Structure−Reactivity Correlations for the Dissociative Uncatalyzed Isomerization of Monoalkylbis(phosphine)platinum(II) Solvento Complexes

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Complexes of the type *cis*-[PtL_2Me_2] (**1**−**14**) (L = an extended series of phosphines of widely different steric and electronic properties) were synthesized, characterized, and used as precursors for the formation of *cis*-monoalkylplatinum(II) solvento species in methanol. The cleavage of the first platinum-alkyl bond by protonolysis is a fast process, but the subsequent cis to trans isomerization of the cationic solvento species [PtL_2(Me)(MeOH)]$^+$ is relatively slow and it can be monitored using ^{31}P NMR or conventional spectrophotometry. A large collection of ^{1}H and ^{31}P NMR data for *cis*-[PtL_2Me_2], *cis*-[PtL_2Me(MeOH)]$^+$, and *trans*-[PtL_2Me(MeOH)]$^+$ complexes showed interesting dependencies upon the size, the σ-donor capacity, and the mutual position of the phosphines in the coordination sphere of the metal. The rate constants for isomerization of *cis*-[PtL_2Me(MeOH)]$^+$ were resolved quantitatively into steric and electronic contributions of the phosphine ligands, by means of correlations with parameters which reflect their σ-donor ability (χ values) and steric requirements (Tolman's cone angles, θ). The electronic and steric profiles obtained for these reactions are discussed within the framework of a mechanism which involves dissociative loss of the solvent molecule and interconversion of two geometrically distinct 3-coordinate T-shaped 14-electron intermediates. The factors controlling the stability of these coordinatively unsaturated species are discussed. The electronic and steric influences of phosphines as "spectator" ligands in a dissociative process are compared with those shown by these ligands when used as nucleophiles in associative substitution processes. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were measured using both conventional isothermal and non-isothermal spectrophotometric kinetics.

Introduction

The course of many reactions of square planar complexes of d^8 transition metals, such as nucleophilic substitution, electron transfer, oxidative addition, reductive elimination, thermal decomposition, and interaction with molecules of biological interest, is dictated by the geometry in the square planar configuration.[1] