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Why Cationic Mono-Organo Bis-Phosphine Solvento Complexes of Platinum(II) Are Short-Lived Species? A Mechanistic and Synthetic Problem

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Complexes of the type *cis*-$[Pt(PR_3)_2(R')(S)]^+$ (PR_3 = tertiary phosphine, R' = alkyl- or aryl group; S = solvent), unlike their *trans* isomers, are short-lived species. These elusive compounds can be formed "in situ" easily by protonolysis of precursor dialkyls or mixed alkyl-aryl platinum complexes. The reason for their instability in solution is a facile conversion into the *trans* isomers with a mechanism which involves dissociative loss of the solvent molecule and interconversion of two geometrically distinct 3-coordinate T-shaped 14-electron intermediates. The application of QALE (quantitative analysis of ligand effects) to NMR and rate data provide a means of ascertaining the relative importance of electronic and steric properties of the "spectator" phosphine ligands in governing the structural characteristics of the precursor dialkyls and the lability of the monoalkyl solvento species. The overall structure-reactivity correlation has been rationalized. The velocity of the geometrical isomerization depends dramatically upon the nature of the ancillary phosphine ligands. The following factors combine to stabilize the 3-coordinate T-shaped transition state and to accelerate the rate of conversion: (*i*) electron release by the

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phosphine ligands, (*ii*) steric repulsions and distortion of the original 4-coordinate square-planar configuration, (*iii*) interaction of the vacant coordination site of the metal with β-hydrogen atoms of the alkyl chain. The stabilization energy involved in the kinetic β-hydrogen effect for *cis*-$[Pt(PR_3)_2(Et)(MeOH)]^+$ is around 24 kJ mol^{-1} at 298 K.

Keywords: *alkyl complexes, cleavage of Pt-CH_3 bond, cis-trans isomerization, β-hydrogen kinetic effect, QALE analysis. non-isothermal spectrophotometric kinetics*

INTRODUCTION

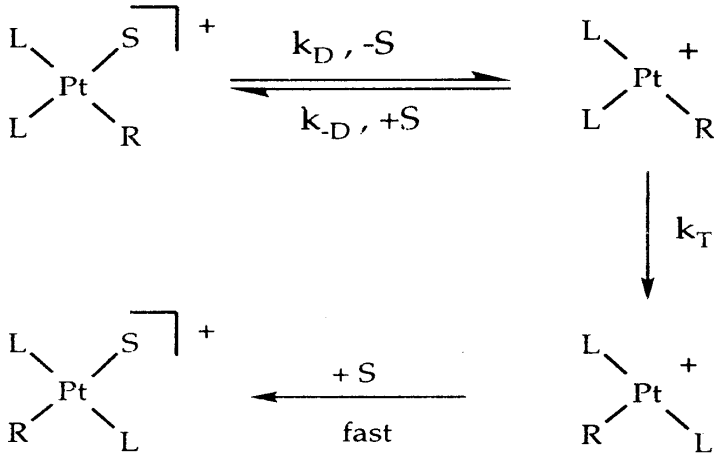
Mono-organo bis-phosphine solvento complexes of platinum(II) of *trans* configuration have been known for many years and investigated in detail in reactions of β-hydrogen elimination[1] and of olefin insertion.[2] Removal of an halide ligand X from neutral *trans*-$[Pt(PR_3)_2(alkyl)X]$ complexes by treatment with AgA (A= a non-coordinating anion), in a solvent S, leads to cationic alkyl solvento complexes of the type *trans*-$[Pt(PR_3)_2(alkyl)(S)]^+$. The marked rate enhancement observed for the β-hydrogen abstraction and olefin insertion processes, with respect to the corresponding neutral species, is due to the generation of a vacant coordination site. These results suggest to create a vacant site adjacent to the alkyl ligand, but removal of a halide ligand from *cis*-$[Pt(PR_3)_2(alkyl)X]$ by silver ions leads invariably to *trans*-$[Pt(PR_3)_2(alkyl)(S)]^+$. This prompted Yamamoto[3] to assert, in 1995, that “no cationic organoplatinum solvento complexes with monodentate tertiary phosphines that have *cis* geometry have been reported so far”. We give here a rational explanation of some of the reasons which make it difficult to synthesize bis-phosphine alkyl solvento complexes of platinum (II) in the *cis* configuration. Two factors, i.e. ligand steric congestion and strong σ-electron donation by the phosphine ligands, combine to accelerate the rate of conversion into the more stable *trans*-isomers. The nature of the bonded organic moiety (linear or branched alkyl group; phenyl or substituted aryl group) is also of overriding importance, especially as far as the presence of β-hydrogen atoms on a alkyl chain is concerned.

RECOGNITION OF MONO-ALKYL AND MONO-ARYL BIS-PHOSPHINE SOLVENTO COMPLEXES

Long before Yamamoto's observation we discovered that these elusive compounds can be formed “in situ” easily by protonolysis of precursor

