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Contribution from the Department of Chemistry and Biochemistry,
San Francisco State University, San Francisco, California 94132

Structural Analysis of Platinum Phosphine Complexes by Two-Dimensional ^{31}P NMR Spectroscopy

Jane V. Zeile Krevor,* Ursula Simonis, and Julianne A. Richter II

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The synthesis and characterization of a new platinum(I) phosphine complex, $[Pt_2(\mu\text{-dppm})(\eta^1\text{-dppm})dppeCl]Cl$, is reported. This unique complex is the first example of a stable Pt(I) dimer in which all three types of coordination possible for a diphosphine ligand are observed. To structurally characterize this complex, we have employed one- and two-dimensional ^{31}P NMR spectroscopy. Using 14 other structurally simpler platinum phosphine complexes, it is established that the ^{31}P homonuclear shift correlated spectroscopy (COSY) technique provides valuable information about both the phosphorus–phosphorus and platinum–phosphorus couplings, especially when the resonances in the one-dimensional spectra are poorly resolved. The $^2J_{Pt-P}$ and $^3J_{Pt-P}$ coupling constants are obtained from the relative positions of the observed cross-correlations with respect to the main phosphorus resonances. From the analysis of the coupling patterns observed and the coupling constants measured from the two-dimensional data sets, determination of the geometrical arrangement of the phosphine ligands is demonstrated. The structural assignment of the new Pt(I) complex is based on the analysis of its ^{31}P COSY map and further supported by the COSY studies of the other platinum complexes.

Introduction

Platinum complexes containing phosphine ligands exhibit diverse chemical properties as evidenced by the different oxidation states for platinum (complexes with Pt(0), -(I), -(II), and -(IV) are well-known) and by the different reactions they will undergo, i.e. substitution, oxidative addition, reductive elimination, electron transfer, and protonation.[1] The characterization of these complexes and their reactions has been greatly aided by the development of ^{31}P NMR spectroscopy.[2] Because of the 100% isotopic abundance of the ^{31}P nucleus ($I = {}^1/_2$), good quality, highly resolved spectra can be obtained on a relatively dilute sample. In addition, the presence of ^{195}Pt (33.8% isotopic abundance, $I = {}^1/_2$) results in platinum–phosphorus coupling patterns which are often characteristic of the geometrical arrangement of the phosphine ligands.[3] Through comparison of a large number of $^1J_{Pt-P}$ and $^2J_{P-P}$ coupling constants, it is now possible to determine which ligands are trans to the coordinated phosphine molecule.[4] Even the relative strength of the Pt–Pt bond in dinuclear Pt(I) complexes can be predicted on the basis of the $^2J_{Pt-P}$ coupling constants of the phosphine ligands.[5]

For mononuclear Pt(II) and symmetrical dinuclear Pt(I) complexes, such as $Pt_2(dppm)_2Cl_2$ (dppm = bis(diphenylphosphino)methane), which often have well-resolved one-dimensional spectra, the assignment of a particular phosphorus ligand to a resonance in the one-dimensional ^{31}P NMR spectrum is generally not difficult. Due to the large spread of the chemical shifts of certain resonances, the Pt–P and P–P coupling constants can usually be determined directly from the highly resolved spectra.[6] For the dinuclear compounds, the coupling constant information is contained in the platinum–phosphorus satellite peaks. However, for unsymmetrical complexes such as $Pt_2(dppm)_2XY^+$, where X is a halide and Y is a hydride or another phosphine ligand, the one-dimensional ^{31}P NMR spectra appear complex and often contain phosphorus resonances that are overlapping and poorly resolved.[7] In these cases, only a limited number of Pt–P or P–P coupling constants have been successfully measured and some of these values could only be determined by spectral simulation.

The use of two-dimensional (2D) ^{31}P homonuclear shift correlated spectroscopy (COSY) for the structural characterization of organometallic compounds containing phosphorus has been reported for just a few complexes,[8] and only a recent report involves a platinum phosphine complex, a platinum–gold cluster, characterized by low-temperature ^{31}P COSY studies.[9] During our own electrochemical investigations of $Pt_2(dppm)_2Cl_2$ and related dimers,[10] we have found that the characterization of the platinum phosphine complexes is readily accomplished using ^{31}P COSY studies. Application of this technique leads to the determination of Pt–P and P–P coupling constants which are not accessible from the poorly resolved one-dimensional (1D) data.[11] In addition, along with the magnitude of the $^2J_{Pt-P}$ coupling constant, its sign can be determined from the relative positions of the cross peaks with respect to the main phosphorus resonances.

Considering the number and significance of platinum-containing phosphine complexes, we wish to demonstrate in this paper that the readily available ^{31}P COSY technique is an important tool for the structural assignment of platinum phosphine complexes. In order to show the general application of this method, we have applied it to the structural characterization of the newly synthesized Pt(I) dimer $[Pt_2(\mu\text{-dppm})(\eta^1\text{-dppm})dppeCl]Cl$ (**1**), shown in Figure 1. In order to substantiate the proposed structure of **1**, we have extended our studies to a series of related platinum(I) and platinum(II) phosphine complexes, **2–15**, also depicted in Figure 1. The analyses of the ^{31}P COSY data for these complexes are also presented.

