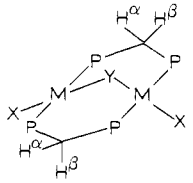
Mechanisms of "A"-Frame Inversion for Binuclear Platinum(II) Complexes with Bis(diphenylphosphino)methane Ligands

Richard J. Puddephatt,*[1a] Kazi A. Azam,[1a] Ross H. Hill,[1a] Michael P. Brown,[1b] Charles D. Nelson,[1b] Roger P. Moulding,[1c] Kenneth R. Seddon,[1c,2] and Martin C. Grossel[1d]

Contribution from the Department of Chemistry, University of Western Ontario, London, Canada, Donnan Laboratories, University of Liverpool, Liverpool L69 3BX, England, Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR, England, and Department of Chemistry, Bedford College, London NW1 4N5, England. *Received December 28, 1982*

Abstract: A mechanism is proposed that accounts for all the known examples of "A"-frame inversion for complexes of the general types $[Pt_2(\mu\text{-dppm})_2(\mu\text{-Y})X_2]^{n+}$ (dppm = bis(diphenylphosphino)methane, $n = 0$ or 1). The key step in this process involves an intermediate with a linear Pt–H–Pt skeleton.

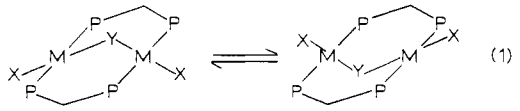
The chemistry of the "A"-frame complexes with bridging bis(diphenylphosphino)methane, dppm, ligands (structure I) has



(I)

been developed rapidly over the past 5 years.[3] A number of reviews of selected areas have been published recently.[4-8]

In the static structure (I) the methylene protons, $CH^{\alpha}H^{\beta}$, of the dppm ligands are nonequivalent and, unless there is an accidental degeneracy of the chemical shifts, should give rise to an AB quartet in the ^1H NMR spectrum.[9-11] However, several cases have been reported in which only one CH_2 signal has been observed, and this generally appears to be due to a fluxional process leading to an inversion of the "A"-frame structure (eq 1). This



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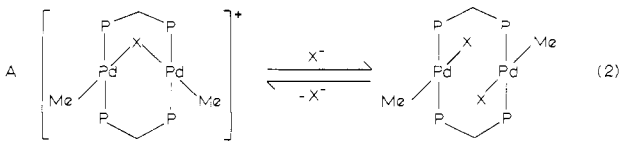
I II

paper presents variable-temperature NMR data obtained on a range of diplatinum "A"-frame molecules[11-15] and new evidence concerning the mechanism of "A"-frame inversion in these complexes.

In an early study[12] of the complex cation $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$, we suggested tentatively that the same fluxional process that led to the equivalence of the terminal and bridging hydride ligands also may have led to the equivalence of the methylene $CH^{\alpha}H^{\beta}$ protons of the dppm ligands. This theory is now disproved (vide infra). More recently, Balch and co-workers[10] have proposed two mechanisms, A and B (eq 2 and 3), by which "A"-frame



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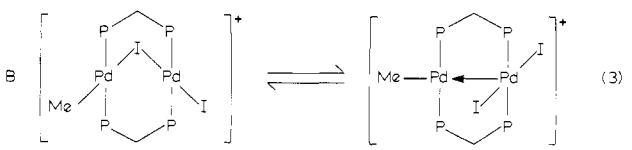

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inversion may occur in dipalladium complexes. Mechanism A requires halide catalysis and is shown in eq 2, while mechanism B involves a bridging-to-terminal ligand exchange (eq 3), similar to that proposed[12] for $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$.

We shall show that there are at least two further mechanisms by which "A"-frame inversion may occur in the diplatinum system.

Results and Discussion

The Mechanistic Possibilities. We shall consider several possible additional mechanisms for the "A"-frame inversion in this section and then proceed to examine some specific examples. These simple, one-step mechanisms, C–F, are shown in eq 4–7 (structures I and II are defined in eq 1).

Mechanism C involves the direct inversion of the "A"-frame complex, via an intermediate in which the X–M–Y–M–X skeleton is linear. We consider that this mechanism is only viable in the specific case where Y = H^+. In other cases, the M–Y–M distance would probably be too great to be spanned by the bridging dppm ligands. Moreover, in many cases (e.g., Y = CH_2), it would

(1) (a) University of Western Ontario. (b) University of Liverpool. (c) University of Oxford. (d) Bedford College.

(2) Present address: School of Molecular Sciences, University of Sussex, Brighton, BN1 9QJ, England.

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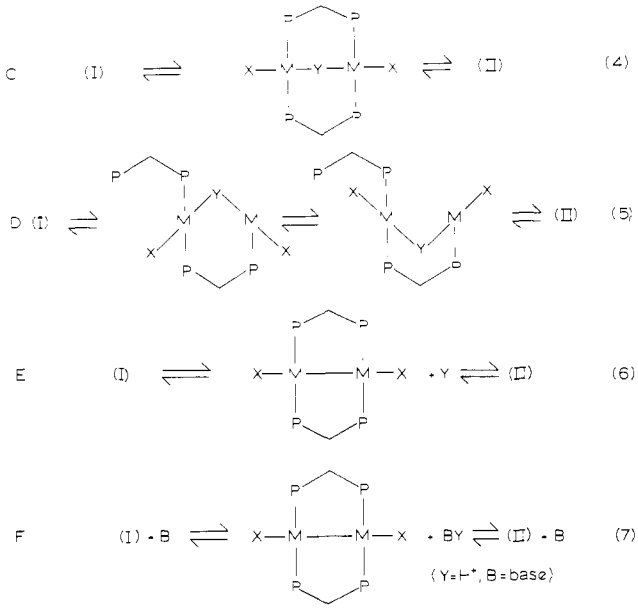

require an unfavorable inversion at the center Y, and in yet other cases (e.g., Y = SCH_2Ph), inversion would be impossible because of steric hindrance. In these difficult cases, it could be envisaged that partial dissociation of a dppm ligand may occur (as illustrated in mechanism D, eq 5). This would then allow the group Y to swing about the M···M axis without invoking a great distortion of the MŶM angle; recoordination of the dangling η^1-dppm ligand would then complete the inversion process. The factor militating against mechanism D is that dissociation of platinum–phosphorus bonds is usually slow, although gross steric hindrance in I *may* lead to some acceleration.

Another very simple, possible, mechanism involves rapid reversible dissociation of the bridging ligand Y (mechanism E, eq 6). The group Y could dissociate as a cation (e.g., Y = H^+) or as a neutral molecule (e.g., Y = CO or SO_2), but loss of Y as an anion (e.g., Y = Cl^-, SR^-, or PPh_2^-) would lead to a coordinatively unsaturated molecule, and is consequently much less likely. Mechanism F (eq 7) represents a simple extension of this mechanism for the special case of Y = H^+, indicating that base catalysis could occur.

Finally, we note that very strong bases (e.g., BuLi) can deprotonate coordinated dppm to give the coordinated $[Ph_2PCHPPh_2]^-$ anion.[17-19] Clearly, if this occurred rapidly, the $CH^\alpha H^\beta$ protons of the dppm ligands would be rendered equivalent without the "A"-frame inversion being necessary. However, since our studies were performed in the absence of a strong base, this mechanism is considered extremely improbable.

The Complex Cations $[Pt_2R_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ (R = H or Me). Perhaps the most instructive example to consider initially is the $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ cation,[12,20] examined as its hexafluorophosphate or its chloride salt. In its ^1H NMR spectrum at ambient temperature (in chlorinated hydrocarbon solvents), individual signals are seen due to the terminal and bridging hydride ligands ($\Delta\nu$ = 100 Hz at 100 MHz), and they show well-resolved coupling to each other (^2J(HH) = 15 Hz) in the $^1H\{^{31}P\}$ NMR spectrum (Figure 1). However, under the same conditions, only a single resonance is observed due to the CH_2P_2 protons. Coalescence of the PtH_t and PtH_b resonances occurs at 65 °C, corresponding to an approximate value of $\Delta G^\ddagger$ of 68 kJ mol^{-1}.[21] On