dialkyl or mixed alkyl-aryl platinum complexes[4] and that the reason for their instability in solution is a spontaneous conversion into the *trans* isomers. The process can be followed very clearly by ^{31}P NMR at low temperature. For example, *cis*-[$Pt(PEt_3)_2(Me)_2$] in CD_3OD at −60 °C gives a ^{31}P resonance at δ 8.81($^1J_{PtP}$ = 1839 Hz). Upon addition of a sufficient excess of ethereal solution of HBF_4 there is an immediate and sharp change of the spectrum, which now shows two ^{31}P resonances $\delta(P_A)$ = 7.91 ($^1J_{PtPA}$ = 1829 Hz) and $\delta(P_B)$ = 23.87 ($^1J_{PtPB}$ = 4344 Hz). The low coupling constant $^1J_{PtPA}$ is typical of phosphorus atoms *trans* to carbon in platinum(II) complexes, while the value $^1J_{PtPB}$ = 4344 Hz is consistent with the presence of a very weak *trans* donor ligand such as MeOD. Thus, the *cis* configuration is retained as a result of the Pt-CH_3 bond breaking. On increasing the temperature at 283 K the isomerization can be followed by ^{31}P NMR through the decrease in the signals associated with *cis*-[$Pt(PEt_3)_2(Me)(MeOD)]^+$ and the parallel and matching increase in the signal of the corresponding *trans* complex which appears at δ = 25.14 with $^1J_{PtP}$ = 2786 Hz. However, the isomerization process is associated with well defined spectral changes in the UV region and the spectrophotometric technique offers the advantage over ^{31}P NMR, among others, of requiring far less complex for a kinetic study. At 303.16 K in methanol the proton attack to the precursor *cis*-[$Pt(PEt_3)_2(Me)_2$] is a fast bimolecular process (k_H = 74000 M^{-1} s^{-1}) while the ensuing *cis*-[$Pt(PEt_3)_2(Me)(MeOH)]^+$ converts more slowly and spontaneously to its *trans* isomer following a first-order rate law. The conversion is complete, the rate is $k_i = 6.73 \times 10^{-3}$ s^{-1}, with $\Delta H^{\ddagger} = 106 \pm 4$ kJ mol^{-1} and $\Delta S^{\ddagger} = +63 \pm 12$ J K^{-1} mol^{-1}. The corresponding phenyl and mesityl solvento complexes, obtained from *cis*-[$Pt(PEt_3)_2(R)(Me)$] (R = $C_6H_5^-$ and 2,4,6-$Me_3C_6H_2^-$) by selective cleavage of the Pt-Me bond, behave likewise. The rate of isomerization is almost insensitive to π effects or steric crowding by the *cis* group, increasing by a factor of four on going from methyl to mesityl. The trend is opposite to that observed for bimolecular processes, such as the protonolysis of the precursors complexes mentioned above or nucleophilic substitution, where the steric destabilization of the five-coordinate transition state produced by the *o*-methyl groups in the mesityl ring provokes a decrease in rate of at least 5 orders of magnitude with respect to that of phenyl.[5] This pattern is consistent with a mechanism in which the breaking of the Pt-S bond is the most important factor determining the rate. The isomerization of *cis*-[$Pt(PR_3)_2(R)(MeOH)]^+$ com-

plexes is described by the simple reaction scheme which involves dissociation of the solvent (S) from the *cis*-solvento species (via k_D), followed by the conversion of a T-shaped 14-electron intermediate (k_T pathway). A rate law of the form, $k_i = k_D/\{1+ (k_{-D}/k_T)[S]\}$, can be derived. The term $(k_{-D}/k_T)[S]$ in the rate law measures the retardation due to the capture of the first intermediate by the bulk solvent. This effect decreases, as the donor properties of the solvent decrease. This mechanism is reminiscent of that assessed for the spontaneous isomerization of mono-alkyl or -aryl halide complexes *cis*-$[Pt(PEt_3)_2(R)X]$[6].



SCHEME 1

THE β-HYDROGEN KINETIC EFFECT

Acidolysis of the diethyl compound *cis*-$[Pt(PEt_3)_2(Et)_2]$ led ineluctably to the formation of *trans*-$[Pt(PEt_3)_2(Et)(MeOH)]^+$, since the rate of isomerization is comparable or faster than that of acidolysis. This rate enhancement was quite unexpected and therefore we decided to perform a thorough study of the proton, temperature and pressure dependencies of the rates of protonolysis of a series of dialkyl complexes *cis*-$[Pt(PEt_3)_2R_2]$ (R = Me, Et, *n*-Pr, *n*-Bu, $CH_2C(Me)_3$, $CH_2Si(Me)_3$)

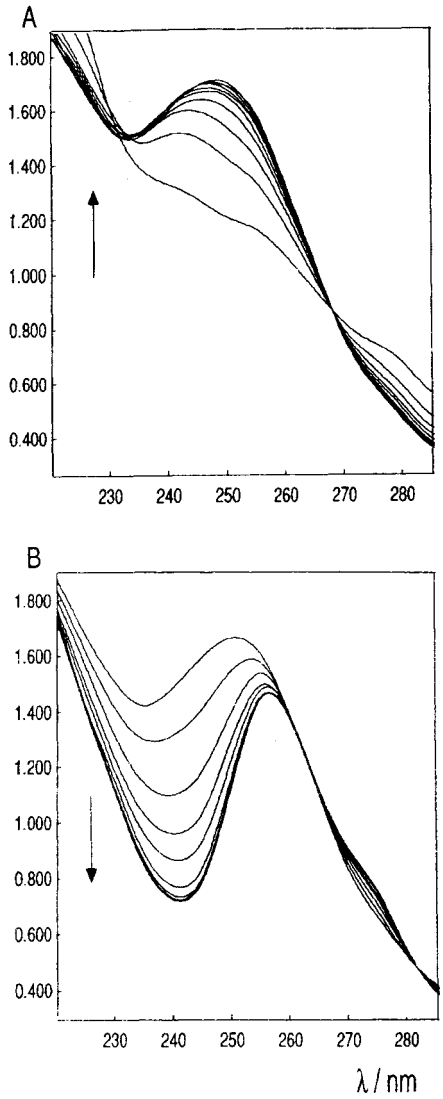


FIGURE 1 Upper plot: spectral changes for protonolysis of *cis*-$[Pt(PEt_3)_2(Et)_2]$ in methanol (T = 298.2 K; $[H^+]$ = 1.0 mM; time between consecutive spectra = 1.25 msec). Lower plot: spectral changes for isomerization of *cis*-$[Pt(PEt_3)_2(Et)(MeOH)]^+$ (T = 298.2 K; time between consecutive spectra = 12.5 msec)

and of mixed alkyl-aryl complexes *cis*-[$Pt(PEt_3)_2(R)(Me)$] (R= Ph, *2*-MeC_6H_4, *2,4,6*-$Me_3C_6H_2$) in methanol and of the rates of *cis-trans* isomerization of the resultant transient solvento complexes.[7] The aim of the work was to investigate the sensitivity of both processes to the nature of the bonded organic moiety (alkyl or aryl), its structure (linear or branched), and/or the availability of β-hydrogen atoms.