Experimental Section

Preparation of Compounds. Platinum complexes **2–15** were synthesized according to published procedures.[6,7,10,12,13,20] Bis(diphenyl-

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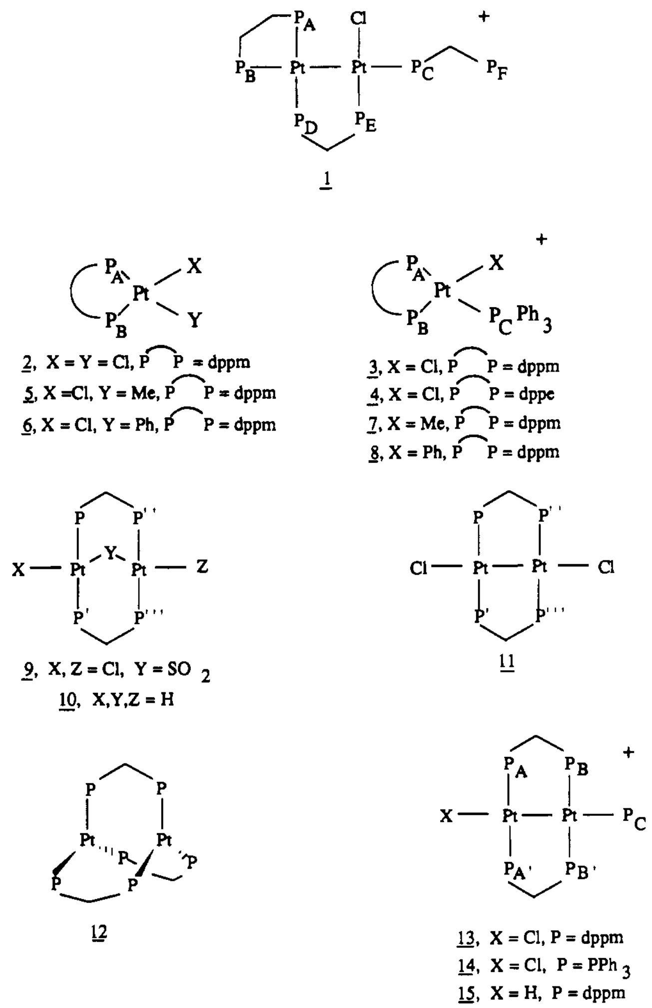

Figure 1. Structures of the Pt(I) and Pt(II) complexes investigated by two-dimensional ^{31}P NMR spectroscopy.

Table I. ^{31}P NMR Chemical Shifts and Coupling Constants for $[Pt_2(dppm)_2dppeCl]^+$

chem shift,[a] ppm	$^1J_{Pt-P}$, Hz	$^2J_{Pt-P}$, Hz	$^2J_{P-P}$, Hz	$^3J_{Pt-P}$
P_A, 46.2	P_A, 3127	P_A, nm[b]	P_AP_D, 389	na[c]
P_B, 45.1	P_B, 1974	P_B, 514	P_BP_A, 36	na
P_C, 23.4	P_C, 2286	P_C, 681	P_CP_B, 214	na
P_D, −12.8	P_D, 3386	P_D, −98	P_DP_E, 43	na
P_E, −8.7	P_E, 4347	P_E, −77		na
P_F, −20.1	na	na	P_FP_C, 29	P_F, +21

[a] Relative to external TMP. [b] Nm = not measured. [c] Na = not applicable.

Table II. ^{31}P NMR Chemical Shifts and Coupling Constants for the Mononuclear Pt(II) Complexes

complex	chem shift,[a] ppm P_A, P_B, P_C	$^1J_{Pt-P}$, Hz P_A, P_B, P_C	$^2J_{P-P}$, Hz P_AP_B, P_BP_C, P_AP_C
2	−67.4	3079	na[b]
3	−52.2, −51.5, 19.8	2002, 3029, 2379	71, 20, 385
4	52.4, 44.9, 22.5	2344, 3516, 2435	8, 23, 382
5	−37.6, −32.6	3957, 1290	41
6	−43.0, −41.3	3915, 1212	42
7	−32.9, −31.4, 25.2	2465, 1348, 2796	41, 36, 392
8	−35.4, −36.1, 18.3	2500, 1275, 2798	36, 22, 390

[a] Relative to external TMP. [b] na = not applicable.

phosphino)methane (Strem), bis(diphenylphosphino)ethane (Strem), triphenylphosphine (Aldrich), 1,5-cyclooctadiene (Aldrich), and sodium borohydride (Aldrich) were used as received. SO_2 gas was generated from the mixture of concentrated HCl (EM Science) and sodium sulfite (Spectrum). Nondeuterated solvents (EM Science) were dried and distilled under nitrogen prior to use. Deuterated solvents (Aldrich) were used as received.