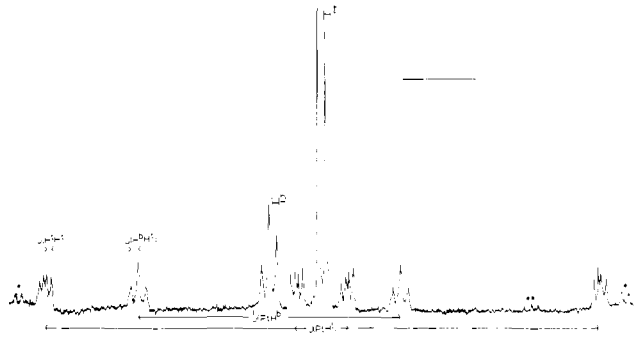

Figure 1. $^1H\{^{31}P\}$ NMR spectrum at 100 MHz of $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$ in CD_2Cl_2 showing only the PtH resonances. The bar represents 150 Hz [δ −6.86, PtH^t, ^1J(PtH) = 1138 Hz, ^2J(PtH) = 103 Hz, $J(H^tH^b)$ = 15 Hz, $J(H^tH^t)$ = 9 Hz; δ −5.86, PtH^b, ^1J(PtH) = 540 Hz]. The peaks marked * and ** are due to the $^{195}Pt_2$ isotopomer (abundance 11%).

cooling, the CH_2P_2 resonance splits into two [$\Delta\nu(CH^\alpha H^\beta)$ = 624 Hz at 400 MHz; Figure 2], the coalescence temperature being −20 °C in the 400-MHz ^1H NMR spectrum. This corresponds to an approximate value of $\Delta G^\ddagger$, of 46.5 kJ mol^{-1}.[21] Despite the approximations implicit in this method of estimating $\Delta G^\ddagger$, the results clearly indicate that the two fluxional processes are not related and that the activation energy for "A"-frame inversion is much lower than for bridging and terminal hydride exchange. This observation immediately rules out mechanism B. Mechanism A is possible in principle, but is excluded by the absence of observable halide catalysis (i.e., the coalescence temperatures for the chloride and hexafluorophosphate salts are the same, within experimental error). Moreover, mechanisms E and F are ruled out by the observation that a mixture of $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ and $[Pt_2D_2(\mu\text{-D})(\mu\text{-dppm})_2]^+$ does not undergo H–D scrambling in solution over a period of several hours.[23]

The experimental evidence does not distinguish between the two remaining possible mechanisms, C and D, and thus either must be considered possible. However, mechanism C is particularly attractive for μ-H salts. Although μ-hydrido complexes of the transition metals invariably possess bent M–H–M groups, the energy difference between this situation and the linear M–H–M group need not be great.[24] If we take the PtH distance to be ca. 1.7 Å in a typical Pt^{II}–H complex, then the Pt---Pt separation in the proposed linear Pt–H–Pt intermediate would have to be ca. 3.4 Å (cf. r(Cr···Cr) = 3.39 Å in $[(\mu\text{-H})Cr_2(CO)_{10}]^-$, with a near linear Cr–H–Cr unit: CrHCr = 159°[25]). Moreover, it is known that a metal–metal distance greater than this can be spanned by a μ-dppm ligands, as (for example) $[Pd_2Cl_2(\mu\text{-}CF_3CCCF_3)(\mu\text{-dppm})_2]$ exhibits r(Pd---Pd) = 3.49 Å.[26] Thus, the linear intermediate of mechanism C should be readily accessible, and to postulate the disfavored phosphine dissociation step required by mechanism D would appear to be unnecessary.

It is likely that mechanism C also operates for $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$, although its fluxional behavior has been investigated less thoroughly. The coalescence temperature for the $CH^\alpha H^\beta$ protons is −90 °C at 100 MHz, and it was not possible to obtain a limiting low-temperature spectrum to give a reliable value of $\Delta\nu(H^\alpha H^\beta)$. It is thus probable, but unproven,[27] that the

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(27) It is possible that $\Delta\nu(H^\alpha H^\beta)$ is much smaller for $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ than for $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$. See, for example, the much smaller $\Delta\nu(H^\alpha H^\beta)$ for $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ compared to $[Pt_2H_2(Cl)(\mu\text{-dppm})_2]^+$ (36 and 464 Hz, respectively, at 400 MHz).