It was possible to measure independently the very fast rates associated with the complexes containing alkyl groups with β-hydrogens by use of rapid-scanning spectrophotometric techniques.[8]

In most of the kinetic runs the amount of acid and the scanning time of the spectrophotometer were regulated properly to collect independently the spectral changes associated with protonolysis and the subsequent isomerization reaction. We will not comment on protonolysis in this paper except by saying that this takes place by a rate-determining bimolecular proton transfer to the substrate. Other specific features, as the site of proton attack, the Pt-C σ-bond[9] or the metal,[10] remain speculative. The associative mode of activation is accredited by the first-order dependence of the rate on the proton concentration, by the strong retardatation induced by steric congestion at the Pt-C bond, by the low enthalpies of activation and by the largely negative entropies and volumes of activation. In contrast, the subsequent slower dissociative process, *cis* to *trans* isomerization of *cis*-[$Pt(PEt_3)_2(R)(MeOH)]^+$, is characterised by high values of enthalpies of activation, positive entropies of activation and largely positive volumes of activation.

The measure of the volumes of activation in the two cases has been shown to be particularly diagnostic in assessing the mechanisms.

Volumes of activation were obtained by a fit of the variable-pressure data to eq 1, where k_0 denotes the rate constant at zero pressure and 24.8°C.

$$\ln k = \ln k_0 - \Delta V^{\ddagger} P/RT \qquad (1)$$

For all the compounds examined (**1, 2, 3, 4**, and **9** in Table I) the natural logarithm of the rate of acidolysis was found to increase linearly with pressure (see Figure 2) and the values of the volumes of activation $\Delta V^{\ddagger}$ are negative, in agreement with the formation of a compact transition state. The natural logatithm of the rates of isomerization goes in opposite direction, decreasing linearly with pressure, and the behavior is perfecly in keeping with a dissociative mechanism, predicting an increase in volume for the transition state with respect to the ground state. All the

$\Delta V^{\ddagger}$ values in Table I are positive, corresponding to an overall expansion, as expected for a process dominated by bond breaking. However, the differences among these values do not seem particularly notable and therefore it must be concluded that the nature of the *cis* group does not play a significant role in controlling the volumes of activation, even though electronic effects from the *cis* group, such as the β-hydrogen kinetic effect, can be of crucial importance in controlling the rates.

TABLE I Rate Constants and Activation Parameters for the Geometrical Isomerization of *cis*-$[Pt(PEt_3)_2(R)(MeOH)]^{+}$[a]

	R	k_i[b]	$\Delta H^{\ddagger}$[c]	$\Delta S^{\ddagger}$[d]	$\Delta V^{\ddagger}$[e]
1	*2,4,6*-$Me_3C_6H_2$	0.0153	106 ± 3	+75 ± 8	+15.6 ± 0.8
2	*2*-MeC_6H_5	0.00527	118 ± 1	+106 ± 2	
3	C_6H_5	0.00474	112 ± 3	+84 ± 8	
4	CH_3	0.00266	106 ± 4	+63 ± 12	
5	C_2H_5	44.9	96.8 ± 0.2	+112 ± 1	+20.1 ± 1
6	*n*-C_3H_7	41.2	93.7 ± 3	+100 ± 15	+16.5 ± 0.5
7	*n*-C_4H_9	49.2	99.4 ± 3	+120 ± 15	+19.8 ± 2
8	$CH_2C(Me_3)$	0.0113	107 ± 5	+78 ± 15	
9	$CH_2Si(Me_3)$	0.0056	100 ± 2	+48 ± 6	

[a] in methanol
[b] (s^{-1}), at 298.2 K
[c] (kJ mol^{-1})
[d] (J K^{-1} mol^{-1})
[e] (cm^3 mol^{-1}); [Complex] = 0.05–0.1 mM.

From the data in Table I it is possible to see that the complexes in which R= Et, *n*-Pr, *n*-Bu isomerize at a much higher rate with respect to that of complexes containing alkyl groups with no β-hydrogen atoms, such as methyl, neopentyl and trimethylsilyl groups. For instance, the reactivity ratio $k_i(Et)/k_i(Me)$ is 1.7 x10^4. Inductive or steric effects cannot account for the large β-hydrogen kinetic effect. A specific interaction of these hydrogen atoms with the metal must be responsible for the large enhancement of the rate of isomerization. The simplest way of

