(33)	299(59)	283(51)
	396(29)	334(4)	279(sh)	266(sh)			
cis—$((C_2H_5)_2(C_6H_5)P)_2PdCl_2$	510(60)	498(69)	468(51)	455(58)	407(sh)	304(84)	288(66)
	397(33)	349(36)	253(55)	247(sh)			
trans—$(C_4H_9)(C_6H_5)_2P)_2PdCl_2$	490(41)	466(40)	448(22)	447(3)	426	350(30)	
trans—$(C_3H_7)(C_6H_5)_2P)_2PdCl_2$	516(73)	490(69)	472(64)	421(36)	403 (29)	352(64)	
$((C_2H_5)(C_6H_5)_2P)_2PdCl_2$	510(65)	488(63)	477(63)	423(38)	358(53)		
	337(56)						
$((CH_3)(C_6H_5)_2P)_2PdCl_2$	524(20)	504(54)	489(42)	419(17)	347(44)		
	358(25)	311(12)	293(21)				

[a] Numbers in parenthesis are relative intensities. [b] Ref. 9 gives 410(10) 374(3) 330(3) 355(39).

Table V. ^{31}P Coordination Chemical Shifts of $(R_nPh_{3-n}P)_2PdCl_2$

cis compounds	$((CH_3)_2(C_6H_5)P$ —53.3	$((C_2H_5)_2(C_6H_5)P$ —42.5		$((C_4H_9)_2(C_6H_5)P$ —46.0
	$((CH_3)(C_6H_5)_2P$ —47.2	$(C_2H_5)(C_6H_5)_2P$ —42.7	$(C_3H_7)(C_6H_5)_2P$ —45.0	$(C_4H_9)(C_6H_5)_2P$ —44.2
trans compounds		$(C_2H_5)_3P$ —38.2	$(C_3H_7)_3P$ —42.2	$(C_4H_9)_3P$ —42.3
	$(CH_3)_2(C_6H_5)P$ —41.9	$(C_2H_5)_2(C_6H_5)P$ —33.2		$(C_4H_9)_2(C_6H_5)P$ —37.1
	$(CH_3)(C_6H_5)_2P$ —35.9	$(C_2H_5)(C_6H_5)_2P$ —31.8	$(C_3H_7)(C_6H_5)_2P$ —33.9	$(C_4H_9)(C_6H_5)_2P$ —33.4

has been observed with platinum(II).[3] The nature of this complex has not yet been elucidated.

Those isomers which were isolated were examined by far infrared spectroscopy. The spectra are recorded in Table IV. The triethyl-, tripropyl-, and tributyl-phosphine complexes each gave one Pd—Cl band (355, 353, and 354 cm^{-1}, respectively). The far infrared spectra of the isolated complexes of dialkylphenyl and alkyl- diphenylphosphine are not always straightforward. For $(C_2H_5)(C_6H_5)_2PdCl_2$ and $((CH_3)(C_6H_5)_2P)_2PdCl_2$, no Pd—Cl stretching assignments could be made and the geometrical configuration was not determined. The crystal structure of *cis*—$((CH_3)_2(C_6H_5)P)_2PdCl_2$ [13] shows no distortion from a square planar structure. The close similarity of the far infrared spectrum of $((C_2H_5)_2(C_6H_5)P)_2PdCl_2$ to that of *cis*—$((CH_3)_2(C_6H_5)P)_2PdCl_2$ confirms the *cis* assignment of the former compound. The ν(Pd—Cl) of the other complexes were assigned with reasonable confidence.

It is well known that the chemical shifts of nuclei other than protons are dominated by the second order paramagnetic term and that the magnitudes of the diamagnetic contributions are quite small.[14] However, ^{31}P studies of tertiary phosphines and phosphonium salts have been interpreted with diamagnetic arguments.[15,16] In light of this, ^{31}P studies of transition metal complexes were undertaken in order to ascertain if diamagnetic contributions could be important in the chemical shifts for these compounds. The study of platinum complexes has been reported.[3]

The ^{31}P chemical shifts of palladium(II) complexes were found to be just the opposite of those of platinum(II), *i.e.*, the chemical shifts of the *trans* Pd- compounds are always upfield from the *cis* isomers while in Pt, the chemical shifts of the *trans* isomers are always downfield from those of the *cis* isomers. Clearly, simple shielding ideas cannot explain these results. There is, however, a consistent trend in the coordinate chemical shifts[3] of the *cis* and *trans* isomers recorded in Table V. The coordination chemical shifts (absolute value) of ethyl-, propyl- and butylphosphines generally increase in that order in both the *cis* and *trans* series, corresponding to an increase in σ-bonding ability in the same order. This trend parallels that found with the analogous platinum(II) complexes. The coordination chemical shift (absolute value) of a complex with a methyl group attached to phosphorus is much larger in all cases than one would predict from diamagnetic arguments. The coordination chemical shifts of trialkyl, dialkylphenyl, and alkyldiphenyl decrease in that order corresponding to a decrease in σ-donor ability as phenyl groups are substituted for alkyls.

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Table VI. Proton and Phosphorus-31 nmr Data for Amine-Phosphine Complexes of Palladium(II)

Amine	Chemical Shift (τ)	$^2J_{P-H}$	*trans*—(amine)($(CH_3)(C_6H_5)_2P$)$PdCl_2$ Chemical Shift (ppm *vs.* H_3PO_4)	Coordination Chemical Shift
pyridine	7.89	12.3	−16.3±0.3	−44.4
aniline	7.97	12.5	−18.6±0.3	−46.7
m-toluidine	7.98	12.4	−17.9±0.3	−46.0
p-toluidine	7.97	12.3	−18.1±0.3	−46.2
cyclohexylamine	7.95	12.2	−14.1±0.3	−42.2
triethylamine	7.95	12.3	−15.5±0.3	−43.6
diethylamine	7.97	12.0	−13.7±0.3	−41.8
piperidine	7.99	12.2	−15.0±0.3	−43.1
propylamine	7.97	12.0	−14.7±0.3	−42.8

The chlorine-bridged dimer of methyldiphenylphosphine was split with a variety of amines for two purposes: (a) to observe the effect that various amines in a *trans* position would have on the ^{31}P chemical shift of the complex and, (b) to measure differences in J_{P-CH_3} which might result with different amine ligands.

The ^{31}P chemical shifts of the amine-phopsphine complexes can be divided into two groups as shown in Table VI. The complexes containing aliphatic amines have ^{31}P chemical shifts which are further upfield than those for complexes containing aromatic amines. No correlation between the basicity of the amine and the chemical shift could be found.

The coupling constants, $^2J_{P-H}$, were found to be nearly independent of the amine as shown in Table VI. The proton chemical shifts are all about the same except for that of pyridine which is further downfield than the shifts of the other amine complexes.