sponding though smaller upfield shift in the methyl or methoxy resonances vs. the free ligands.

Addition of free ligand to a solution of any of the $M(SbR_3)_4$ (M = Pd, Ni) complexes simply added the resonances of the ligands to the spectra, indicating little dissociation and slow exchange or type I behavior as discussed by Tolman.[7] Analogous $P(p\text{-}CH_3C_6H_4)_3$ complexes exhibit extensive dissociation and fast exchange,[5] i.e., type IV behavior.[7]

The steric bulk of the triarylphosphine and stibine ligands can be compared by methods previously outlined.[6,7] The covalent radius of the coordinated antimony is about 0.3 Å larger than for phosphorus[31] and results in a lengthening of the M–Sb and Sb–C bonds such that the cone angle for the $SbPh_3$ is <132° vs. that for PPh_3, 145°. The steric bulk is more similar to that of $P(p\text{-}CH_3C_6H_4O)_3$, 128°, which also exhibits type I behavior.[22]

The ^1H NMR spectrum of $Pd(PPh_3)_2(SbR_3)_2$, R = p-$CH_3C_6H_4$, exhibited a single methyl resonance (peak width at half-height 7 Hz) and a very complex phenyl region. Examination of the phenyl region indicated the presence of several species, consistent with the redistribution of $Pd(PPh_3)(SbR_3)_2$ in solution

$$2Pd(PPh_3)_2(SbR_3)_2 \rightleftharpoons Pd(PPh_3)_3(SbR_3) + Pd(PPh_3)(SbR_3)_3$$

The observation of a single broadened methyl resonance is consistent with nearly identical methyl chemical shifts for the species present. The material obtained from solution analyzing as $Pd(PPh_3)_2(SbR_3)_2$ could be either a single product or a complex mixture, $Pd(PPh_3)_n(SbR_3)_{4-n}$ (n = 4–0), in appropriate ratios.

The ^1H NMR spectrum of $Pt(PPh_3)_2(SbR_3)_2$ showed methyl resonances at τ 7.73 and 7.77. The aromatic region was again more complex than expected for a single species. ^1H NMR spectra of the complexes obtained from $Pt(PPh_3)_3$, $Pt(CS_2)(PPh_3)_2$, or $Pt(PPh_3)_2(C_2H_4)$ were identical. An equilibrium similar to that for $Pd(PPh_3)_2(SbR_3)_2$ must again be proposed.

Triarylstibinerhodium(I) complexes favor five-coordination in the solid state whereas analogous phosphine complexes are four-coordinate.[12] We now find that $M(SbR_3)_4$ (M = Pd, Ni) are not extensively dissociated in solution, unlike the analogous phosphine complexes. These observations can be rationalized on the basis of steric considerations. Measurements of cone angles indicate the steric nature of SbR_3 is closer to that of $P(OR)_3$ than of PR_3. It appears that, compared with triarylphosphine ligands, the lower steric requirements of the triarylstibine ligands allow higher coordination and do not force dissociation in such systems.

Registry No. $Ni[Sb(p\text{-}CH_3C_6H_4)_3]_4$, 57527-33-0; $Ni[Sb(p\text{-}CH_3OC_6H_4)_3]_4$, 57527-34-1; $Pd[SbPh_3]_4$, 23854-68-4; $Pd[Sb(p\text{-}CH_3C_6H_4)_3]_4$, 57527-39-6; $Pd[Sb(p\text{-}CH_3OC_6H_4)_3]_4$, 57527-40-9; $Pd(PPh_3)_2[Sb(p\text{-}CH_3C_6H_4)_3]_2$, 57527-35-2; $Pd(PPh_3)_2(SbPh_3)_2$, 14263-83-3; $Pt(PPh_3)_2(SbPh_3)_2$, 57527-36-3; $Pt(PPh_3)_2[Sb(p\text{-}CH_3C_6H_4)_3]_2$, 57527-37-4; $Pt(PPh_3)_2[Sb(SPh)_3]_2$, 57527-38-5; $Ni(acac)_2$, 3264-82-2; $Ni(COD)_2$, 1295-35-8; $Pd(acac)_2$, 14024-61-4; $Pd(PPh_3)_4$, 14221-01-3; $Pd(PPh_3)_2CS_2$, 57527-52-3; $Pt(PPh_3)_3$, 13517-35-6; $Pt(PPh_3)_2CS_2$, 50588-64-2; $Pt(PPh_3)_2(C_2H_4)$, 12120-15-9; $AlEt_3$, 97-93-8.