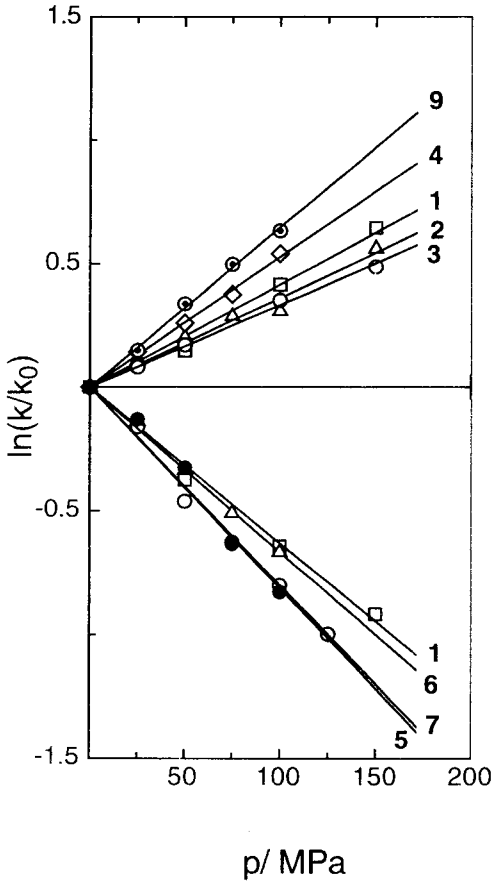


FIGURE 2 Upper plot: Pressure dependence of the second-order rate constants k_H for the cleavage of the Pt-R′(alkyl) bond in *cis*-[Pt(PEt_3)$_2$(R)(R′)] complexes. Lower plot: Pressure dependence of the pseudo-first-order rate constants (k_i) for isomerization of *cis*-[Pt(PEt_3)$_2$(R)(MeOH)]$^+$ complexes. Numbers refer to the compounds as listed in Table I

envisaging this interaction comes from the structural characterization of a very interesting example of β-agostic interaction reported by Spencer, Orpen et al.[11] for the cation [Pt(P-P)(Et)]$^+$ (P-P = (*t*-Bu)$_2$P(CH_2)$_3$

P(*t*-Bu)$_2$) where the chelating ligand prevents isomerization and the platinum-hydrogen interaction is so extended as to favor the formation of a well defined 3-center-2-electron Pt-H-C bond. The structure of the 3-coordinate T-shaped transition state for isomerization, containing modentate phosphines, is expected to be similar to that of the 14-electron Orpen's compound, the only difference being related to the extent of Pt-H interaction, which is less than in [Pt(P-P)(Et)]$^+$. However, this interaction satisfies partly the coordinative unsaturation of *cis*-[Pt(Pet$_3$)$_2$(Et)]$^+$, decreases its energy, and favors its fluxionality.

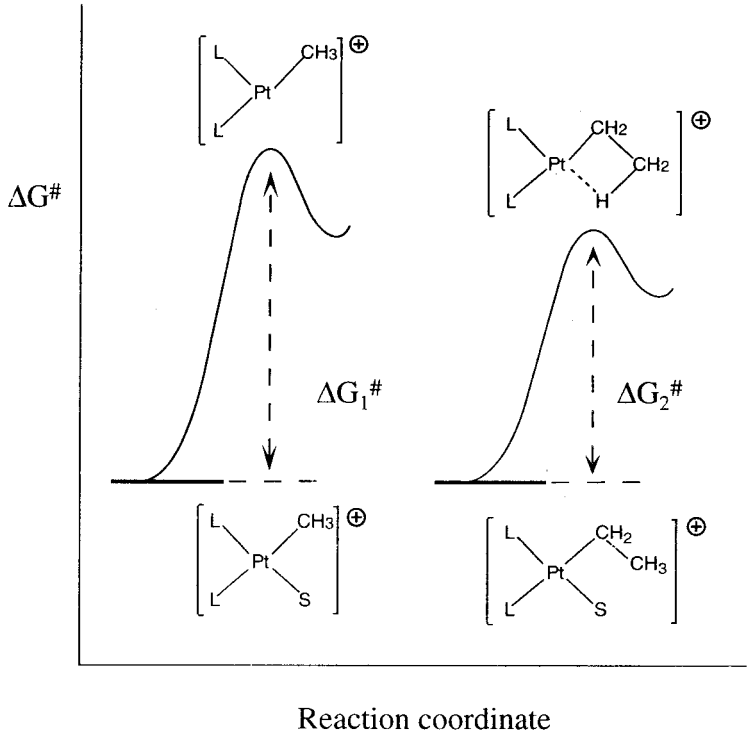


FIGURE 3 Energy profiles accounting for the kinetic β-hydrogen effect

A tentative calculation of the free energy involved in the kinetic β-hydrogen effect can be performed, based on the reasonable assump-

tion that the relative energies of the square-planar *cis*-[Pt(PEt_3)$_2$(Me)(S)]$^+$ and *cis*-[Pt(PEt_3)$_2$(Et)(S)]$^+$ complexes are not greatly different. The free energy of activation for the methyl solvento complex (from the data in Table I) is 87.2 kJ mol^{-1} at 298 K whereas that for the ethyl complex is 63.4 kJ mol^{-1}. The difference between these two values, 23.8 kJ mol^{-1}, should reflect entirely the free energy involved in the kinetic β-hydrogen effect.

KINETIC AND STRUCTURAL EFFECTS OF CIS-PHOSPHINES

We can implement the knowledge of these systems searching for a correlation between the lability of bis-phosphine monoalkyl solvento complexes of *cis* geometry and the nature of the coordinated phosphines. Thus, a series of known and new complexes of the type *cis*-[Pt(PR_3)$_2$$Me_2$] ($PR_3$ = an extended series of phosphines of widely different steric and electronic properties), were synthesized and used as precursors for the formation of *cis*-[Pt(PR_3)$_2$(R)(MeOH)]$^+$ in methanol.[12] In our hands the best method to synthesize the dialkyl-bisphosphine complexes was to use as a synthon the complex *cis*-[Pt(Me_2SO)$_2$(Me)$_2$][13] and to react it with an extended series of phosphines, according to eq.2

$$cis\text{-}[\mathrm{Pt(Me_2SO)_2Me_2}] + 2\ \mathrm{PR_3} \longrightarrow cis\text{-}[\mathrm{Pt(PR_3)_2Me_2}] + 2\ \mathrm{Me_2SO} \quad (2)$$

The removal of both molecules of sulfoxide from the starting material by the PR_3 groups is fast and easy, the reactions go to completion and the desired products were obtained in high yield and purity. All attempts to prepare the compound with P(*t*-Bu)$_3$ failed, as a consequence of the strong steric congestion of the bulky phosphines occupying *cis* positions. A collection of ^{31}P NMR data for the dialkyl complexes can be found in Table II, together with the rates and activation parameters for isomerization of *cis*-[Pt(PR_3)$_2$(R)(MeOH)]$^+$ in methanol and some parameters which measure the steric ed electronic properties of the phosphine ligands.

