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ANALYSIS OF THE ^{1}H NMR SPECTRUM OF DI-n-BUTYL-2,2-d_2-BIS(TRIPHENYLPHOSPHINE)PLATINUM(II)

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SUMMARY

The deuterium-decoupled ^{1}H NMR spectrum of di-n-butyl-2,2-d_2-bis(triphenylphosphine)platinum(II) (I) has been analyzed.

INTRODUCTION

Qualitative analyses of ^{1}H NMR spectra have been useful in establishing the configurations of organometallic compounds containing two phosphine and two σ-alkyl ligands[1,2]. Typically, spectra have been examined for evidence of strong spin–spin coupling between phosphorus nuclei. If a spectrum under analysis has the qualitative form expected to result from strong virtual coupling of σ-alkyl protons to *both* phosphorus nuclei, the phosphine ligands are assumed to be *trans*; if the spectrum shows little or no evidence of virtual coupling, the phosphine ligands are assumed to be *cis*[3].

Although accurate determinations of the spectral parameters characterizing organometallic compounds having the composition R_2ML_2 would both increase confidence in the assigned configurations and provide physical data of use in discussions of other aspects of their structure, few detailed analyses of the $AA'X_nX'_n$ spin systems characteristic of these substances have been described. This shortage of spectral data arises in part because the quality of the NMR spectra of these organometallic compounds is frequently such that the low-intensity lines necessary for precise analyses are difficult to identify, and in part because the analyses have proved difficult to carry out, even given spectra of good quality. We recently required a configurational assignment for di-n-butyl-2,2-d_2-bis(triphenylphosphine)platinum(II) (I) as part of a study of the mechanism of thermal decomposition of this substance[4]. Our attempts to analyze the deuterium-decoupled ^{1}H NMR spectrum of (I) encountered certain ambiguities associated with examinations of spin systems of the $AA'X_2X'_2$ type. We summarize the results of our efforts here, both to illustrate these ambiguities, and to provide a starting point for other analyses in similar systems.

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RESULTS AND DISCUSSION

The general features of $AA'X_nX'_n$ spin systems have been discussed theoretically, under the assumption that $J(XX')=0$[5]. The H portion of an $PP'H_2H'_2$ spectrum may have a total of five pairs of lines centered about $\nu(H)$. Half of the total intensity lies in a doublet (lines 1 and 2 in Fig. 1) with a separation $N=J(PH)+J(PH')$. The remaining intensity is divided between two pairs of "inner" transitions (4,5 and 8,9) and two pairs of "outer" transitions (3,6 and 7,10), the latter having low and often negligible intensity. The "inner" lines fall outside of lines 1,2 if $J(PH)$ and $J(PH')$ have opposite signs. Neither the magnitudes of the coupling constants $J(HH)$ and $J(H'H')$, nor the relative signs of $J(PP')$ and $J(PH)$ [or $J(PH')$] can be determined from the H portion of the spectrum.

The portion of the spectrum of (I) (Fig. 2) assigned to the methylene protons adjacent to the platinum atom is the apparent "quartet" centered at δ 1.04 ppm. One ^{195}Pt satellite (35% natural abundance) is visible at 1.40 ppm [$J(^{195}Pt\ ^1H)=72$ Hz]; the second is hidden under the resonances due to the ethyl group between 0.4–0.9 ppm.

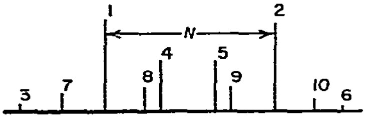

Fig. 1. Schematic ^{1}H spectrum of a $PP'H_2H'_2$ spin system having $J(PH) > J(PH') > 0$ and $J(PP') > J(HH') \sim 0$.

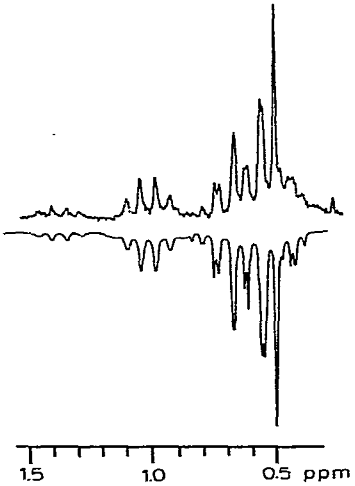

Fig. 2. Observed (upper) and calculated (lower) 100 MHz, deuterium-decoupled, ^{1}H NMR spectra of *cis*-di-n-butyl-2,2-d_2-bis(triphenylphosphine)platinum(II), (I) in methylene chloride solution. Parameters used to calculate the theoretical spectrum are listed in Table 1.