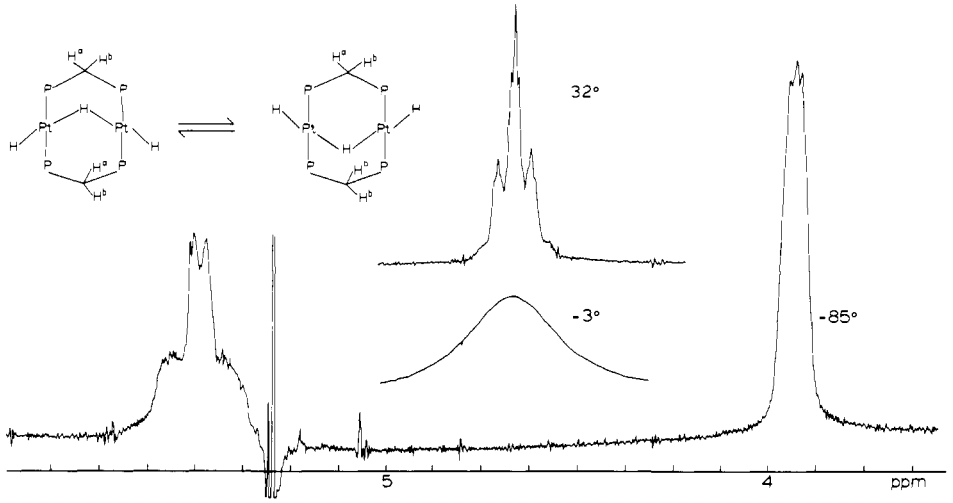
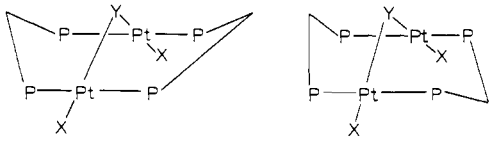


Figure 2. Variable-temperature ^1H NMR spectra (400 MHz) of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2][PF_6]$ in CD_2Cl_2 showing only the CH_2P_2 resonances. The peak at δ 5.32 is due to $CHDCl_2$ solvent impurity.

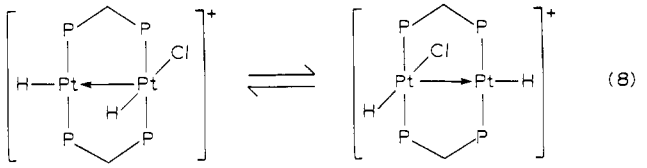
activation energy for the inversion of $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ is significantly lower than that for $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$. It is relevant here to note that the usual orientation of the CH_2P_2 groups is illustrated in III, but that $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$



(III) (IV)

possesses the pseudo-chair conformation (IV).[14] The "A"-frame inversion for complexes of conformation III must be accompanied by inversion of the pseudo-boat, and this may contribute a small amount to the activation energy; no such process is required for complexes of conformation IV. The conformation of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ is not known, so that this explanation must be considered very tentative.[27]

The Complex Cations $[Pt_2R_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$ (R = H or Me). As in the previous section, it is most instructive to consider the hydrido complex, $[Pt_2H_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$,[12] initially. The first important feature concerning this complex is that, although ambient-temperature ^1H and ^{31}P NMR spectra suggest it is a symmetrical "A"-frame complex of structure I,[12] low-temperature ^{31}P, ^{195}Pt, and ^1H NMR studies have recently unequivocally established that this is an artifact of the rapid equilibrium illustrated in eq 8[28] and that the complex really has structure V. This structure,



(8)

(V)

like the "A"-frame structure I, leads to the $CH^\alpha H^\beta P_2$ protons being nonequivalent. At ambient temperatures, however, not only does the fluxional behavior illustrated in eq 8 occur, but also the CH_2P_2 protons give rise to only a single resonance. Clearly, as the fluxionality of eq 8 does not remove the nonequivalence of the $CH^\alpha H^\beta$ protons, then the equivalencing must occur by a different mechanism. The coalescence temperature for these protons occurs at −16 °C at 400 MHz [$\Delta\nu(H^\alpha H^\beta)$ = 464 Hz], corresponding to an approximate $\Delta G^\ddagger$ of 47.8 kJ mol^{-1}.[21] This is ca. 7 kJ mol^{-1} larger than the activation energy for the process represented in eq 8, and so is clearly a distinct process. Arguments similar to those presented in the previous section clearly suggest that the mechanism for inversion is essentially mechanism C, as modified for structure V in eq 9. Spectra are shown in Figure 3.