The spectroscopic data for the dimethylbis(phosphine)platinum(II) system compare well with those reported more recently by Nolan et cow.[14] for the same complexes obtained in a calorimetric study of the reaction of phosphines with CODPtMe_2(COD = η^4-1,5-cyclooctadiene).

TABLE II Stereoelectronic Properties of Phosphine Ligands, ^{31}P NMR Data for *cis*-[Pt(PR_3)$_2$$Me_2$], Rate Constants and Activation Parameters for the Geometrical Isomerization of *cis*-[Pt(PR_3)$_2$Me(MeOH)]$^+$ in Methanol

	Phosphine	χ^a	θ^b	E_{ar}	$\delta(^{31}P)^c$	$10^3k_i{}^d$	$\Delta H^{\ddagger}$(VTK)^e	$\Delta S^{\ddagger}$(VTK)^f
1	PMe_3	8.55	118	0	–23.1 (1761)	0.018	125 ± 1[g]	84 ± 1
2	$PPhMe_2$	10.6	122	1	–10.0 (1794)	0.017		
3	PEt_3	6.3	132	0	9.3 (1843)	2.95	108 ± 1[g]	67 ± 1
4	P(*n*-Pr)$_3$	5.4	132	0	–0.1 (1828)	9.26	119 ± 1[g]	116 ± 1
5	PPh_2Me	12.1	136	2	7.6 (1851)	0.071	125 ± 1[g]	94 ± 3
							127 ± 1[h]	103 ± 1
6	PPh_3	13.2	145	2.7	28.0 (1910)	5.31	121 ± 1[g]	120 ± 1
							122 ± 1[h]	121 ± 1
7	P(*4*-MeC_6H_4)$_3$	11.5	145	2.7	26.0 (1924)	17.9	119 ± 1[g]	119 ± 1
							120 ± 1[h]	123 ± 1
8	P(*4*-ClC_6H_4)$_3$	16.8	145	2.7	26.7 (1887)	0.543	129 ± 1[g]	124 ± 1
							127 ± 1[h]	117 ± 1
9	P(*4*-$MeOC_6H_4$)$_3$	10.5	145	2.7	24.7 (1930)	62.0	120 ± 1[g]	134 ± 1
10	P(*i*-Pr)$_3$	3.45	160	0	29.8 (1866)			
11	P(*3*-MeC_6H_4)$_3$		148	2.7	28.1 (1923)	7.97	120 ± 1[g]	116 ± 1
							120 ± 1[h]	118 ± 1
12	P(*3*-ClC_6H_4)$_3$	18.4	145	2.7	29.5 (1876)	0.141	119 ± 1[g]	80 ± 1
							124 ± 1[h]	96 ± 1
13	PCy_3	1.4	170	0	20.1 (1828)			
14	P(*2*-$MeOC_6H_4$)$_3$			2.7	9.5 (1839)			

a. values in cm^{-1} taken from ref 18
b. Cone angle in deg data taken from ref 19
c. ^{31}P chemical shifts for *cis*-[Pt(PR_3)$_2$$Me_2$] (in ppm from H_3PO_4 at 253 K; solvent = 3:1 CD_2Cl_2/CD_3OD (v:v); $^1J_{PtP}$ in Hz are given in parentheses)
d. First-order rate constants (s^{-1}) for isomerization of *cis*-[Pt(PR_3)$_2$Me(MeOH)]$^+$ at 298.16 K
e. Enthalpies of activation (kJ mol^{-1}) from variable temperature kinetics
f. Entropies of activation (J K^{-1} mol^{-1}) from variable temperature kinetics
g. Temperature gradient α = 0.0166°C /s^{-1}
h. Temperature gradient α = 0.0083°C /s^{-1}

QUANTITATIVE SEPARATION OF STERIC AND ELECTRONIC EFFECTS

In the last few years, numerous papers by Giering, Prock and coworkers[15] and by Poë and coworkers[16] have reported methods to perform a quantitative analysis (QALE) of the stereoelectronic properties of ligands of the type AR_3, AR_nAr_{3-n}, and $A(4\text{-}XC_6H_4)_3$. A large body of kinetic and physicochemical properties can be analyzed successfully with the general equation[17]

$$\text{property} = \omega + \alpha(\chi) + \beta(\theta) + \beta'(\theta - \theta_{st})\lambda + \gamma(\mathrm{E_{ar}}) \qquad (3)$$

or with one of its reduced forms, where χ is an infrared parameter[18] which measures the σ donicity of the ligand (the electron-donor ability decreases as χ increases), θ is Tolman's cone angle,[19] that measures the steric requirements of the ligand, θ_{st} is the steric threshold, below which no steric effects are evident, λ is a switching function that equals 0 when $\theta < \theta_{st}$ and equals 1 when $\theta > \theta_{st}$, E_{ar} is the aryl-effect parameter,[15d,16a] which depends on the number of pendent aryl groups of AR_nAr_{3-n} and $A(4\text{-}XC_6H_4)_3$ but is independent of any substituents on the aryl rings. α, β, β', and γ are regression coefficients that measure the relative importance of electronic, steric and aryl factors in the process. The response of the property to χ is assumed to be *linear* over the entire range of ligands, while the response to the steric parameter (θ-θ_{st}) is not linear. The presence of so many variables makes the results from regression analysis questionable, especially in the detection of a meaningful value for the steric threshold. Having in mind this difficulty, very recently Giering, Prock *et al*.[17] have proposed a combined method of graphical and regression analysis of ligand effect data, based essentially on the use of data obtained from graphical analysis to control the results of the regression analysis. To perform the stereoelectronic analysis of the NMR and kinetic data in Table II we followed the protocol suggested by Giering.[17]

