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A Carbon-13 NMR Study of Some Phosphine, Arsine and Amine Complexes of Palladium

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The ^{13}C NMR spectra of a series of Pd^{2+} complexes containing phosphine, arsine and amine ligands, have been measured. The ^{13}C chemical shift of the carbon atom adjacent to the donor atom, and the para-*carbon in corresponding phenyl derivatives can be useful probes for the determination of complex geometry. Triple resonance measurements* e.g. *$^{13}C\{^1H, ^{31}P\}$ are shown to be a valuable aid in assigning ^{13}C spectra of phosphine complexes. The mixed complexes* trans-*$PdCl_2LL'$ (L = phosphine, arsine; L' = amine) exist as stable species in $CDCl_3$ solution and do not disproportionate to yield the symmetrical bis derivatives.*

Introduction

Although the applications of ^{13}C nuclear magnetic resonance (NMR) techniques in organic chemistry are quite common [1], the value of this technique to the transition metal chemist has only recently become clear [2, 3]. Although much effort has been expended in the study of the ^{13}C characteristics of metal carbonyl [3] and metal alkyl [4] complexes the number of investigations concerned specifically with phosphine, arsine and amine ligands when complexed to palladium have been limited. Many of the measurements involving complexes of these ligands have centered around platinum chemistry since ^{13}C studies involving this metal afford both chemical shift and coupling constant, $^nJ(Pt, C)$, information. In a number of studies changes in this latter parameter have been related to the NMR *trans* influence [5]. In those relatively few cases in which palladium complexes were studied interest has centered on square planar bis phosphine complexes and, in particular, the number of lines appearing in the AA'X or ABX (A, A' or A, B = ^{31}P, X = ^{13}C) spin system [6]. Although earlier [7] ^1H studies on related systems have been useful in distinguishing between *cis* and *trans* isomers the appearance of the ^{13}C multiplet for C_α (see scheme) is now recognized not to be sufficient for proof of structure [6, 8]. A recent study [9] has proposed that the magnitude of $^1J(P, C_\alpha)$ can be of value in deciding whether one has a *cis* or a *trans* complex. We have recently [10] suggested that δ $^{13}C_\alpha$ in some platinum complexes may also provide a hint in the assignment of complex geometry and in order to extend our knowledge in this area we have synthesized and measured ^{13}C NMR spectra for a series of symmetrical and mixed dichloro palladium complexes. Of special interest to us are the complexes $PdCl_2$(amine)(arsine) since these cases have neither metal–ligand nor ligand–ligand couplings which may assist in the structural assignment.

Experimental

^{13}C NMR spectra were measured as $CDCl_3$ solutions at 22.63 MHz using a Bruker HX–90 spectrometer operating in Fourier transform mode. Chemical shifts are referred to TMS and are estimated to be correct to ±0.1 ppm. The probe temperature was ~31 °C. The third frequency for the $^{13}C\{^1H, ^{31}P\}$ triple resonance measurements was provided by a Bruker frequency synthesizer. We routinely used the synthesizer to drive the broad band ^1H decoupler and the built-in ^{31}P decoupling channel for the selective decoupling. The latter frequency was applied *via* the unused transmitter coil of an HX–90 system operating in single coil mode.

The mixed complexes under consideration were synthesized by cleaving the dimers, $Pd_2Cl_4L_2$ (L = phosphine or arsine), in CH_2Cl_2 solution with two equivalents of L' (L' = phosphine, arsine or amine) dissolved in the same solvent. In our hands these reactions proceed smoothly at room temperature to afford complexes which after removal of solvent and recrystallization give satisfactory ^{31}P and ^{13}C NMR spectra as well as good microanalyses. These latter, the results for some of which are shown in Table I, are important since, although they do not differentiate between 2 mol of $PdCl_2LL'$ and 1 mol of $PdCl_2L_2$ plus 1 mol $PdCl_2L'_2$, they do confirm that we are dealing with analytically pure materials. The compounds $PdCl_2L_2$ and $Pd_2Cl_4L_2$ were synthesized using standard methods [11].

TABLE I. Elemental Analyses[a] for Some Mixed Complexes.