$[Pt_2(dppm)_2dppeCl]Cl$ (1). To a suspension of $Pt_2(dppm)_2Cl_2$ (**11**) (0.150 g, 0.122 mmol) in 2.5 mL of $CDCl_3$ was added 0.050 g (0.12 mmol) of dppe. The suspended solid dissolved immediately, and a dark yellow solution formed. A yellow solid was precipitated by addition of petroleum ether to the solution. The precipitate was separated by filtration, washed with petroleum ether, and dried under vacuum to yield 0.184 g of **1** (92.6%, based on **11**). The solid was recrystallized at −10 °C from a 4:1 mixture of methylene chloride/hexane: decpt 174 °C; ^1H NMR ($CDCl_3$) δ 8.34–6.02 (m, 12 H, C_6H_5), 5.00–4.21 (m, 2 H, μ-PCH_2P), 2.43 (br, m, 2 H, η^1-PCH_2P), 2.27 (br, s, 4 H, PCH_2CH_2P); UV/vis (CH_2Cl_2) λ_{max} 392 nm, ϵ 1.76×10^4 M^{-1} cm^{-1}. Anal. Calcd for $C_{76}H_{68}Cl_2P_6Pt_2$: C, 56.06; H, 4.21. Found: C, 56.85; H, 4.61.

NMR Spectroscopy. Room-temperature one-dimensional proton NMR spectra were recorded on a General Electric QE-300 300-MHz NMR spectrometer equipped with a 1280 computer system, locked on solvent deuterium, and referenced to tetramethylsilane (TMS) as an internal standard. Solvents most frequently used were $CDCl_3$ and CD_2Cl_2, and the concentration of the samples was about 0.03 M. Typically, one-dimensional ^1H spectra of the platinum phosphine complexes were acquired by using spectral widths of 6024 Hz, 16K data points, and a 1-s repetition time. In general, 32 transients were obtained with a 3-μs pulse (90° pulse = 9 μs).

One-dimensional ^{31}P NMR spectra of all complexes were recorded at room temperature on the General Electric GN-300 300-MHz NMR spectrometer equipped with a 1280 computer system and a process controller using a 10-mm broad-band probe. Typically, data were acquired by using spectral widths of 20 000 Hz, 16K data points, a recycle delay of 5 s, and broad-band proton decoupling. In general, 256 transients were obtained with a 18-μs 90° pulse. A solution of trimethyl phosphate (TMP) in deuterobenzene served as an external standard.

Two-dimensional ^{31}P homonuclear shift correlated (COSY) spectra were recorded on the General Electric GN-300 300-MHz instrument. Quadrature detection was used with typically a sweep width of 6024 Hz in F_2 and ±3012 Hz in F_1. The original size in F_2 was 1024 w (words). A total of 256 FIDs were taken in F_1 with 256 scans each. The recycle delay was set to 1 s to give a total measuring time of about 18 h. Either a nonshifted sine bell function or a sine bell function of 18 deg was used to process the two-dimensional data sets. The data were zero-filled once in F_1 to give a final matrix of 512 w × 512 w. No proton decoupling was applied.

Results and Discussion

The platinum complexes investigated by two-dimensional ^{31}P NMR spectroscopy are shown in Figure 1. Complexes **2–8** are monomers which contain a chelating bis(diphenylphosphino)methane, dppm, or a chelating bis(diphenylphosphino)ethane, dppe, ligand whereas complexes **9–15** represent important dimeric dppm compounds. The structurally uncharacterized complex **1** is unique because it exhibits all three possible coordination geometries (monodentate, chelating, or bridging) for a diphosphine ligand. This complex was synthesized by addition of 1 equiv of bis(diphenylphosphino)ethane, dppe, to a solution of $Pt_2dppm_2Cl_2$ (**10**) in $CDCl_3$, via a ligand substitution reaction, in which a chloride ligand is displaced by a phosphine molecule, a reaction well-known to occur for both mononuclear and dinuclear platinum complexes.[12] The proposed structure for this complex, shown in

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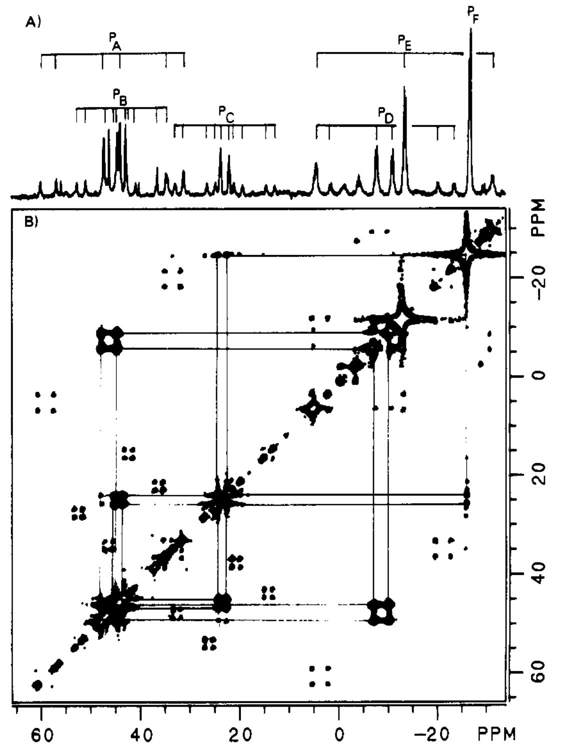

Figure 2. (A) One-dimensional and (B) two-dimensional ^{31}P NMR spectra of [Pt(dppm)$_2$dppeCl]Cl (**1**) in CDCl$_3$. Resonances are assigned according to the structure shown in Figure 1. Coupling pathways between the main phosphorus resonances are indicated by the boxes drawn.