The central resonances of the methylene "quartet", separated by 6.0 Hz, must include the 1 and 2 transitions (and perhaps other lines) since they account for more than half of the intensity of the total pattern. Therefore the quantity $N=J(PH)+J(PH')$ must equal 6.0 Hz. The remaining pair of lines must be assigned to the "inner" transitions 4, 5, 8, and 9 (or to the 4,5 transitions alone, or to the 8,9 transitions alone). Since the

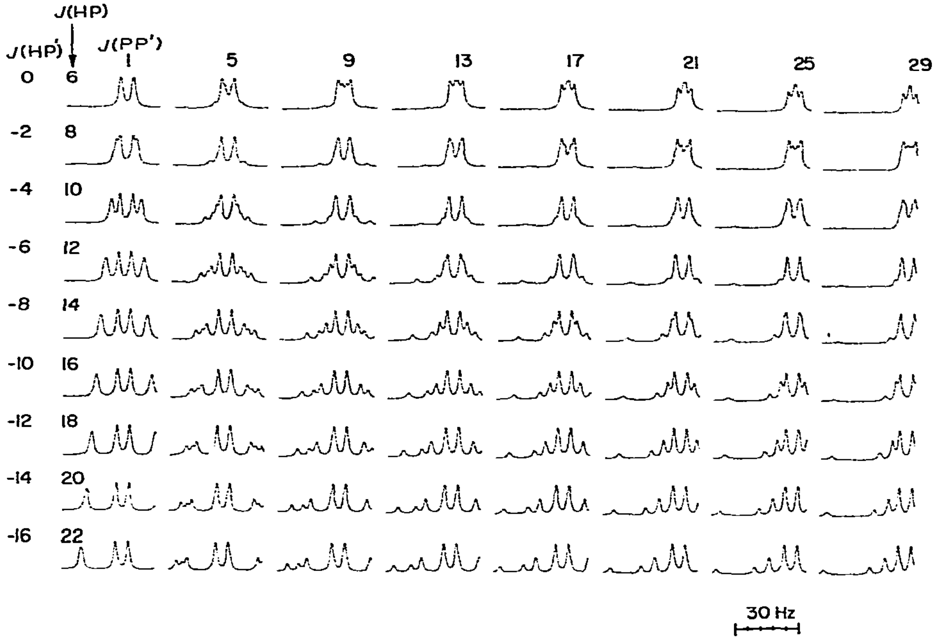

Fig. 3. ^{1}H spectra calculated for a $PP'H_2H'_2$ spin system as a function of $J(PP')$ and $J(HP)$, with the assumptions that $J(HP')+J(HP)=6$ Hz, and that $J(HH)=J(HH')=0$. Magnitudes of coupling constants are expressed in Hz. Spectra are symmetric around their midpoint; some lines on the right side of spectra have been omitted to conserve space.

"inner" lines fall outside the 1 and 2 transitions, $J(PH)$ and $J(PH')$ must have opposite signs*.

Since the magnitude of the geminal coupling constant $J(HH)=J(H'H')$ has no influence on the H portion of the spectrum, the spectral line shape is determined by the three independent variables $J(PH)$ [or $J(PH')$], $J(PP')$ and $J(HH')$. Spectra were thus calculated** for $+6\text{ Hz}\leqslant J(PH)\leqslant +22$ Hz and $\pm 1\text{ Hz}\leqslant J(PP')\leqslant \pm 29$ Hz, with the restricting condition that $J(PH)+J(PH')=+6$ Hz and the assumption that $J(HH')=0$ Hz; these spectra are shown in Fig. 3. The sign of $J(PP')$ had no influence on the spectra. Additional spectra could in principle be calculated for values of $J(PP') > 29$ Hz and for $J(PH) > 22$ Hz without duplicating those included in Fig. 3; however, extending the matrix of spectra to the left [$J(PP') < 0$ Hz] or top [$J(PH')+J(PH) = 6$ Hz, $J(PH) < 6$ Hz] duplicates spectra already shown. Large values of $J(PP')$ were not examined, since the magnitudes of $J(PH)$ and $J(PH')$ required to bring the calculated spectra into even casual agreement with experimental spectra for such values are unreasonably large.

Two features of the calculated spectra of Fig. 3 are pertinent to attempts to fit a calculated spectrum to the observed spectrum of (I). First, wide ranges of $J(PP')$ and $J(PH)$ can be found which give closely similar, although not identical, spectra. Thus,

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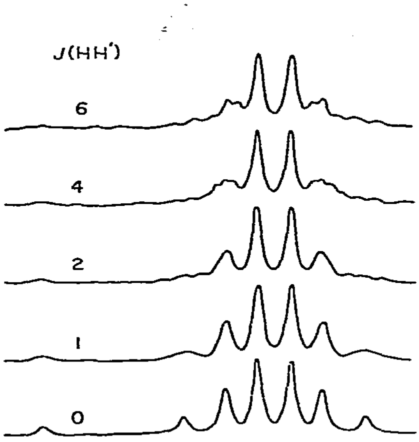
* Values of $J(PH)$ and $J(PH')$ having the *same* signs, and magnitudes such that $N=6$ Hz, do not yield calculated spectra resembling the observed spectrum.

** Calculations were performed using a slightly modified version of the program LAOCN3[6].



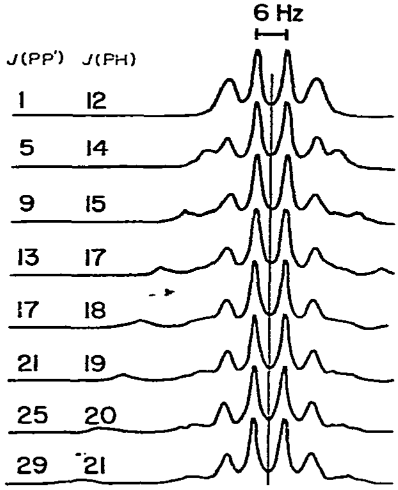


Fig. 4. Calculated ^{1}H PP'H$_2$H'$_2$ spectra with J(HH)=0, J(PP)=33, J(HP)=22, and J(HP')=16 Hz, showing the effect of the magnitude of J(HH') on the appearance of the spectra.

Fig. 5. Calculated ^{1}H PP'H$_2$H'$_2$ NMR spectra that represent potential matches to the observed spectrum of (I) with J(HH)=0, J(HH')=1.5, and J(HP)+J(HP')=6 Hz.

it is unlikely that spectral analysis in spin systems resembling that of (I) will lead to accurate values of coupling constants, unless spectra of very high resolution are available. Second, in fact, none of the spectra calculated over the range of values of coupling constants represented by Fig. 2 closely matches the observed spectrum.

The major source of the discrepancy between calculated and observed spectra was found to be the assumption that J(HH')=0. Fig. 4 demonstrates that the effect of values of J(HH') >0 on the shape of spectra is to broaden or split the lines, with this effect being most pronounced on the "outer" lines. The spectra of Fig. 4 with J(HH')=1 or 2 Hz are in satisfactory agreement with the observed spectra, since the weak and broadened outer lines might be hidden either by noise or by the ^{195}Pt satellites*. This selective broadening of outer transitions also takes place when non-zero values of J(HH') are introduced into the other spectra of Fig. 3 which resemble the observed spectrum. The calculated spectra reproduced in Fig. 5 illustrate the range of values of J(PP') and J(PH) which can be brought into reasonable apparent agreement with the observed spectrum by adjustment of values of the various coupling constants.

The final parameters chosen to describe the spectrum of (I) were selected somewhat subjectively on the basis of the apparent relative intensities of the inner and outer lines of the methylene "quartet". For low values of J(PP'), the inner and outer lines have approximately equal intensities; for high values of J(PP'), intensity from the outer lines of the quartet is transferred to the unobserved broad lines in the wings of the spectra. Since the *cis*-J(PH) coupling is believed to be small**, the minimum possible magnitude was chosen for J(PH), consistent with a value for J(PP') sufficient-

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* For other spectra in which the outer lines are not observed see ref. 7.

** Available evidence also indicates that *cis*-J(PH) < *trans*-J(PH) in compounds resembling (I)[8].

ly large to give intensities for the inner and outer lines of the "quartet" in reasonable agreement with those observed. Table 1 summarizes the parameters used to calculate the theoretical spectrum shown in Fig. 2. These parameters are not in close agreement with those reported for *cis*-$(CH_3)_2Pt[P(C_2H_5)_3]_2$[9] [$J(PP') \sim 2$ Hz, $J(PH) = \mp 6.5$, $J(PH') = \pm 8.2$] and *cis*-$(CH_3)_2Pt[PhP(CH_3)_2]_2$[2] [$J(PP') \sim 0$ Hz, $J(PH) = \mp 6.3$, $J(PH') = \pm 8.2$], although the values of J(Pt, H) observed for these compounds (67.6 and 67.1 Hz respectively), and for *cis*-$(CH_3)_2Pt(PPh_3)_2$ (69 Hz)[10], are similar to that found here. It is not presently clear whether these differences are artifacts of the spectral analyses, or whether they reflect real differences in the magnetic parameters characterizing these compounds*.

TABLE 1

CHEMICAL SHIFTS (ppm) AND COUPLING CONSTANTS (Hz) FOR *cis*-DI-n-BUTYL-2,2-d_2-BIS(TRIPHENYLPHOSPHINE)PLATINUM(II) (I)

Chemical shifts butyl protons $\overset{a}{CH_3}-\overset{b}{CH_2}-CH_2-\overset{c}{CH_2}-Pt$		Coupling constants	
δH_a	0.52	$J(PH)$ *cis*[a]	∓ 13
δH_b	0.72	$J(PH')$ *trans*[a]	± 19
δH_c	1.04	$J(PP')$	21
		$J(HH')$	1.5
		$J(PtH)$	72
		$J(H_aH_b)$	7.3

[a] The assignment of $J(PH)$ and $J(PH')$ to *cis*- and *trans*-couplings is made by analogy with previous work[1,7].

Although this work accomplished its original intent of establishing the *cis*-stereochemistry for (I), and provides a set of coupling constants which are believed to be reasonably accurate, it also points out the potential ambiguities which must be resolved in carrying out spectral analyses of spin systems of the type exemplified by (I).

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* The relatively large value of $J(HH')$ used in this work has some precedent in coupling constants observed for $(CH_3)_nX$ compounds[11], and for $(CH_3)_2Hg$ [$J(HH') = 0.45$ Hz][12].

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