Compound	% C	% H	% N
PdCl$_2$(pyridine-N-oxide)(PEt$_2$Ph)	39.95 (41.08)	4.35 (4.60)	3.28 (3.19)
PdCl$_2$(pyridine)(PEt$_2$Ph)	42.80 (42.63)	4.85 (4.77)	3.39 (3.31)
PdCl$_2$(NHEt$_2$)(PEt$_2$Ph)	40.75 (40.36)	6.19 (6.29)	3.35 (3.36)
PdCl$_2$(NHEt$_2$)(PBu$^n_3$)	42.64 (42.45)	8.63 (8.46)	3.19 (3.09)
PdCl$_2$(AsTol$_3$[b])(PBu$^n_3$)	54.64 (54.45)	6.97 (6.65)	
PdCl$_2$(AsBu$^n_3$)(PBu$^n_3$)	45.97 (46.06)	8.60 (8.70)	
PdCl$_2$(PTol$_3$[b])(PBu$^n_3$)	58.25 (57.95)	6.87 (7.07)	
PdCl$_2$(NHEt$_2$)(AsEt$_3$)	29.04 (29.11)	6.32 (6.35)	3.31 (3.40)
PdCl$_2$(piperidine)(AsEt$_3$)	31.65 (31.12)	6.13 (6.17)	3.31 (3.30)
PdCl$_2$(pyridine)(AsEt$_3$)	31.55 (31.57)	4.80 (4.82)	3.43 (3.35)
PdCl$_2$(piperidine)(PTol$_3$[b])	54.92 (55.09)	5.66 (5.69)	
PdCl$_2$(NHEt$_2$)(PTol$_3$[b])	54.18 (54.12)	5.86 (5.81)	2.74 (2.53)

[a]Calculated values in parenthesis. [b]Tol = *p*-Tolyl.

Results and Discussion

The ^{13}C chemical shifts for C_α of the aliphatic chain and C_4 of the aromatic moiety are shown in Table II. The ^{13}C chemical shifts for C_β–C_δ (butyl groups) are relatively insensitive to changes in complex geometry as are C_2 and C_3 of the aromatic sections of the ligands. C_1 for the tri-*para*-tolylphosphine derivatives seems relatively insensitive, although in other alkyl–aryl phosphine derivatives there seems to be a tendency for C_1 *cis* to be at slightly higher field than C_1 *trans*. Since, as we shall show, the determination of the exact position of this resonance in such phosphine complexes is not always straightforward, we have restricted the ^{13}C chemical shift and coupling constants data given (Table II and III) to those resonances which show the largest effects.

Examples of ^{13}C spectra for compounds of the type PdCl$_2$LL' are shown in Figure 1 in which we show the region of the aromatic phosphine ^{13}C resonances. The problem of assignment in these cases is trivial and the ^{13}C shifts and $^nJ(P, C)$ values can be measured without difficulty. Consider, however, the trace shown in Figure 2a which represents the aromatic carbon resonances of PdCl$_2$(PEt$_2$Ph)$_2$. The spectrum shows all the signals which arise from the equilibrium mixture of the *cis* and *trans* isomers (predominantly *trans*). The ^{31}P NMR spectrum of this mixture has been reported previously [12] and confirmed by us for our sample. We expect *at least* ten lines for the *trans* isomer (three triplets for C_1, C_2 and C_3 which are the X parts of the ABX system with a relatively large J(A, B) coupling, and a singlet for C_4) and *at least* seven lines for the *cis* isomer (doublets for C_1, C_2 and C_3 and a singlet for C_4). In reality C_1 *cis* is not a doublet and C_4 for both isomers may be coupled to phosphorus. A preliminary assessment of 2a suggests that there *may be* a low field triplet (C_2 *trans*) and a high field triplet (C_3 *trans*) as well as a sharp triplet centered at about 130 ppm with approximately the correct magnitude for $^1J(P, C_1)$. A considerable simplification of this spectrum is made possible by simultaneously decoupling both ^{1}H (broad band) and ^{31}P (selective) and the results for these are shown in Figure 2b and 2c. Irradiation at the frequency corresponding to δ ^{31}P *trans* (2b) collapses all three of the presumed triplets ($\delta C_1 = 130.0$, $\delta C_2 = 131.7$, $\delta C_3 = 128.0$) and sharpens δC_4 (129.7), while simultaneously exposing the doublets for C_2 *cis* and C_3 *cis* and a broad resonance which contains at least C_4 *cis*. Irradiation at the corresponding ^{31}P frequency of the *cis* isomer (2c) collapses the doublets for C_2 *cis* and C_3 *cis*, clearly reveals the C_2 and C_3 triplets, markedly sharpens C_4 *cis* and introduces a new resonance at 129.3 ppm which we believe is C_1 *cis*. The triplet, C_1 *trans*, remains unchanged. Given the new resonance at 129.3 one can backtrack and, from spectrum 2a, select the lines (doublet of doublets) which most likely correspond to C_1 *cis*. As shown, in 2a there is a dependence of δC_4 on complex geometry and we shall comment further on this later.