Figure 1, was deduced from one- and two-dimensional ^{31}P NMR spectroscopy. As can be clearly seen from the one-dimensional spectrum in Figure 2A, the new complex **1** shows a very complex 1D spectrum. This is a direct result of P–P and Pt–P couplings due to the four overlapping spin systems associated with the Pt nucleus (one with no ^{195}Pt, two with one ^{195}Pt, one with two ^{195}Pt). To unambigously assign all resonances observed and to determine the sign and magnitude of all coupling constants, it was necessary to analyze its COSY map shown in Figure 2B.

The analysis of the ^{31}P COSY spectrum of **1** is facilitated by first analyzing the simple spectra of the related mononuclear complexes **2**–**4**, the structures of which can readily be deduced from the one-dimensional ^{31}P NMR spectra. The chemical shifts and the $^1J_{\text{Pt-P}}$ and $^2J_{\text{Pt-P}}$ coupling constants for these monomers are reported in Table II and agree well with values previously reported for these types of complexes.[12b,13]

The one- and two-dimensional ^{31}P NMR spectra of **2**, the simpliest of the monomers studied, can readily be predicted from its known structure. The 1D spectrum (supplementary material, Figure 5A) consists of a singlet at −67.5 ppm due to the chemically equivalent phosphorus nuclei present in the molecules that do not contain ^{195}Pt whereas the doublet centered around the main phosphorus resonance, the platinum satellite peaks, are derived from Pt–P interactions. That these satellite peaks are indeed a result of Pt–P couplings can be determined from the ^{31}P COSY map (supplementary material, Figure 5B), which shows, as expected, only the three diagonal cross-correlations representing the resonances in the 1D spectrum. No off-diagonal peaks are observed among the satellite resonances under any experimental condition since these are derived from Pt–P and not P–P couplings. However, off-diagonal peaks are observed between satellite resonances in the 2D spectra of the other monomeric and dimeric complexes and are a result of P–P couplings. These cross-correlations are essential for the unambiguous assignment of either overlapping or poorly resolved main phosphorus resonances as will be discussed below.

The one-dimensional spectrum of **3**, [PtdppmPPh$_3$Cl]Cl, shown in Figure 3A, is characteristic of a square planar complex which contains three chemically inequivalent phosphorus nuclei coordinated to platinum.[14] All of the resonances are marked according to the structure shown in Figure 1. The resonances of the dppm ligand, P$_A$ and P$_B$, are shifted upfield from uncoordinated dppm which resonates at −23 ppm. This upfield shift upon coordination is typical of the dppm ligand and is due to the formation of a four-membered ring.[15] The upfield portion of the spectrum is complicated by the small chemical shift difference of P$_A$ and P$_B$, but upon closer investigation of this spectral area, the expected doublet of doublets that result from cis and trans P–P coupling is observed. On the basis of previous investigations,[12b,14] P$_A$ was assigned to the resonance which has the larger coupling constant (385 Hz, Table II) consistent with the phosphorus atoms being trans to each other. P$_B$ is coupled to both P$_A$ and P$_C$ with the larger coupling constant (71 Hz) due to ^2J(P$_A$,P$_B$). The signals due to the triphenylphopshine ligand, P$_C$, are shifted downfield from the phosphorus resonance of free PPh$_3$ and resonate at about −5 ppm.

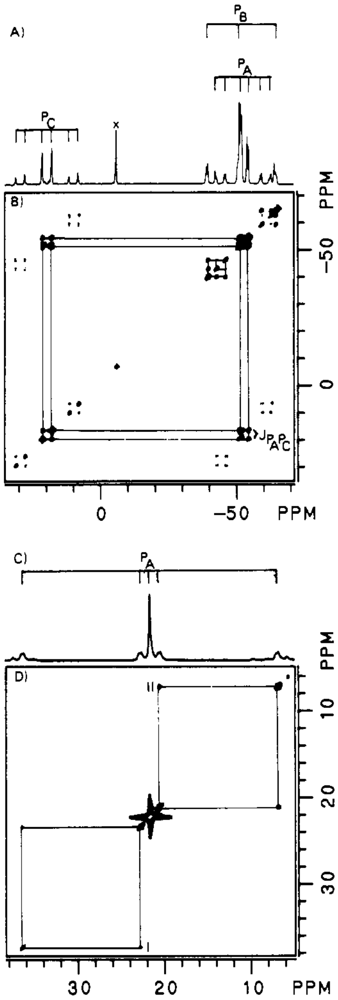

Figure 3. (A) One-dimensional and (B) two-dimensional ^{31}P NMR spectra of [PtdppmPPh$_3$Cl]Cl (**3**). The resonance marked × in (A) is due to free PPh$_3$. Coupling pathways between the main phosphorus resonances in **3** are indicated by the boxes drawn. In (C) and (D) are shown the one- and two-dimensional ^{31}P NMR spectra of Pt$_2$(dppm)$_2$Cl$_2$SO$_2$ (**9**). The boxes drawn indicate the cross-correlations between satellite peaks. The horizontal separation of cross-peaks I and II is a measure of the $^2J_{\text{Pt-P}}$ coupling constant.