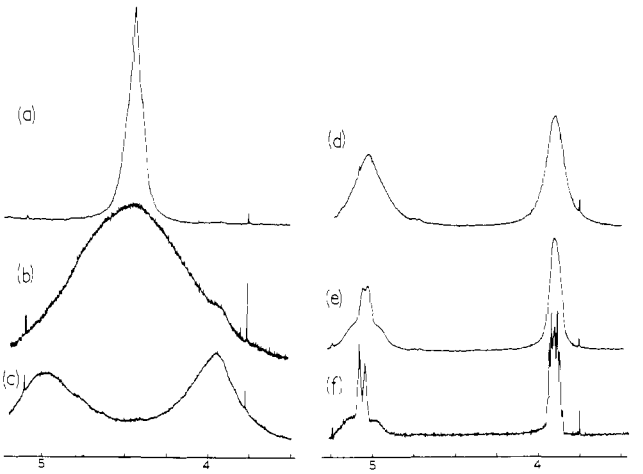
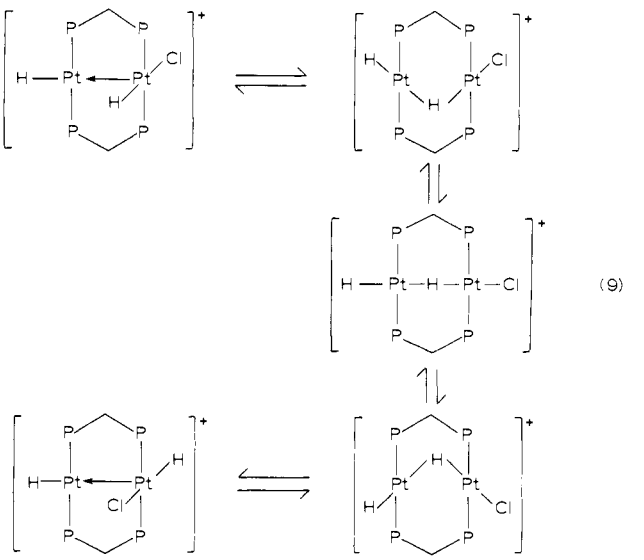


Figure 3. ^1H NMR spectra (400 MHz) of $[Pt_2H_2Cl(\mu\text{-}dppm)_2][PF_6]$ in CD_2Cl_2 in the region of the CH_2P_2 resonances. Spectra were recorded at (a) ambient temperature, (b) −16 °C, (c) −25 °C, (d) −37 °C, (e) −50 °C, and (f) −77 °C. The spectrum at −77 °C is Gaussian enhanced to show the fine structure: $\delta(H^a)$ 5.09, $^2J(H^aH^b)$ = 14 Hz, $^3J(PtH^a)$ = ~60 Hz; $\delta(H^b)$ 3.93, $^2J(H^aH^b)$ = 14 Hz, $^2J(PH) + {}^4J(PH)$ = 11 Hz.



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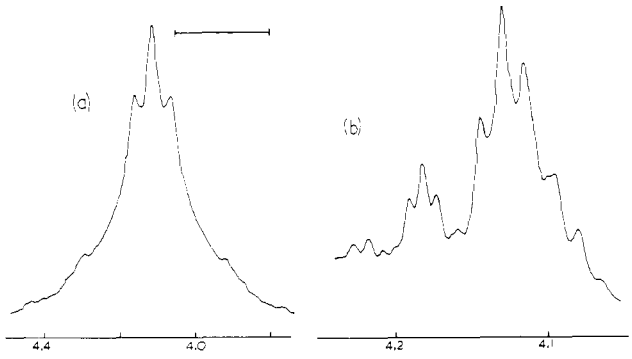


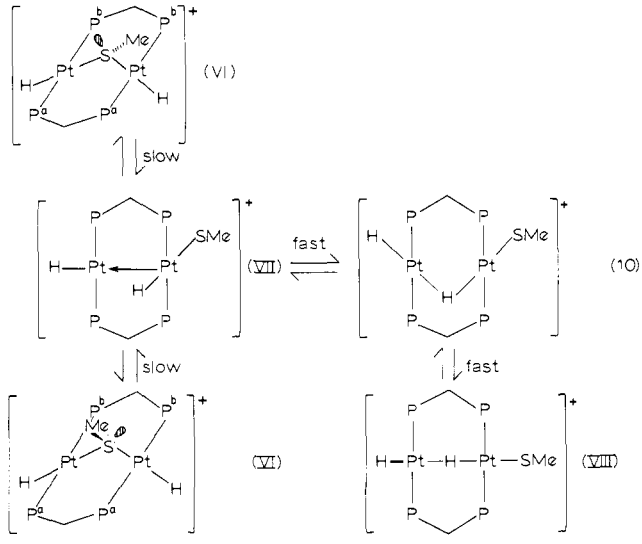
Figure 4. ^{1}H NMR spectra of $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2][PF_6]$ in the region of the CH_2P_2 resonances: (a) Spectrum at 100 MHz. (b) Spectrum at 400 MHz; $\delta(H^a)$ 4.20, $^2J(H^aH^b)$ = 14 Hz, $^2J(PH) + {}^4J(PH)$ = 7 Hz; $\delta(H^b)$ 4.11, $^2J(H^aH^b)$ = 14 Hz, $^4J(PH) + J(PH)$ = 12 Hz.