The aliphatic region of the carbon spectrum of PdCl$_2$(piperidine)(PBu$^n_3$) presents a similar problem. The "normal" spectrum, Fig. 3a, shows doublets for the α and β carbons of the piperidine group as well as singlets* for C_β and C_δ of the phosphine chain. Unfortunately, the high field resonance of the phosphine C_γ doublet, the low field resonance of the phosphine C_α doublet and C_γ of the piperidine all overlap. This overlap is clearly proven when the appropriate ^{31}P frequency is irradiated since the two doublets associated with the phosphine collapse (Figure 3b) to reveal the hidden piperidine resonance**. In general we have found the

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*C_β of the phosphine shows a relatively small phosphorus coupling which is not resolved in this spectrum. A small $^2J(P, C)$ is to be expected [9] and is observed in C$_6$D$_6$ solution.

**We have subsequently observed that all of the resonances are well separated in C$_6$D$_6$ solution.

TABLE II. Some Carbon-13 Chemical Shifts[a] (TMS) in the Complexes.

Compound $Pd_nCl_{2n}L_{2-m}L'_m$				$\delta C_\alpha(L)$	$\delta C_{para}(L)$	$\delta P(L)$
1.	sym.	*trans*	$Pd_2Cl_4(PMe_2Ph)_2$	14.3	131.6	
2.		*cis*	$PdCl_2(PMe_2Ph)_2$	15.9	130.7	5.9
3.		*trans*	$PdCl_2(PMe_2Ph)_2$	11.9	130.5	– 5.3
4.	sym.	*trans*	$Pd_2Cl_4(PMePh_2)_2$	15.0[b]	131.7	22.3
5.		*cis*	$PdCl_2(PMePh_2)_2$	17.8	130.7	18.2
6.		*trans*	$PdCl_2(PMePh_2)_2$	12.2	130.2	7.4
7.	sym.	*trans*	$Pd_2Cl_4(PEt_2Ph)_2$	16.8	131.3	36.2
8.		*cis*	$PdCl_2(PEt_2Ph)_2$	18.1	130.6	24.7
9.		*trans*	$PdCl_2(PEt_2Ph)_2$	14.5	129.7	15.4
10.		*trans*	$PdCl_2(PEt_2Ph)(py\rightarrow O)$	17.4	130.6	34.4
11.		*trans*	$PdCl_2(PEt_2Ph)(py)$	16.7	130.5	26.9
12.		*trans*	$PdCl_2(PEt_2Ph)(NHEt_2)$	16.4	130.3	25.4
13.	sym.	*trans*	$Pd_2Cl_4(AsMe_2Ph)_2$	10.6	131.1	–
14.		*trans*	$PdCl_2(AsMe_2Ph)_2$	8.3	129.9	–
15.	sym.	*trans*	$Pd_2Cl_4(AsMePh_2)_2$	10.6	131.3	–
16.		*trans*	$PdCl_2(AsMePh_2)_2$	8.4	130.2	–