Although the structure of **3** can be assigned from the one-dimensional data alone, it is important to establish that the same result can be more easily obtained from the analysis of the two-dimensional spectrum shown in Figure 3B. As expected from the structure of **3**, the strongest cross-peaks observed in the 2D COSY map indicate coupling between the two main phosphorus resonances, P$_A$ and P$_B$. In addition, strong cross-peaks are observed between P$_A$ and P$_C$ and P$_B$ and P$_C$. The less intense correlations are due to the P–P couplings among the satellite peaks of the main phosphorus resonances, P$_A$, P$_B$, and P$_C$, and can be used to assign these couplings. For example, cross-peaks are observed between the satellite resonances of P_A and P_B as clearly marked in Figure 3, indicating that P_A and P_B are indeed coupled to each other. Weaker cross-correlations are also observed between the satellite peaks of P_A and P_C but not between those of P_B and P_C. This result suggests that the coupling between P_B and P_C is smaller than that between P_B and P_A and P_A and P_C. Presumably, because P_C and P_B are cis to each other and only one coupling pathway exists between them, the coupling will be weaker than that between P_A and P_B, where two two-bond coupling pathways are present.[12b] Although this conclusion is supported by the measured coupling constants, $^2J_{P_BP_C}$, 20 Hz, being smaller than $^2J_{P_AP_B}$, 71 Hz, it is made with some caution since there is no theoretical verification that the intensity of a cross-peak is directly related to the magnitude of the coupling.[16] When more than one coupling pathway exists, the signs of the contributing coupling constants may be opposite, rendering a coupling constant value that is small in magnitude even when the coupling is considered strong.[17]

The one-dimensional spectrum of [PtdppePPh$_3$Cl]Cl (**4**) (supplementary material, Figure 6A) is somewhat more difficult to analyze than that of **3** because all of the phosphorus resonances have similar chemical shift values resulting in resonance overlap. However, the identification of the resonances due to the triphenylphosphine ligand and the dppe ligand was easily accomplished from the analysis of the COSY spectrum (supplementary material, Figure 6B). Once these resonances were identified, it became clear that the one-dimensional spectrum displayed the expected doublet of doublets for both P_A and P_C and only a narrow doublet for P_B. Since P_B is cis to both P_A and P_C, the P_B–P_C coupling should be weaker than the P_B–P_A coupling because only one coupling pathway is present between P_B and P_C. However, the small coupling constant $J_{P_AP_B}$ of 8 Hz is most likely a result of the combination of a positive two-bond coupling through the metal and a negative three-bond coupling through the ethylene carbon atoms. In the two-dimensional spectrum, the only cross-peaks that are observed are between the two strongly coupled phosphorus nuclei that are trans to one another, P_A and P_C.

The one- and two-dimensional ^{31}P NMR spectra of complexes **5–8** can be analyzed in the same manner as described for **3** and **4**. These spectra are included in the supplementary material, Figures 7–10, and the chemical shifts and coupling constants are reported in Table II. All structural assignments were based on the cross-peak information provided by the two-dimensional data and were further substantiated by the coupling constants determined from the one-dimensional spectra.

In order to structurally characterize the new complex **1**, it was necessary to explore some examples of known Pt(I) dimers with more complex spin systems. A number of dinuclear Pt(I) complexes containing two bridging dppm ligands have been well characterized by NMR, X-ray crystallography, and elemental analysis.[6,7,18] We investigated the COSY spectra of seven of these dimers starting with the symmetrical complexes **9–12**, which have the least complicated spectral appearance, in order not only to obtain the magnitude of the coupling constants but also to establish the sign of the $^2J_{Pt-P}$ coupling using the methods described by Carty et al. and us in earlier investigations.[8c,11] This study was concluded with three unsymmetrical complexes, **13–15**, which contain three and four chemically inequivalent phosphorus nuclei.

The fairly simple one- and two-dimensional ^{31}P NMR spectra of **9** are shown in Figure 3C,D, respectively. The central resonance at 21.8 ppm in the one-dimensional spectrum arises from the four equivalent phosphorus nuclei in molecules that contain no ^{195}Pt. The two sets of platinum satellite peaks at 7.4, 36.6 and 20.8, 23.2 ppm are due to two overlapping spin systems, an AA′A″A‴X system and an AA′A″A‴XX′ system as previously discussed in detail.[6b] The splitting pattern observed for the satellite peaks at 7.4 and 36.6 ppm is a direct result of long-range coupling of P to P″ and P‴, whereas the splitting pattern observed for the other set of satellite peaks which arise from the two-bond coupling to P″ to the same ^{195}Pt nucleas is a result of coupling between P″ and P, P′. Coupling constants based on the analysis of the satellite peaks and chemical shift values are listed in Table III.

Table III. ^{31}P NMR Chemical Shifts and Coupling Constants for the Dinuclear Complexes

complex	chem shift,[a] ppm P_A, P_B, P_C, P_D	$^1J_{Pt-P}$, Hz P_A, P_B, P_C	$^2J_{Pt-P}$, Hz P_A, P_B, P_C	$^3J_{Pt-P}$, Hz P_D
9	21.8	4451	+52	na[b]
13	−3.5, −0.3, −3.5, −28.8	2844, 2913, 2071	−76, −54, 583	+58
14	−3.5, −0.2, 2.5	2886, 2856, 2207	−84, −137, 1232	na
15	9.0, 10.4, 19.5, −29.7	3533, 2874, 2720	−85, −12, 1364	+24

[a] Relative to external TMP. [b] Na = not applicable.