The value of $\Delta G^\ddagger$ for the process represented in eq 9 is satisfactorily close to that for the inversion of $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ by mechanism C, and this similarity would suggest that for $[Pt_2H_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$, the rate-determining step is probably the formation the linear H–Pt–H–Pt–Cl intermediate, rather than the initial formation of the μ-hydrido "A"-frame intermediate. Again, while mechanism D cannot be excluded by the experimental evidence, it would appear to be unnecessary to invoke the disfavored Pt–P bond dissociation.

Turning to the cation $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$,[13] this is a genuine "A"-frame complex of structure I.[28] In its 60- and 100-MHz ^{1}H NMR spectra at ambient temperatures, there appears to be only a single asymmetric resonance due to CH_2P_2, which is not greatly affected by cooling to −90 °C. However, the 400-MHz ^{1}H spectrum clearly shows two distinct but very close [$\Delta\nu(H^\alpha H^\beta)$ = 36 Hz] resonances at ambient temperatures, which were not resolved at the lower field strengths (see Figure 4). Thus, for $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$, inversion is slow on the NMR time scale, and must be associated with a $\Delta G^\ddagger > 64$ kJ mol^{-1}. If it is accepted that $[Pt_2H_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ and $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ invert by mechanism C, with $\Delta G^\ddagger \sim 47$ kJ mol^{-1}, then the rigidity of $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ is as expected, since mechanism C is not accessible to this complex [r(Pt–Cl–Pt) for a linear intermediate would have to be >4 Å]. However, if the fluxionality of the first two complexes was due to mechanism D, then the result for $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ would be very surprising, as the rate-determining steps (dissociation of the Pt–P bond) should involve similar activation energies. Thus, the rigidity of $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ strongly supports mechanism C over mechanism D for all the cases discussed so far. It is expected that the Balch mecanism A will be less favorable for platinum(II) than for palladium(II), in view of the known lower reactivity of platinum(II) in nucleophilic substitution.[10]

The Complex Cations $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2]^+$ and $[Pt_2H_2(\mu\text{-PPh}_2)(\mu\text{-dppm})_2]^+$. The complex $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2]^+$ also shows an "A"-frame inversion reaction,[11] with a coalescence temperature of 40 °C at 100 MHz [$\Delta\nu(CH^\alpha H^\beta P)$ = 80 Hz]. At the coalescence temperature and higher, the proton resonance due to μ-SCH_3 displays well-resolved coupling to the two platinum atoms (giving rise to a 1:8:17:8:1 quintet pattern). Thus, mechanism A (with catalysis by adventitious MeSH or MeS^-) and mechanism E can be eliminated, since they would give rise to a loss of $^3J(^{195}PtSCH_3)$ coupling in the high-temperature limiting spectrum. Mechanism B can also be eliminated as it cannot lead to the equivalency of the $CH^\alpha H^\beta$ protons (the rocking motion does not, of itself, give rise to a plane of symmetry containing the $[Pt_2P_4]$ unit). Experiments have established that the coalescence temperature is concentration independent, and so any intermolecular exchange mechanism (which is, in any case, difficult to envisage) can be ruled out. Mechanism C is, on this occasion, impossible to envisage, as there is not room enough for the SMe group to pass through the $[Pt_2P_4]$ unit. This would then appear to leave only mechanism D as a possible mechanism, which would be very surprising for the reasons already discussed in earlier sections.