STEREOELECTRONIC ANALYSIS OF $^1J_{PtP}$ COUPLING CONSTANTS

The values of $^1J_{PtP}$ coupling constants of the *cis*-$[Pt(PR_3)_2(Me)_2]$ complexes in Table II were analyzed with eq. 3, setting apart the value for

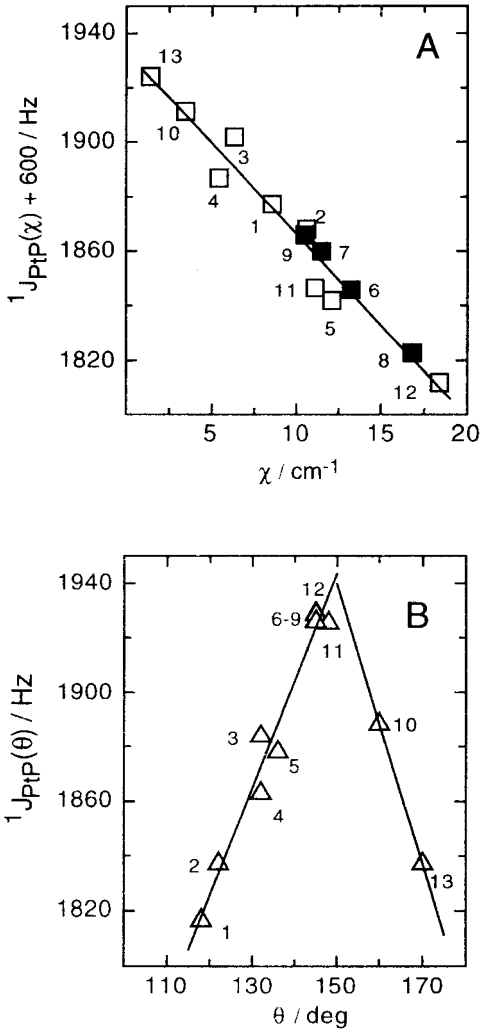


FIGURE 4 (A) Electronic profile, showing the dependence of the coupling constants $^1J_{PtP}$ upon the electronic parameter χ for *cis*-[Pt$(PR_3)_2(Me)_2$] compounds; (B) Steric profile, showing the dependence of $^1J_{PtP}$ upon the Tolman's cone angle. See text for the description of each plot. Numbers refer to the ligands as listed in Table II. Full squares refer to isosteric P(*4*-X-$C_6H_4)_3$ ligands

complex **14**, and using the values of χ, θ, and E_{ar} as stereoelectronic parameters of the ligands. The results of a regression analysis of all data points (n = 13), performed using equation 3 and the MicroMath SCIENTIST program,[20] were: $\alpha = -6.00 \pm 1$ Hz cm; $\beta = +4.0 \pm 0.4$ Hz deg^{-1}; $\beta' = -8.9 \pm 1$ Hz deg^{-1}; $\chi = 23.9 \pm 5$ Hz; $\omega = 1338 \pm 58$ Hz and $\theta_{st} = 149°$. As measure of goodness-of-fit we used the coefficient of determination, DC = 0.982, which measures the fraction of the total variance accounted for by the model. When dealing with a multiplicity of possible models, a more appropriate index of goodness-of-fit is the value of MSC = 3.26 (Model Selection Criterion).[21] The most appropriate model will be that with the largest MSC. A supplementary statistical criterion is given by the value of $r^2 = 0.995$ for the linear plot of $^1J_{PtP(calc)}$ *vs* $^1J_{PtP(obs)}$ where $^1J_{PtP(calc)}$ is obtained by introducing the calculated coefficients in eq.3. An appropriate index of goodness-of-fit is given also by the correspondence between the values of α (- 6.00 ± 1 Hz cm) obtained from full regression analysis and the value of α (-6.89 ± 0.2 Hz cm) obtained from a plot of $^1J_{PtP(obs)}$ *vs* χ for the isosteric ligands P(*4*-$XC_6H_4)_3$, where θ and E_{ar} remain constant.

The results of QALE analysis can be now displayed as electronic, steric and aryl profiles. The electronic profile (Figure 4A) represents the sensitivity of the $^1J_{PtP}$ coupling constants to the inductive effects brought about by substituents on phosphorus, and can be constructed by subtracting the contributions of all the terms of the regression equation, except that of the variable of interest, *i.e.* α (χ), from the $^1J_{PtP}$ experimental data, according to the equation:

$$(^1J_{PtP})(\chi) = J_{PtP}(obs) - [\omega + \beta(\theta) + \beta'(\theta - \theta_{st})\lambda + \gamma(E_{ar})] \quad (4)$$

Likewise, the steric profile (Figure 4B) and the aryl plot can be constructed using similar equations[12].