17.	sym.	*trans*	$Pd_2Cl_4(AsTol_3)_2$[c]	–	141.1	–
18.		*trans*	$PdCl_2(AsTol_3)_2$	–	139.8	–
19.			$PdCl_2(AsTol_3(py)$	–	140.2	–
20.			$PdCl_2(AsTol_3)(NHEt_2)$	–	140.2	–
21.			$PdCl_2(AsTol_3)(AsEt_3)$	–	139.9	–
22.		*trans*	$PdCl_2(AsTol_3)(PBu^n_3)$	–	139.4	–
23.	sym.	*trans*	$Pd_2Cl_4(PTol_3)_2$	–	141.8	31.5
24.		*trans*	$PdCl_2(PTol_3)_2$	–	140.1	21.4
25.			$PdCl_2(PTol_3)(py)$	–	141.0	27.3
26.		*trans*	$PdCl_2(PTol_3)(pip)$	–	140.9	26.4
27.		*trans*	$PdCl_2(PTol_3)(NHEt_2)$	–	140.8	25.2
28.		*trans*	$PdCl_2(PTol_3)(PBu^n_3)$	–	140.0	17.9[d]
29.			$PdCl_2(pip)_2$[e]	51.0	–	–
30.		*trans*	$PdCl_2(pip)(AsEt_3)$	48.9	–	–
		trans	$PdCl_2(pip)(PTol_3)$	48.8	–	–
31.		*trans*	$PdCl_2(pip)(PBu^n_3)$	48.2	–	–
32.			$PdCl_2(NHEt_2)_2$[e]	48.4	–	–
			$PdCl_2(NHEt_2)(AsTol_3)$	47.2	–	–
33.		*trans*	$PdCl_2(NHEt_2)(AsEt_3)$	46.7	–	–
		trans	$PdCl_2(NHEt_2)(PTol_3)$	46.6	–	–
34.		*trans*	$PdCl_2(NHEt_2)(PBu^n_3)$	46.3	–	–
		trans	$PdCl_2(NHEt_2)(PEt_2Ph)$	46.2	–	–
35.	sym.	*trans*	$Pd_2Cl_4(AsBu^n_3)_2$	23.7	–	–
36.		*trans*	$PdCl_2(AsBu^n_3)_2$	20.8	–	–
37.		*trans*	$PdCl_2(AsBu^n_3)(PBu^n_3)$	20.5	–	–
38.	sym.	*trans*	$Pd_2Cl_4(AsEt_3)_2$	16.6	–	–
39.		*trans*	$PdCl_2(AsEt_3)_2$	13.6	–	–
40.			$PdCl_2(AsEt_3)(py)$	15.7	–	–
			$PdCl_2(AsEt_3)(NHEt_2)$	14.9	–	–
			$PdCl_2(AsEt_3)(pip)$	14.6	–	–
			$PdCl_2(AsEt_3)(AsTol_3)$	14.4	–	–
41.	sym.	*trans*	$Pd_2Cl_4(PBu^n_3)_2$	23.9	–	39.7
42.		*trans*	$PdCl_2(PBu^n_3)_2$	21.5	–	10.0
43.			$PdCl_2(PBu^n_3)(py)$	23.9	–	27.3
		trans	$PdCl_2(PBu^n_3)(pip)$	23.3	–	24.6
		trans	$PdCl_2(PBu^n_3)(NHEt_2)$	23.3	–	24.0
		trans	$PdCl_2(PBu^n_3)(AsTol_3)$	22.4	–	20.4
		trans	$PdCl_2(PBu^n_3)(PTol_3)$	22.0	–	16.1[d]
		trans	$PdCl_2(PBu^n_3)(AsBu^n_3)$	21.7	–	13.2

[a] Chemical shifts are for $CDCl_3$ solutions and are estimated to be ±0.1 ppm. [b] In $DMSO/CD_2Cl_2$ 1:4. [c] Tol = *para*-tolyl. [d] Calculated for $^2J_{PP}$ between 500 and 600 Hz. [e] Assumed to be *trans* complexes.

TABLE III. Phosphorus–Carbon Coupling Constants[a] in Some Pd^{2+} Complexes.