A more plausible explanation for the inversion can be obtained if two of the above mechanisms are combined. Mechanism B would produce an intermediate of structure type V, which could then invert according to the scheme outlined in eq 9, a scheme based on mechanism C. Thus, eq 10 represents the simplest



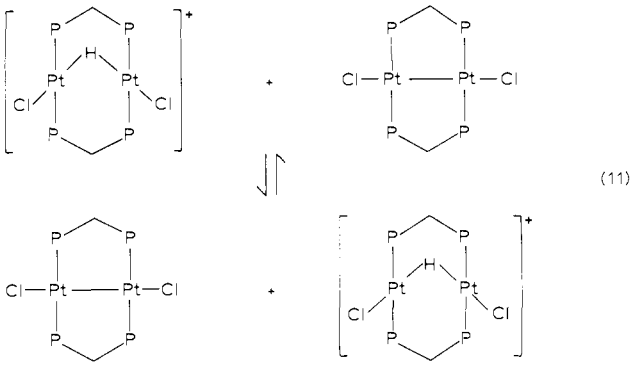
mechanism that is consistent with the experimental data. In eq 10 we take the inversion process only as far as the symmetric intermediate or transition state VIII.

There are several points of interest with this mechanism. Firstly, $\Delta G^\ddagger$ for the process is 63.5 kJ mol^{-1},[21] significantly higher than for the other processes (vide supra) involving mechanism C as the key step. This would imply that, in eq 10, the rate-determining step is the dissociation of the Pt–S bond, an observation perfectly in accord with chemical intuition. Secondly, in all the examples so far considered, the presence of a hydride ligand in either the terminal or bridging position has been *essential* to the occurrence of the "A"-frame inversion: this point will be returned to later.

Implicit in the mechanism illustrated in eq 10 is that inversion at the sulfur center should occur at the same rate (or faster, if it occurs by an independent mechanism) as "A"-frame inversion. This inversion has been studied by $^{31}P\{^1H\}$ NMR spectroscopy [T_c = 50 °C; $\Delta\nu(P^aP^b)$ = 76 Hz at 40.5 MHz], giving $\Delta G^\ddagger$ = 63.5 kJ mol^{-1}.[21] The agreement between this value and the activation energy for "A"-frame inversion is remarkably good and provides strong evidence for the above mechanism, with rate-determining cleavage of a PtS bond according to eq 10.

The complex $[Pt_2H_2(\mu\text{-PPh}_2)(\mu\text{-dppm})_2]^+$ is not fluxional up to +60 °C and gives separate $CH^aH^bP_2$ signals in the ^{1}H NMR spectrum due to the dppm ligands ($\Delta\nu$ 110 Hz at 100 MHz). This falls neatly into the series, since the very strongly bonded $Pt_2(\mu\text{-PPh}_2)$ group is not expected to break down to a terminal $PtPPh_2$ group under mild conditions.

The Complex Cation $[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$. Previous studies[12,20] have shown that this complex is easily deprotonated in the presence of added base to give $[Pt_2Cl_2(\mu\text{-dppm})_2]$. This apparent "A"-frame inversion is catalyzed by the presence of $[Pt_2Cl_2(\mu\text{-dppm})_2]$, according to eq 11.[20] This represents a special case of mechanism F, where $[Pt_2Cl_2(\mu\text{-dppm})_2]$ functions as the base (cf. eq 7). In the absence of free $[Pt_2Cl_2(\mu\text{-dppm})_2]$, achieved by the addition of an excess of $H[BF_4]$ to the system, the ambient-temperature ^{1}H spectrum in the CH_2P_2 region consists of a single broad resonance. Upon cooling, the fluxional behavior became slow on the NMR time scale, leading to the now familiar resolution of the peak into α and β components ($\Delta\nu$ = 292.5 Hz; T_c = +10 °C at 400 MHz; $\Delta G^\ddagger$ = 54.0 kJ mol^{-1}). This, again, is in accord with mechanism C. We note a series of increasing activation energy for the actual inversion step along the series (dppm ligands omitted) $[HPt(\mu\text{-H})PtH]^+$, $[HPt(\mu\text{-H})PtCl]^+$, and $[ClPt(\mu\text{-H})PtCl]^+$. It seems that terminal ligands with a high



(11)

trans influence (namely hydride in this series) lead to a lower activation energy for inversion.