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Contribution from the Department of Chemistry, University of Nevada, Reno, Nevada 89507, and the Life Sciences Division,
Stanford Research Institute,
Menlo Park, California 94025

Investigation of the Utility of "Virtual Coupling" in the $^{13}C\{^1H\}$ Nuclear Magnetic Resonance Spectra of Bis-Phosphite Complexes of Palladium and Platinum. Algebraic Cancelation of Spin–Spin Coupling

A. W. Verstuyft,[1a] J. H. Nelson,*[1a] and L. W. Cary[1b]

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Following the early observation of "virtual coupling" in the ^1H NMR spectra of bis-organophosphorus compounds by King[2] and by Jenkins and Shaw,[3] this phenomenon has become a fundamental tool for geometry assignment. Several hundred articles have appeared in which it has been utilized to assign the geometry of transition metal–phosphine complexes. Unfortunately, there are a large number of compounds for which ^1H NMR virtual coupling is not applicable. The method generally cannot be applied unless the phosphorus ligand bears an α-methyl, α-methoxy, α-methylene, or ortho methylene group which is not coupled to other protons. This excludes such commonly utilized ligands[4] as triphenylphosphine, triethylphosphine, and triethyl phosphite for which the method is applicable only in fortuitous circumstances.[5] Because of this limitation as well as the increasing availability of Fourier transform spectrometers $^{13}C\{^1H\}$ NMR has been briefly investigated for similar use.[6] In several instances it has been shown that ^{13}C NMR can provide structural information where ^1H NMR cannot.[7] Yet few systematic investigations have appeared. In the course of our studies, we noted that the $^{13}C\{^1H\}$ NMR spectrum of *cis*-$[(MeO)_3P]_2PdCl_2$ was a singlet instead of the anticipated multiplet.[6] We had also observed other instances of the apparent lack of phosphorus–carbon coupling, e.g., in the aryl groups of arylphosphine complexes.[8] In order to seek an explanation for this phenomenon and to investigate the general utility of $^{13}C\{^1H\}$ NMR for geometry assignments we undertook an investigation of the $^{13}C\{^1H\}$ NMR spectra of complexes of the type L_2MCl_2, where L is a phosphite or phosphine and M is Pd(II) or Pt(II). The chosen ligands are ones for which ^1H virtual coupling for the most part is not applicable. Furthermore, no previous $^{13}C\{^1H\}$ studies of phosphite complexes have been reported. For comparison, a few compounds of the type *cis*-$LL'PdCl_2$ were also investigated.[9] While this work was being completed, a similar study of phosphine complexes appeared.[7b] Our results on the

Table I. $^{13}C\{^1H\}$ NMR Data for Phosphites $(RO)_3P^a$

R	$\delta(C_1)$	$^2J_{PC}$, Hz	$\delta(C_2)$	$^3J_{PC}$, Hz	$\delta(C_3)$	$^4J_{PC}$, Hz	$\delta(C_4)$	$^5J_{PC}$, Hz
Methyl	24.2	10.6						
Ethyl	57.4	11.4	16.7	4.8				
Allyl	63	11.0	116	0	134.7	5.1		
Isopropyl	40.9	12.9	24.2	14.4				
n-Butyl^b	62	10.6	33.4	4.8	19.1	0	13.7	0
Neopentyl	72.2	8.9	32.3	2.6	26.9	0		
Phenyl^b	151.5	3.6	120.6	7.1	129.5	0		

[a] $CDCl_3$ solution; δ relative to TMS internal standard. [b] L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley, New York, N.Y., 1972.