The cross-peaks present in the COSY map shown in Figure 3D are derived from the coupling between P and P″, P‴ as well as between P″ and P, P′. The horizontal separation of the cross-peaks marked I and II in Figure 3D is a direct measure of the magnitude of the $^2J_{Pt-P}$ coupling constant, whereas the vertical separation is a measure of the magnitude of the $^1J_{Pt-P}$ coupling constant, which is always positive.[19] The position of I and II relative to the central phosphorus resonance is indicative of a positive $^2J_{Pt-P}$ coupling constant as described in detail in a previous paper.[11]

The complexity of the one-dimensional ^{31}P NMR spectrum increases significantly when the dinuclear complex is no longer symmetrical because of the overlapping spin systems of the four possible isotopomers.[20] An example is the one-dimensional spectrum of the complex salt [Pt$_2$(μ-dppm)$_2$(η^1-dppm)Cl]Cl (**13**) shown in Figure 4A. As can be seen, the main phosphorus resonances are not well resolved and the satellite peaks are broad and ill-defined even at very high resolution (biggest block size and smallest spectral width possible). Hence, it is not possible to measure the $^2J_{PtP_A}$ or $^2J_{PtPB}$ coupling constant for this complex from the one-dimensional spectrum. Coupling constants that are determined from the 1D spectrum are given in Table III and agree well with those previously reported for this complex.[7,10]

The assigned structure of **13** (Figure 1) is fully supported by its ^{31}P COSY spectrum displayed in Figure 4B. The major cross-peaks observed are indicative of the coupling present between P_A and P_B, P_B and P_C, and P_C and P_D, respectively. The fact that P_A and P_C overlap does complicate the initial interpretation of the one-dimensional spectrum, but the presence of the cross-peaks marked d in the 2D spectrum, which show correlations only to the platinum satellite peaks of P_C, verifies the coupling of P_D to P_C. This in turn substantiates the resonance overlap of P_A and P_C since a major cross-peak is observed between P_D and the overlapping signals of P_A and P_C. The relative positions of the peaks marked d to the main P_D resonance is indicative of the $^3J_{Pt-P}$ coupling between P_D and Pt_B in the molecules where this platinum nucleus is ^{195}Pt. This coupling has not been previously reported and is not observed in the one-dimensional spectrum. The magnitude and sign of the $^3J_{Pt-P}$ coupling constant measured from the horizontal separation of the cross-peaks and their position relative to the main phosphorus resonance for P_D is determined to be +58 Hz. The vertical separation determines the magnitude of the $^1J_{Pt(B)-P_C}$ and $^2J_{Pt(A)-P_C}$ coupling constants. In the same way, the positions of the cross-correlations present between the P_A and P_B satellite peaks were used to measure the magnitude and sign of the previously unreported $^2J_{Pt(A)-P_B}$ and $^2J_{Pt(B)-P_A}$ coupling constants as well as the $^1J_{Pt-P}$ coupling constants for P_A and P_B (Table III). Thus, the analysis of the positions of the cross-peaks involving the platinum satellite peaks does provide coupling constant information that cannot be obtained from the one-dimensional spectrum. This demonstrates one of the major advantages of using the ^{31}P COSY experiment for the characterization of platinum phosphine organometallic complexes.

The ^{31}P COSY spectra of complex **14** was also analyzed to determine the $^2J_{Pt-P_A}$ and $^2J_{Pt-P_B}$ coupling constants from the positions of the cross-peaks with respect to the corresponding main phosphorus resonances. These are reported in Table III. The ^{31}P COSY spectrum of **14**, which is part of the supplementary material, Figure 11, clearly shows coupling between P_A and P_B and

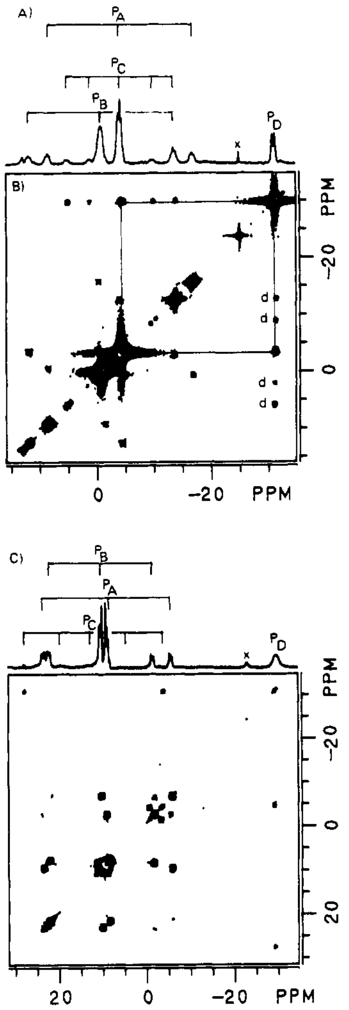

Figure 4. (A) One- and (B) two-dimensional ^{31}P NMR spectra of $[Pt_2(dppm)_3Cl]Cl$ (**13**). The boxes drawn indicate the coupling between the main phosphorus resonances, P_A and P_B and P_C and P_D. The resonance marked × in (A) is due to free dppm. In (C) and (D) are shown the one- and two-dimensional ^{31}P NMR spectra of $[Pt_2H(dppm)_3]Cl$ (**15**). The resonance marked × in (C) is due to free dppm.

between P_B and P_C. No coupling is observed between P_C and P_A.