Compound			$^1J(P, C_\alpha)$	$^2J(P, C_\beta)$	$^3J(P, C_\gamma)$	Ref.
sym.	*trans*	$Pd_2Cl_4(PMe_2Ph)_2$	39.6			This Work
	cis	$PdCl_2(PMe_2Ph)_2$[b]	36.6			This Work
	trans	$PdCl_2(PMe_2Ph)_2$[b]	32.2			This Work
sym.	*trans*	$Pd_2Cl_4(PMePh_2)_2$[c]	40.3			This Work
	cis	$PdCl_2(PMePh_2)_2$[b]	37.4			This Work
	trans	$PdCl_2(PMePh_2)_2$	32.2			This Work
sym.	*trans*	$Pd_2Cl_4(PEt_2Ph)_2$	34.4	3.7		This Work
	cis	$PdCl_2(PEt_2Ph)_2$[b]	33.0	1.4		This Work
	trans	$PdCl_2(PEt_2Ph)_2$[b]	27.8	n.o.		This Work
	trans	$PdCl_2(PEt_2Ph)(py{\rightarrow}O)$	35.9	3.7		This Work
	trans	$PdCl_2(PEt_2Ph)(py)$	35.2	2.9		This Work
	trans	$PdCl_2(PEt_2Ph)(NHEt_2)$[c]	33.7	n.o.		This Work
sym.	*trans*	$Pd_2Cl_4(PBu^n_3)_2$	30.8	2.9	16.1	This Work
	trans	$PdCl_2(PBu^n_3)_2$[b]	26.4	n.o.	13.2	9
	trans	$PdCl_2(PBu^n_3)(py)$	32.2	n.o.	13.2	8
	trans	$PdCl_2(PBu^n_3)(pip)$[c]	30.9	n.o.	14.0	This Work
	trans	$PdCl_2(PBu^n_3)(NHEt_2)$[c]	32.2	n.o.	13.2	8
	trans	$PdCl_2(PBu^n_3)(AsTol_3)$	27.8	n.o.	14.6	8
	trans	$PdCl_2(PBu^n_3)(PTol_3)$[d]	23.9	n.o.	13.2	8
	trans	$PdCl_2(PBu^n_3)(AsBu^n_3)$[e]	26.4	n.o.	14.6	8

[a] Coupling constants are ±0.7 Hz. The phosphorus coupling (or sum of couplings) to C_1, C_2 and C_3 were of the order of 40–60 Hz, 8–13 Hz and 9–12 Hz respectively. Coupling to C_4, when observed, was of the order of 3 Hz [8]. We have not observed phosphorus coupling to C_δ. [b] Sum of the couplings $^nJ(P, C) + {}^{n+2}J(P, C)$ given. [c] $^3J(P–Pd–N–C)$ varies from 2.9–3.7 Hz in these complexes. [d] Calculated using ^{13}C and ^{31}P spectra. [e] $^3J(P–Pd–As–C) = 4.4$ Hz.

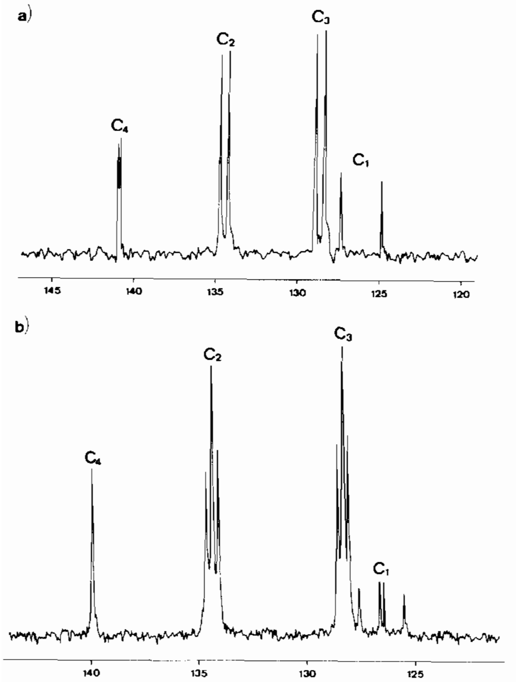

Figure 1. a) ^{13}C resonances in the aromatic region for the complex *trans*-$PdCl_2(piperidine)(PTol_3)$. b ^{13}C resonances in the aromatic region of the complex *trans*-$PdCl_2(PTol_3)(PBu^n_3)$.

$^{13}C\{^1H, {}^{31}P\}$ measurements to be quite useful and especially valuable when one deals with molecules containing more than one phosphorus atom.