The most relevant feature of the stereolectronic analysis of the NMR data is that, before the steric threshold (Figure 4B), both electron release and steric encumbrance of substituents on phosphorus concur to increase the value of $^1J_{PtP}$, with the latter factor playing a somewhat major role. After the steric threshold the overload of steric congestion leads to a sharp decrease of $^1J_{PtP}$ that must be associated with severe distortions of the P-Pt-P bond angle and lengthening of Pt-P bond distances.[22] Under these circumstances, steric repulsion prevents maximum overlap of phosphorus and platinum bonding orbitals and changes the s character present in the metal-phosphorus bond. Thus, the steric

threshold in the plot of $^1J_{PtP}$ *vs* the cone angles, and the sharp change in the direction of the steric effects, can be assumed as a signal that marks the onset of significant changes in the structure of the *cis*-[$Pt(PR_3)_2Me_2$] complexes. This has been confirmed recently by Nolan *et al.*[14] by determining the reaction enthalpies of a variety of such complexes and the X-ray molecular structure when PR_3 = PEt_3, PMe_2Ph, P(pyrrolyl)$_3$ and PCy_3. The relative stability of the dimethyl-bisphosphine platinum(II) complexes was found to be strongly influenced by the size of the phosphine, with larger cone angles resulting in less thermodinamically stable complexes. For instance, *cis*-[$Pt(PCy_3)_2Me_2$] (PCy_3, θ =170°) which is one of the two points that together with P(*i*Pr)$_3$ (θ =160°) lies beyond the steric threshold in Figure 4B, has the lowest value of enthalpy of formation (-ΔH = 19.2 kcal/mole), the longer Pt-P bond separation (2.252(2) Å) and the largest P-Pt-P bond angle (P_1-Pt-P_2= 108.60(5) deg).

STEREOELECTRONIC ANALYSIS OF KINETIC DATA

The cationic solvento complexes *cis*-[$Pt(PR_3)_2(Me)(MeOH)]^+$ were obtained from the corresponding dimethyl compounds, following the procedure described above, and their rates of isomerization were monitored with spectrophotometric techniques. For the most sterically hindered complexes, containing P(*i*-Pr)$_3$ and PCy_3, the rate of isomerization was too fast to be followed.

The QALE analysis for the isomerization process has been performed according to the protocol described before. The regression analysis of the kinetic data in Table II (11 data points) led to the equation:

$$\begin{aligned}\log k_{\mathrm{i}} = {} & (-0.27 \pm 0.06\ \mathrm{cm})(\chi) \\ & + (0.13 \pm 0.03\,\mathrm{deg}^{-1})(\theta) + (0.066 \pm 0.3)(\mathrm{E_{ar}}) \\ & - 17.8 \pm 4 \end{aligned} \tag{5}$$

(r^2 = 0.995, DC = 0.982, MSC = 3.26) which corresponds to steric and electronic contributions of 58% and 40%, respectively, and only of about 2% for the aryl contribution.

The electronic profile (Figure 5A) and the steric profile (Figure 5B) for the overall set of ligands were constructed by using the parameters in equation 5 and the same absolute vertical scale for the two plots. As

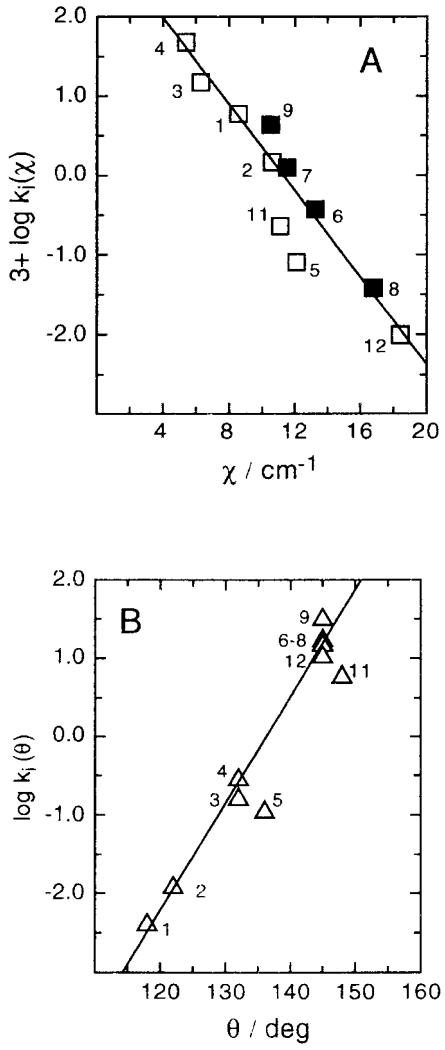


FIGURE 5 Stereoelectronic analysis of the rate constants k_i s^{-1} for the uncatalyzed isomerization of *cis*-$[Pt(PR_3)_2(Me)(MeOH)]^+$ compounds, at 298.16 K in methanol. (A) Electronic profile. (B) Steric profile. Numbers refer to the ligands as listed in Table II

expected, the rates of isomerization increase with increasing electron-donating ability of the substituents on the phosphorus atoms. Electron-donation facilitates the departure of MeOH with its previously bonding electron pair and stabilizes the electron-deficient transition state. The linear plot of Figure 5B describes the steric dependence of the rates of these reactions and the slope of the plot measures the sensitivity of the isomerization to steric effects. An increase of 10° in cone angle of the phosphines accounts for more than one order of magnitude increase in reactivity. The steric dependence is the result of the different response of the energy of the ground and the transition states to changes in the size of the "spectator" ligands. There is significant release of steric strain on going from the highly congested 4-coordinate *cis*-bisphosphine solvento compounds to the more flexible 3-coordinate T-shaped transition state. For a number of dissociative processes of carbonyl compounds the steric profile is a straight line as that shown in Figure 5B, but the values of the slopes are very much less than the value of $\beta = 0.13 \pm 0.03$ deg^{-1} found for isomerization.[23] Since the electronic effect is also much larger than in the CO dissociation reactions, the isomerization is thought to occur with a very late transition state and with MeOH being totally outside the coordination sphere of the metal. It is worth mentioning that, when phosphines are used as entering groups in nucleophilic substititution reactions, the rates are retarded as the size of the ligand increases (negative sign of β).[24] In these associative processes steric effects are operative through a continuous increasing destabilization of the five-coordinate transition state.