The one-dimensional ^{31}P NMR spectrum of complex **15**, shown in Figure 4C, is complicated by the fact that the monodentate dppm ligand is involved in an exchange process,[20a] which results in a broad resonance for P_D and very weak resonances for P_C, almost buried in the baseline. In fact, assignment of these resonances for this spectrum based on the one-dimensional results is rather difficult, if not impossible. Of main interest here are the structural results obtained from the COSY spectrum, shown in Figure 4D, analyzed in detail to determine the Pt–P coupling constants and the assignment of P_C. Although the main cross-peaks expected for the phosphorus resonances of P_A and P_B are partially obscured by the intensity of the diagonal peaks, the cross-correlations between the P_A and P_B satellite peaks do show that P_A and P_B are coupled to one another. From the position of these cross-peaks the magnitude and sign of the ${}^2J_{Pt-P_A}$ and ${}^2J_{Pt-P_B}$ coupling constants are determined and listed in Table III. Coupling between P_C and P_D is also observed through the cross-correlations involving P_D and the P_C satellite peaks. On the basis of these cross-correlations, the resonances at −3.4, 17, and 27 ppm can be assigned to P_C and two of its satellite peaks. As was discussed for **13**, the positions of these particular cross-peaks show that P_D is coupled to Pt_B, a coupling that is reported not to be observed in the one-dimensional spectrum.[20a] The magnitude and sign of the ${}^3J_{Pt-P_D}$ coupling constant for **15** is +24 Hz. We believe that this coupling constant is very sensitive to the PCP angle of the dppm ligand and may lead to an understanding of the exchange mechanism for the monodentate dppm ligand. An investigation of this exchange is currently underway in this laboratory.[21] All chemical shifts and coupling constants for **15** are reported in Table III.

Figure 2 depicts the one- and two-dimensional ^{31}P NMR spectra of the new dimer, $[Pt_2(\mu\text{-dppm})(\eta^1\text{-dppm})dppeCl]Cl$ (**1**), which has the most complicated one-dimensional spectrum of this series of complexes. The proposed structure, shown in Figure 1, is based on the analysis of the 1D and 2D ^{31}P spectra. The chemical shifts and coupling constants for this complex are given in Table I.

The assignments of the chemical shifts were made for each of the six phosphorus atoms beginning with P_F on the basis of the following assumptions: Because P_F represents the uncoordinated phosphorus atom of the monodentate dppm ligand, it should not have any observable Pt–P satellite peaks in the one-dimensional spectrum. According to the analysis of the ^{31}P COSY spectrum of complex **13**, the two-dimensional spectrum should show only cross-peaks due to couplings between P_C and P_F. The only resonance that fits this criteria is the one at −20.1 ppm and hence is assigned to P_F. The chemical shift value of this resonance supports its assignment since it is similar to that of the same type of phosphorus in complex **13**. This resonance has no satellite peaks, and all of its cross-peaks present in the two-dimensional spectrum are associated with only one other resonance, which is therefore assigned to P_C. Because P_C is trans to P_B with respect to the platinum–platinum bond, it is expected to be strongly coupled to P_B. It should also be strongly coupled to P_F. Cis coupling to P_E is expected to be weak and may not be prominent in the COSY spectrum. The cross-peaks observed for P_C do show strong coupling to P_F and strong coupling to one other resonance, assigned to P_B. The chemical shift of 45.1 ppm for P_B is similar to that found for the dppe ligand in complex **4**. Besides being strongly coupled to P_C, P_B should show weaker cis coupling to P_A and P_D. The coupling to P_A should be stronger than to P_D, since the chelate ring provides a second pathway for coupling to P_B. Thus, coupling with P_A should be observed in the COSY spectrum whereas coupling to P_D may not be observed. The main cross-correlations present for P_B indicate strong coupling between P_B and P_C and a weaker coupling of P_B with one other resonance. This resonance is therefore assigned to P_A. Since P_A is part of the dppe ligand, the chemical shift of this resonance is in the expected downfield region of the spectrum. In addition to being coupled to P_B, P_A should be coupled to P_D. This coupling should be strong since P_D is trans to P_A. Coupling to P_E or P_C should be weak and may not be observed. Indeed cross-correlations are observed between P_A and P_B and between P_A and another resonance assigned to P_D as depicted in the COSY spectrum in Figure 2B. The chemical shift of P_D is similar to that of a coordinated phosphorus atom in a bridging dppm ligand, as observed for complexes **9**–**15**. P_D should not only be coupled to P_A but should also be coupled less strongly to P_E. Weaker coupling to P_B and P_C may not be observed. The cross-peaks present for P_D show strong correlations with P_A and weaker ones with one other resonance. This resonance is assigned to P_E. Once again, the chemical shift of P_E is in the range expected for this type of phosphorus nucleus. In the COSY map only cross-peaks between P_E and P_D are observed, consistent with the assignment of P_E. The absence of coupling between P_E and P_C is not unusual, since cis coupling with P_C is weak and has not been observed in the previous examples where only one coupling pathway exists between the cis phosphorus atoms.