Before going further it is appropriate, at this point, to reaffirm [12, 13] the existence and relative stability in $CDCl_3$ solution of the mixed complexes $PdCl_2(amine)L$ (L = phosphine or arsine) since these points have recently been questioned [14]. In particular $PdCl_2(piperidine)(PBu^n_3)$ definitely does not disproportionate to any significant extent in $CDCl_3$ solution since the ^{13}C NMR and ^{31}P NMR parameters for this complex differ clearly from the two bis-complexes. We observe long-range phosphorus–carbon coupling through the metal to C_α of the piperidine group (~3.7 Hz) for both the PBu^n_3 (see Fig. 3) and the $PTol_3$ derivatives and feel these observations to be additional evidence in favor of a structure in which piperidine exchange must be slow on the NMR time scale. Although devoid of any intraligand coupling the chemical shift values for $PdCl_2(amine)(AsEt_3)$ (amine = $NHEt_2$ or piperidine) confirm that these complexes have not disproportionated either. Additionally, as we shall show, the combined ^{13}C NMR data from several sources suggest a *trans* geometry for mixed complexes. We have observed some disproportionation a) when $Pd_2Cl_4(PTol_3)_2$ was cleaved with $AsBu^n_3$ and b) in the cleavage of $Pd_2Cl_4(PEt_2Ph)_2$ with $AsTol_3$.

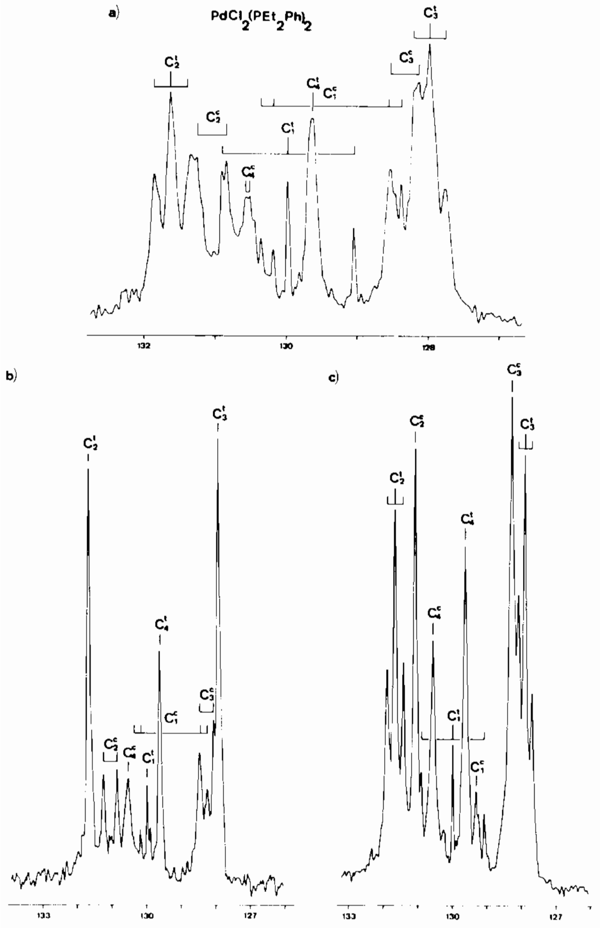

Figure 2. ^{13}C resonances in the aromatic region for the equilibrium mixture of the *cis* and *trans* isomers of $PdCl_2(PEt_2Ph)_2$ a) with ^{1}H decoupling, b) with ^{1}H and ^{31}P (*trans* only) decoupling and c) with ^{1}H and ^{31}P (*cis* only) decoupling.