Table II. $^{13}C\{^1H\}$ NMR Data^a for Complexes of the Type $[(RO)_3P]_2MCl_2$

R	Geometry^b	M	$\delta(C_1)$	J,^{c} Hz	$\delta(C_2)$	J,^{c} Hz	$\delta(C_3)$	J,^{c} Hz	$\delta(C_4)$	J,^{c} Hz
Methyl	Cis	Pd	54.6	0						
Methyl	Cis	Pt	51.2	0^d						
Ethyl	Cis	Pd	64	0	16.1	0				
Allyl	Cis	Pd	68.5	0	118.65	0	132.1	0		
Isopropyl	Trans	Pd	73.5	4.7 t	24.0	4.7 t				
Isopropyl	Cis	Pt	72.9	e	23.9	0				
Neopentyl	Trans	Pd	76.1	0	32.4	12 t	26.4	0		
Neopentyl	Trans	Pt	75.8	0	32.1	6 t	25.9	0		
Phenyl	Cis	Pd	150.8	12 d	120.6	0	125.7	0	129.8	0
Phenyl	Cis	Pt	150.0	12 d	120.5	0	125.5	0	129.7	0
$(EtO)_3P, PPh_3$^{f}	Cis	Pd	64.1	6.3 d	15.7	6.3 d				
$(MeO)_3P, Et_3As$^{f}	Cis	Pd	54.4	4.2 d						
$(PhO)_3P, Ph_3P$^{f}	Cis	Pd	131.8	3.3 d	129.9	4.0 d	120.95	9.9 d	125.8	0

[a] $CDCl_3$ solutions; δ relative to TMS internal standard. [b] Geometries were assigned by using ^1H or $^{31}P\{^1H\}$. For the $^{31}P\{^1H\}$ NMR assignment technique see A. W. Verstuyft, J. H. Nelson, and L. W. Cary, *Inorg. Nucl. Chem. Lett.*, **12**, 53 (1976). [c] $J = |^nJ_{PC} + {}^{n+2}J_{PC}|$; d ≡ doublet; t ≡ 1:2:1 triplet. [d] $J_{Pt-C} = 10.7$ Hz. [e] $J_{Pt-C} = 62$ Hz, $^2J_{PC} = 3.52$ Hz, $^4J_{PC} = -1.28$ Hz, and $^2J_{PP} = 1.13$ Hz calculated from a five-line spectrum. [f] Only the phosphite resonances are reported.

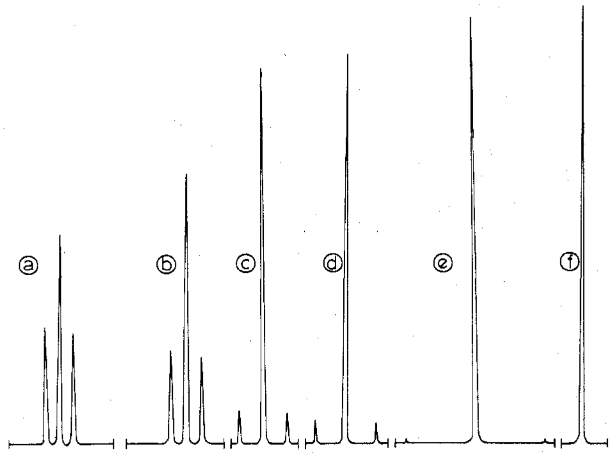

Figure 1. Spin simulation of the $[A]_2X$ spin system exhibiting the algebraic cancelation of J_{AX} and $J_{A'X}$ as a function of J_{AA}. A, A' ≡ ^{31}P, X ≡ ^{13}C, $J_{PC} = -J_{PC'} = 10$ Hz throughout with the following values of $^2J_{PP}$: a, 0; b, 5; c, 15; d, 20; e, 50; f, 500 Hz. Line widths at half-height are 0.5 Hz.

phosphine complexes are in total agreement with these[7b] and consequently will not be reported.

Experimental Section

All compounds were prepared by standard literature methods,[9,10] and most have been reported elsewhere. $[P(o\text{-allyl})_3]_2PdCl_2$ and $[P(o\text{-neopentyl})_3]_2MCl_2$ (M = Pd or Pt) have not been previously reported. Each complex was isolated, recrystallized, and characterized by its melting point, and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra. Satisfactory elemental analyses were obtained for the new compounds. All operations involving phosphorus ligands were conducted under an atmosphere of dry prepurified nitrogen. NMR spectra were obtained as previously described.[11] The data are listed in Tables I and II.

Results and Discussion

The spin system for each of the carbon atoms in the $(R_3P)_2MX_2$ type complexes is of the ABX or $[A]_2X$ (A, B = ^{31}P, X = ^{13}C) limiting type.[6,7b] Theoretically, several possible line shapes can arise for this spin system,[6] depending upon the signs and magnitudes of $\Delta\nu_{AB}$, J_{AB}, J_{AX}, and J_{BX} as illustrated in Figures 1 and 2 and figure 2 of ref 6. Normally the ^{13}C resonances for the cis isomers of these complexes should appear as a quintet, a non 1:2:1 triplet, a doublet of doublets, or a doublet.[8] The ^{13}C resonances for the trans isomers always appear as 1:2:1 triplets. These line shapes will be observed as long as one or both of the phosphorus–carbon coupling constants is not zero.