The assignment of each of these resonances is further substantiated by the pattern of the resonances observed in the one-dimensional ^{31}P NMR spectrum and by the relative magnitudes of the coupling constants reported in Table I. For example, P_E is trans to a chloride ligand, whereas P_D is trans to P_A. It is well-known that the ${}^1J_{Pt-P}$ coupling constant for a coordinated phosphorus atom in a position trans to a chloride ligand is larger than that of a phosphorus atom trans to another phosphorus atom.[4] This difference is due to the trans effect of a chloride versus a phosphorus ligand. For complex **1**, ${}^1J_{Pt-P_E}$ is 4347 Hz and ${}^1J_{Pt-P_D}$

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is 3386 Hz. Also the larger doublet separation for P_A (P_A exhibits a doublet of doublets) matches that of P_D, which further supports their assignment as being trans to each other. For P_B, the larger doublet separation matches that of P_C, indicating that these two nuclei are trans to each other. The additional satellite peaks observed for P_B and P_C substantiate their position trans to the Pt–Pt bond, where strong $^2J_{Pt-P}$ coupling is present.

Complex **1** is the first example of a stable compound in which all three types of coordination geometries possible for a bidentate phosphine ligand are observed. The structural characterization of this particular Pt(I) dimer is important for several reasons. First of all, it supports the characterization made by low-temperature ^{31}P NMR spectroscopy of the $[Pt_2(dppm)_2PPh_3Cl]^+$ intermediate proposed by Blau and Espenson in which one of the dppm ligands is bridging and the other is chelating.[12a] Second, the formation of **1** can only result from the dissociation of one end of the bridging dppm ligand, a mechanistic step that has been previously proposed to occur in both mononuclear and dinuclear complexes during ligand substitution reactions.[12b,22] We suggest that the geometrical arrangement of the phosphine ligands in **1** results from the preference of the dppe ligand to chelate[23] and the ability of the dppm ligand to choose both a bridging and a monodentate position. Thus, the structure of **1** also emphasizes the coordination flexibility that makes the dppm ligand somewhat unique among phosphines.[24]

Conclusions

Our results show not only the general application of the homonuclear ^{31}P COSY experiment for the structural analysis of platinum phosphine complexes but also the following advantages of this technique: (1) the pulse sequence for the COSY experiment is available on all high-field instruments and is easy to use; (2) the positions of the observed cross-correlations provide the magnitude and sign of the $^2J_{Pt-P}$ coupling constants for the dinuclear complexes even when the one-dimensional satellite resonances are poorly resolved allowing the unambiguous assignment of the positions of the nonphosphine ligands; (3) the cross-peaks present between the satellite peaks facilitate the definitive assignment of the main phosphorus resonances, even when the main resonances are overlapping; (4) weaker couplings that cannot be determined in the one-dimensional spectra may be observed in the COSY spectra, i.e. $^3J_{Pt-P}$ found for **1**, **13**, and **15**; (5) the structures of compounds with relatively complex spin systems, such as **1**, can be assigned with confidence.

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Supplementary Material Available: Figures showing one- and two-dimensional ^{31}P NMR spectra of complexes **5–8** and **14** (8 pages). Ordering information is given on any current masthead page.

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Contribution from URA 454, Université Paul Sabatier, 31062 Toulouse Cedex, France, and Laboratoire de Physico-Chimie Moléculaire, URA 474, Université de Pau et des Pays de l'Adour, Avenue de l'Université, 64000 Pau, France

Diphosphiranes: Formation and Ionic Ring Opening, a Theoretical Approach

C. Tachon,[‡] M. Gouygou,[‡] M. Koenig,[‡] M. J. Hervé,[§] D. Gonbeau,[§] and G. Pfister-Guillouzo*[,§]

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The process of addition of methylene to diphosphene was studied theoretically using ab initio theory (SCF + CI level). Two possible mechanisms (addition to the π system and addition to the lone pair of phosphorus) were analyzed. The preferential process corresponds to a π addition leading to the diphosphirane ring. The cationic and anionic ring opening processes of the diphosphirane have been investigated at the same level of theory (ab initio SCF + CI). The results were analyzed by comparison with those of cyclopropane and in terms of the Woodward–Hoffmann rules. For the cations, the cleavage of the P–P bond (disrotatory motion) leads directly to an exo–endo open-chain structure. In the case of the anions, in contrast, a cyclic intermediate was located, which leads to an exo–exo open-chain species in a conrotatory ring opening.

Introduction

The chemistry of phosphorus analogues of cyclopropane has only been developed recently.[1] Since 1986, some of us have reported that the reactivity of various carbenoids on the diphosphene series leads to stable functionalized diphosphiranes.[2,3]

Further work indicated the ability of these strained molecules to undergo ring opening under thermal,[4] photochemical,[5] anionic,[6] and cationic[7] reaction conditions. The resulting products were fully characterized.

In this paper, using ab initio theory (SCF + CI level), we have studied the possible mechanisms of attack of methylene. Although carbene addition to alkenes has been extensively studied, little work has been done on the reactivity of carbenes toward heteroatomic π bonds; in particular, the problem of the preferential site of addition (π system or lone pair)[8] has not been fully elucidated.

[‡] Université Paul Sabatier.

[§] Université de Pau et des Pays de l'Adour.

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