It may be seen from Table II that there is a dependence of the chemical shift of C_α in the mixed alkylphenylphosphine derivatives on complex geometry, with *cis* isomers appearing at lower field (≃3–5 ppm) than the corresponding *trans* derivatives [1–9]. Further, the phosphine and arsine dimeric species, $Pd_2Cl_4L_2$ [1, 4, 7, 13 and 15] also show C_α at lower field than the corresponding *trans* isomers, although to a lesser extent (2–3 ppm). Of particular interest in this connection, are the PEt_2Ph compounds [7–12]. In all but 9 the phosphine is *trans* to a group with a weak *trans* influence and we find C_α at relatively low field. Since the compounds *cis*-$PdCl_2(PBu_3)_2$ and *cis*-$PdCl_2(AsR_3)_2$ are unknown we are not certain of the magnitude of this dependence in trialkyl phosphine and arsine derivatives; however, we note that a 2–3 ppm difference in C_α exists between the sym. *trans* dimers and the *trans*-monomers. This latter difference in the chemical shift of C_α, although somewhat small, when combined with the dependence [8] of $^1J(P, C_\alpha)$ and $\delta\,^{31}P$ on complex geometry provides a useful structural probe. In Table III are shown the relevant $^nJ(P, C)$ values. Thus the product of cleaving $Pd_2Cl_4(PBu^n_3)_2$ with two moles of $AsBu^n_3$ shows δC_α (phosphine) = 21.7 ppm, δC_α (arsine) = 20.5 ppm, $^1J(P, C_\alpha)$ = 26.4 Hz and $\delta\,^{31}P$ = 13.4 ppm, all in good agreement for phosphorus (and arsenic) *trans* to a ligand with a relatively strong *trans* influence (see for example, 42, Table II). Previous ^{31}P NMR studies [8, 12] on related systems have suggested the order of *trans* influence $PBu_3 > AsBu_3 > PTol_3 > AsTol_3 > NHEt_2 >$ pyridine, which is roughly confirmed by the carbon NMR data (see C_α for the PBu_3 derivatives in Table II). This ranking is not completely unexpected [15]. The suggestion that dialkyl amines have a higher *trans* influence than pyridine is supported by the ^{31}P data from a previous study of the derivatives *trans*-$PdCl_2(amine)(PEtPh_2)$ [12].

A somewhat more subtle but constant dependence exists at the *para* position, C_4, of the aryl containing phosphines and arsines. Thus, for a complex possessing a weaker ligand (chloride, bridging chloride, amine) *trans* to either phosphorus or arsenic we find a C_4 resonance shifted about one ppm to lower field relative to the bis *trans* complex (compare 1 and 3, 4 and 6, 7 and 9, 13 and 14, 15 and 16, 17 and 18). We are thus able to confirm our previous assignment [8] of a *trans* structure* for the mixed complex $PdCl_2(PBu^n_3)(PTol_3)$ since the chemical shift of both C_4 140.0 ppm of the *p*-tolyl group (140.1 for $PdCl_2(PTol_3)_2$; 141.8 for sym. *trans*-$Pd_2Cl_4(PTol_3)_2$; 141.0 for $PdCl_2(pyridine)(PTol_3)$) and C_α of the aliphatic phosphine, in combination with $^1J(P, C_\alpha)$ and the ^{31}P chemical shift all point to a *trans* structure. Somewhat more tenuous is the assignment of a *trans* geometry to 21, $PdCl_2(AsEt_3)(AsTol_3)$. The position of C_4 is correct for a *trans* structure but C_α of the aliphatic arsine has its resonance rather close to 33, $PdCl_2(NHEt_2)(AsEt_3)$. Dipole moment and NQR measurements could be helpful here. Interestingly, the position of C_4 for a given ligand tends to reflect the *trans* influence series mentioned above (see 17–22 in Table II), although in view of the small spread of values a firm conclusion would be presumptuous.

We have commented on the possibility that the *trans* influence of the groups in the complex may, in part, determine the position of C_α; however, it has not been suggested previously that a similar effect may be responsible for the change in position of C_4. If one accepts that *cis* isomers have the phosphine (arsine) more strongly bound to the metal than do

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*The ^{31}P spectrum shows only the two most intense lines of a tightly coupled AB system.

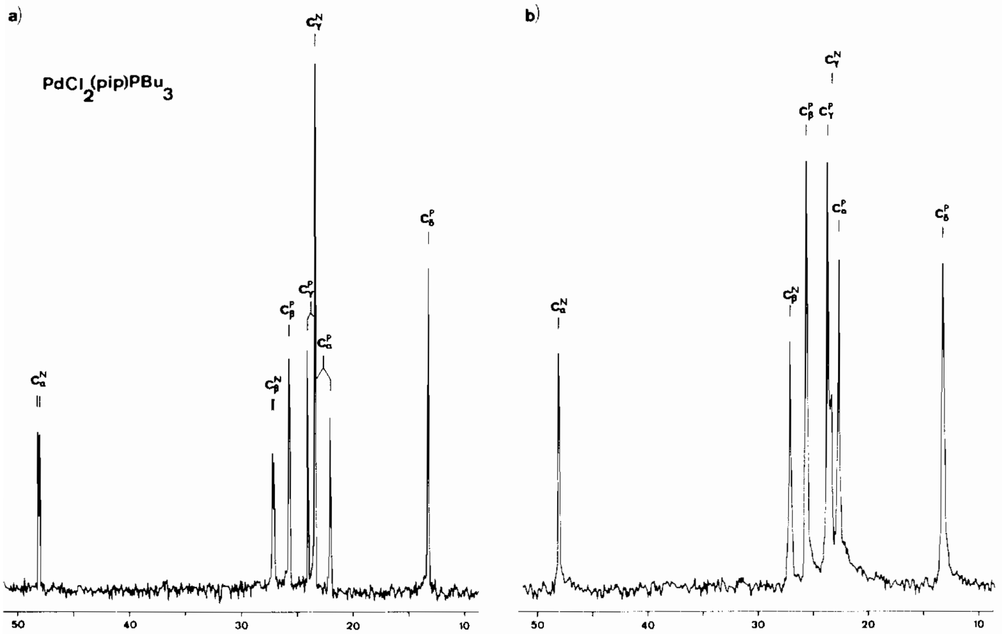
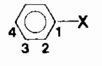