ACTIVATION PARAMETERS

We mentioned before the utility of using the values of the volumes of activation as a clear-cut diagnostic tool to assess the molecularity of the reactions (proton attack on *cis*-[Pt(PEt_3)$_2$(R)(Me)] complexes and *cis-trans* isomerization of the ensuing solvento complexes). High values of enthalpy of activation and large positive entropies of activation are usually associated to the geometrical conversion, according to a dissociative mode of activation. In the case of *cis*-[Pt(PR_3)$_2$(Me)(S)]$^+$ complexes the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were measured using for the first time non-isothermal spectrophotometric kinetics[25] as a routine method. The method requires a controlled change of the temperature with time by use

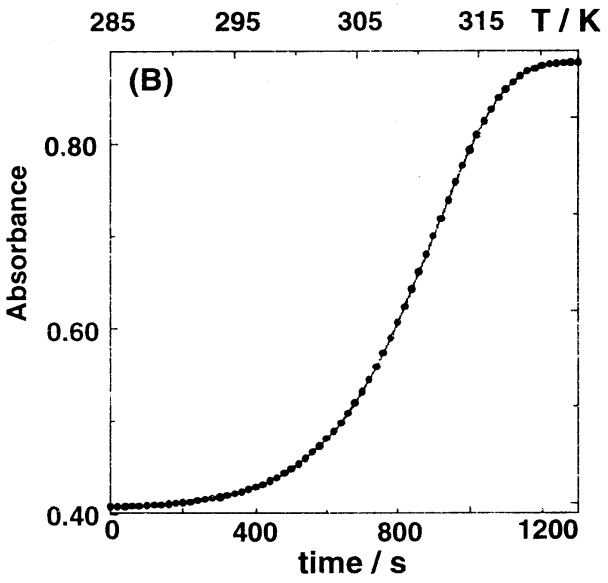


FIGURE 6 Change in absorbance at 240 nm during the geometrical isomerization of *cis*-[Pt (P(*4*-$ClC_6H_4)_3)_2$(Me)(MeOH)]$^+$ in methanol at the variable temperature T(K) = 285 ± 0.05 + 0.033 t (s)

of a Peltier temperature programmer and the automatic collection of the absorbance-time data by a spectrophotometer, at a fixed wavelength. Plots as that featured in the D_t*vs t* profile of Figure 6 have the form of a sigmoidal curve and can be analyzed with a program, such as Micro-Math SCIENTIST,[20] which allows to solve the differential equation

$$-\mathrm{d}(\mathrm{D}_t - \mathrm{D}_\infty)/\mathrm{d}_\mathrm{t} = k(\mathrm{T}_0 + \alpha t)/h \exp[\Delta \mathrm{S}^{\ddagger}/\mathrm{R}] \exp[-\Delta \mathrm{H}^{\ddagger}/\mathrm{R}(\mathrm{T}_0 + \alpha t)](\mathrm{D}_t - \mathrm{D}_\infty) \quad (6)$$

with D_∞, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the parameters to be optimized (T_0 is the starting temperature, α is the temperature gradient, D_t is the absorbance at the time *t*, D_∞ is the absorbance at completion of the reaction. A k_{obs} (T) profile (k_{obs} = rate of reaction; T = temperature) can be obtained simply by dividing the time derivative of the absorbance data to the normalised value of the absorbance (D_t-D_∞).

The advantages offered by the non-isothermal (VTK) method over the traditional isothermal (CTK) method are straightforward: (*i*) it permits fast and easy collection and processing of enormous amounts of data, (*ii*) the whole set of data is from a single experiment carried-out in homogeneous conditions, *(iii)* with a single kinetic run it is possible to obtain a $\underline{k}(T)$ profile instead of a single rate constant, saving time and chemicals (*iv*) the statistical error associated with the calculated values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is very low. The VTK treatment described requires accuracy and precision in temperature measurements and it applies only to a first-order process. Potential caveats to this method are associated to the use of large ranges of temperature or of temperature gradients, to a possible thermal expansion of the solvent that affects the concentration of the absorbing species, and to the temperature dependence of various factors (pH, ionic strength, etc.) that are considered constants.

CONCLUSIONS

This work gives a rational explanation of some of the reasons which make it difficult to synthesize bis-phosphine alkyl solvento complexes of platinum (II) in the *cis* configuration. The quantitative analysis of ligand effects (QALE), and the derived steric and electronic profiles for NMR and rate data, have provided invaluable information to rationalize the overall structure-reactivity correlation. For the complexes *cis*-$[Pt(PR_3)_2Me_2]$, the steric threshold observed in the steric profile of the $^1J_{PtP}$ coupling constants, corresponds to a value of Tolman's cone angle (149°) above which the P_A-Pt-P_B angle and the Pt-P bond separation of the two phosphine ligands suddenly increase (as for PCy_3), as a result of a strong steric congestion at the square coordination plane. Steric repulsion and distortion of the square planar configuration and electron release by the phosphine "spectator" ligands combine to accelerate the rate of isomerization of *cis*-monoalkyl-bisphosphine platinum(II) compounds. The nature of the bonded organic moiety is also of overriding importance, especially as far as the presence of β hydrogen atoms on an alkyl chain is concerned. All this information allows to understand why complications arise in the synthesis of the compounds *cis*-$[Pt(PR_3)_2(Me)_2]$ with the most sterically demanding ligands such as P(*2*-$MeC_6H_4)_3$ (θ = 194°), P(*2*-$MeOC_6H_4)_3$ or for P(*t*-$Bu)_3$) (θ = 182°) and why the rate of *cis*-*trans* conversion of *cis*-$[Pt(PR_3)_2(alkyl)(S)]^+$

complexes with phosphines having a cone angle greater than 150° or an alkyl group with β hydrogen atoms is too fast to be followed with conventional NMR or spectrophotometric techniques.

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