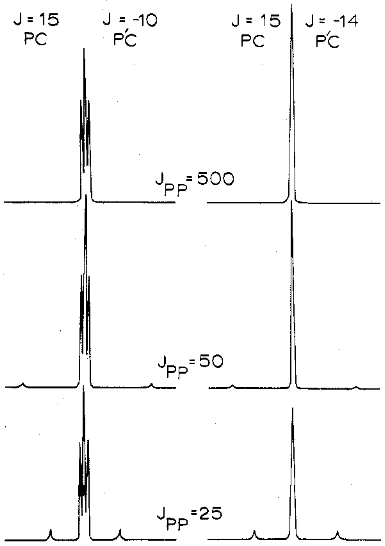

Figure 2. Spin simulation of the $[A]_2X$ spin system showing that algebraic cancelation of J_{AX} and $J_{A'X}$ may occur even if J_{AX} is not exactly equal in magnitude to $J_{A'X}$. If $\nu_A - \nu_B > 1$ Hz in the ABX system and $J_{AX} - J_{BX} > 1$ Hz, singlets will not be observed for any value of $J_{AB} \equiv {}^2J_{PP}$ if the resolution is greater than 0.5 Hz. Line widths at half-height are 0.5 Hz.

The observation of a singlet in the ^{13}C NMR spectra of *cis*-$[(MeO)_3P]_2MCl_2$[12] (M = Pd, Pt)[12] might imply one of two things: either ligand exchange is rapid or $^2J_{PC}$ and $^4J_{PC}$ are zero. That neither of these is the case can be shown by the following arguments. Spin–spin coupling (J_{PH} and J_{PP}) results in "filled-in" doublet methyl resonances[12] in the ^1H NMR of these two complexes, and not the singlet or doublet which are characteristic of phosphorus ligand exchange in systems of this type.[13] Platinum sattelites are observed in the $^{13}C\{^1H\}$ spectrum of *cis*-$[(CH_3O)_3P]_2PtCl_2$ (Table II). Moreover, carbon–phosphorus coupling is seen in the *cis*-$LL'PdCl_2$ complexes (Table II) though the coupling constants differ from those of the free ligands (Table I). It has been shown[14] that J_{POCH} is positive for both the free ligand[15] and Ni(II) complexes of phosphites, phosphonites, and phosphinites. For the free ligands[15] J_{POC} is positive, but it may change sign upon coordination since J_{POC} is negative in pentavalent phosphorus compounds.[15] The analogous complexes *cis*-$[(CH_3O)_nP(C_6H_5)_{3-n}]_2PdCl_2$ ($n = 1, 2$) each exhibit "filled-in" doublets for their ^1H methyl resonances[16] and non 1:2:1 triplets[6] for their $^{13}C\{^1H\}$ methyl resonances.[17] For the complexes *trans*-$[P(o\text{-neopentyl})_3]_2MCl_2$ (M = Pd, Pt) the C_1 carbon resonance is a singlet, yet the C_2 carbon resonance is a triplet (Table II). Thus, it can be concluded that rapid exchange is not occurring and neither $^2J_{PC}$ nor $^4J_{PC}$ are zero for the $[(RO)_3P]_2MCl_2$ complexes.

The separation[6,7] of the most intense lines in the X part of the $[A]_2X$ multiplet is given by $|^nJ_{PC} + {}^{n+2}J_{PC}|$. Using the above arguments, this implies that when singlets are observed for the C_1 carbon resonances, $^nJ_{PC} = -{}^{n+2}J_{PC}$; that is, the two phosphorus–carbon coupling constants are equal in magnitude and opposite in sign and algebraically cancel! A complete analysis was possible for the complex $[P(o\text{-}i\text{-Pr})_3]_2PtCl_2$, where a five-line spectrum was observed for the C_1 resonance and $^2J_{PC}$ and $^4J_{PC}$ had opposite signs (Table II). Thus, a singlet can arise for these resonances depending upon the magnitude of $^2J_{PP}$ and the relative magnitudes of $^2J_{PC}$ and $^4J_{PC}$. As can be seen in Figure 2, it is not necessary that $^2J_{PC}$ exactly equal $^4J_{PC}$ in order to observe a singlet.