Figure 3. Aliphatic ^{13}C resonances of the complex *trans*-PdCl$_2$(piperidine)(PBu$_3^n$) a) with ^{1}H decoupling and b) with ^{1}H and ^{31}P decoupling.

the *trans* counterparts, then one can consider the *cis* isomers as more phosphonium (arsonium)-like in character. The partial charge on the phosphorus polarizes the π-system of the aromatic such that C_4 develops a small positive charge and is thus slightly shifted to lower field. A structure somewhat like III is clearly extreme, but presents the idea. In support



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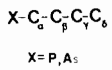
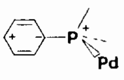


II



III

of this concept we note the following ^{13}C values in CDCl$_3$ for C_4: AsMePh$_2$ = 128.0; *trans*-PdCl$_2$(AsMePh$_2$)$_2$ = 130.2; sym. *trans*-Pd$_2$Cl$_4$(AsMePh$_2$)$_2$ = 131.3; AsMePh$_3^+$I$^-$ = 133.8. The selection of the triphenylmethyl arsonium ion is somewhat arbitrary; however, if one considers that the *para* carbon chemical shifts, $\delta\,^{13}C_4$, for AsPh$_3$R$^+$I$^-$ (R = CH$_3$, Et, Pr^n, Bu^n, Ph) are: 133.8, 133.8, 133.8, 133.8 and 134.6 ppm, respectively, then perhaps the compound taken is not an unreasonable model.

If the *trans* influence is an important factor in determining the C_α chemical shift in the phosphine and arsine derivatives, it is not unreasonable to expect this effect to influence C_α in amine complexes. That this is the case is demonstrated by comparing C_α in the complexes PdCl$_2$(NHEt$_2$)$_2$ and PdCl$_2$(piperidine)$_2$ with C_α in the mixed complexes 12, 20, 27, 33, 34 and 26, 30, 31. In both bis-amine complexes we observe that the resonance appears 1.5–2.5 ppm to lower field than in the mixed complexes. We take this to suggest that the amine is situated opposite to a group with a relatively strong *trans* influence (*e.g.* phosphine or arsine) in the mixed complexes.

Lastly, current and earlier ^{13}C measurements for mixed dichloro palladium complexes suggest that the recent [14] assignment of the *cis* structure to PdCl$_2$(AsEt$_3$)(PBu$_3^n$) should be reconsidered. If one assumes that the given assignment of C_β in the phosphine is actually C_α (C_α in PBu$_3^n$ complexes of Pd(II) is normally found at higher field than C_β and in this case shows the expected larger $^1J(P, C_\alpha)$ value) then the observed NMR parameters for C_α (21.54 ppm, $^1J(P, C)$ = 25.4 Hz) are in good agreement with the ^{13}C parameters for *trans*-PdCl$_2$(PBu$_3^n$)$_2$ (δC_α = 21.5 ppm, $^1J(P, C_\alpha) + {}^3J(P, C_\alpha)$ = 26.4 Hz. The complex sym. *trans*-Pd$_2$Cl$_4$(PBu$_3^n$)$_2$ has δC_α = 23.9 ppm, $^1J(P, C_\alpha)$ = 30.8 Hz).

Concluding, we feel that ^{13}C chemical shift values can be helpful in the determination of molecular structure in square planar complexes of palladium.

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