Complexes That Are Not Fluxional. A number of the diplatinum complexes examined are not fluxional on the NMR time scale at ambient temperatures. These include $[Pt_2Cl_2(\mu\text{-}Y)(\mu\text{-dppm})_2]$ (Y = CH_2, S, or SO_2)[11] and $[Pt_2Cl_2(\mu\text{-}CF_3C{=}CCF_3)(\mu\text{-dppm})_2]$.[28] Although it was originally reported[11] that $[Pt_2Cl_2(\mu\text{-S})(\mu\text{-dppm})_2]$ appeared to be showing some evidence of fluxionality, a variable temperature ^{31}P and ^{195}Pt study has shown that this is not the case, and the poorly resolved nature of the ^{31}P spectrum is due to a fortuitous combination of coupling constants. These derivatives either do not contain terminal or bridging hydride ligands (in which case mechanism C is not accessible to them) or, in the case of $[Pt_2H_2(\mu\text{-}PPh_2)(\mu\text{-dppm})_2]^+$ and hydrido derivatives of $[Pt_2Cl_2(\mu\text{-}CF_3C{=}CCF_3)(\mu\text{-dppm})_2]$,[28] which are also static, contain a bridging ligand that would eliminate the mechanism illustrated in eq 10, owing to the disfavored nature of the first step (viz. mechanism B).

General Conclusions

We have shown that all of the diplatinum complexes examined that undergo "A"-frame inversion on the NMR time scale have a bridging hydride ligand or are capable of rearranging rapidly to a complex with a bridging hydride. The "A"-frame inversion then occurs through an intermediate with a linear Pt–H–Pt group.

For the diplatinum complexes, mechanisms of "A"-frame inversion involving attack of external nucleophiles on platinum (mechanism A) do not lead to fluxionality on the NMR time scale, but this mechanism can be important in analogous dipalladium complexes.[10] This is consistent with earlier results from associative ligand substitution reactions which have shown that square planar palladium(II) complexes react 10^5–10^6 times more rapidly than analogous platinum(II) complexes with external nucleophiles.[29] However, it seems that the reactions shown in eq 3, 9, and 10 in which *intramolecular* displacement of a bridging ligand by nonbonding d-electrons on a metal, with formation of a donor–acceptor metal–metal bond, can be rapid in both the palladium and platinum complexes. These donor–acceptor metal–metal bonds, first established in diplatinum complexes in the cation $[Pt_2Me_3(\mu\text{-dppm})_2]^+$, are fast becoming a dominant feature in this area of chemistry.[10,23,28,30,31]

Finally, we note that the free energy of activation for "A"-frame inversion in the complex $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ of 46.5 kJ mol^{-1} probably represents an upper limit of the free energy difference between the bent and linear $Pt_2(\mu\text{-H})$ bond strengths and, as far as we know, this represents the first case in which such an energy difference between bent and linear $M_2(\mu\text{-H})$ groups has been determined. Unfortunately, the contribution toward the overall activation energy from distortion of the μ-dppm ligands is not known.

Experimental Section

Syntheses and characterization of complexes have been reported elsewhere.[11-15] For this work variable-temperature NMR spectra were recorded on Jeol FX-90Q, Varian XL-100 and XL-200, and Bruker WH-400 or WP-400 spectrometers. Data for $[Pt_2H_2(\mu\text{-}PPh_2)(\mu\text{-dppm})_2][PF_6]$ have not been reported before: ^1H NMR (CD_2Cl_2) δ −4.65 (^1J(PtH) = 874 Hz, ^2J(PtH) = 18 Hz, PtH), 2.85 (^3J(PtH) = 59 Hz, CH_2P_2), 3.95 (^3J(PtH) = 11 Hz, CH_2P_2); ^{31}P NMR (trimethyl phosphate) δ 8.10 (^1J(PtP) = 3010 Hz, ^2J(PtP) = 52 Hz, dppm), 39.3 (^1J(PtP) = 2605 Hz, Pt_2PPh_2). A low-temperature limiting ^{31}P NMR spectrum was recorded for $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$ to give $\Delta\nu$ (P^aP^b, dppm) = 76 Hz at 40.5 MHz. The value reported earlier[11] was of a partly coalesced spectrum and is inaccurate. For definition of P^aP^b see eq 10.

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Registry No. $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]PF_6$, 86392-86-1; $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl$, 81533-18-8; $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$, 75862-26-9; $[Pt_2H_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$, 81533-21-3; $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$, 75862-28-1; $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2]^+$, 69215-81-2; $[Pt_2H_2(\mu\text{-}PPh_2)(\mu\text{-dppm})_2]^+$, 81557-31-5; $[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$, 81646-40-4; $Pt_2Cl_2(\mu\text{-dppm})_2$, 86392-87-2.

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