From the data in Table II it can be concluded that for phosphite complexes of palladium(II) and platinum(II), except those of $(C_6H_5O)_3P$, $^2J_{PC} \simeq -{}^4J_{PC}$ in general. Also, $|^3J_{PC} + {}^5J_{PC}|$ may be zero for the same reason. Similarly, it may be concluded from the spectral data[7] on alkylphosphine complexes of these metals that $^2J_{PC} = -{}^4J_{PC} \neq 0$ and $|^1J_{PC} + {}^3J_{PC}| \neq 0$ in line with the above arguments. For organodiphosphines of the type $R_2PCH_2CH_2PR_2$ it appears[18] that $^1J_{PC} = -{}^2J_{PC}$. Consequently, algebraic cancelation of coupling in $[A]_2X$ spin systems of compounds containing two phosphorus nuclei may be fairly common in ^{13}C NMR.

Conclusion

Although it was hoped at the outset of this investigation that the geometry of phosphite complexes of the type ML_2X_2 could be determined from their ^{13}C NMR spectra, it appears that this will be the exception rather than the rule. This is so, since $^2J_{PP}$ is generally larger than 25 Hz for the palladium(II)–phosphorus ester complexes regardless of geometry.[19] Generally, however, the geometry may be ascertained by utilizing a combination of ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra.[8,19,20]

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Registry No. $(MeO)_3P$, 121-45-9; $(EtO)_3P$, 122-52-1; $(o\text{-allyl})_3P$, 102-84-1; $(i\text{-PrO})_3P$, 116-17-6; $(o\text{-neopentyl})_3P$, 14540-52-4; *cis*-$[(MeO)_3P]_2PdCl_2$, 17787-26-7; *cis*-$[(MeO)_3P]_2PtCl_2$, 28374-51-8; *cis*-$[(EtO)_3P]_2PdCl_2$, 15649-89-5; *cis*-$[(o\text{-allyl})_3P]_2PdCl_2$, 57738-91-7; *trans*-$[(i\text{-PrO})_3P]_2PdCl_2$, 57738-92-8; *cis*-$[(i\text{-PrO})_3P]_2PtCl_2$, 21869-63-6; *trans*-$[(o\text{-neopentyl})_3P]_2PdCl_2$, 57738-93-9; *trans*-$[(o\text{-neopentyl})_3P]_2PtCl_2$, 57738-94-0; *cis*-$[(PhO)_3P]_2PdCl_2$, 38897-83-5; *cis*-$[(PhO)_3P]_2PtCl_2$, 30053-58-8; *cis*-$[(EtO)_3P][Ph_3P]PdCl_2$, 57738-95-1; *cis*-$[(MeO)_3P][Et_3As]PdCl_2$, 57739-00-1; *cis*-$[(PhO)_3P][Ph_3P]PdCl_2$, 57738-96-2; ^{13}C, 14762-74-4.

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Contribution from the Departments of Chemistry,
St. Louis University and Fontbonne College,
St. Louis, Missouri 63103

Synthesis and Spectroscopic Studies of β,β',β''-Triaminotriethylamine Chelates of the Trivalent Lanthanide Perchlorates

Mary F. Johnson and John H. Forsberg*

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Few NMR isotropic shift studies of lanthanide complexes with strictly nitrogen donors have been attempted[1] although the volume of literature concerning the paramagnetic lanthanide shift reagents involving oxygen-donor ligands has been substantial. The mechanism of interaction between the paramagnetic lanthanide ion and ligand protons has been shown to be a combination of contact and dipolar effects for the nitrogen-donor ligands, while the isotropic shifts of substrate protons in the presence of lanthanide shift reagents are thought to be primarily dipolar in nature.[2]

High-coordinate lanthanide complexes derived from the strongly basic nitrogen donors, ethylenediamine,[3] 1,2-propanediamine,[4] and diethylenetriamine[5] with a variety of anions utilizing a nonaqueous solvent as the reaction medium have been isolated. In addition, both the mono- and bis(β,β',β''-triaminotriethylamine (tren)) chelates of the lanthan-

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* To whom correspondence should be addressed at St. Louis University.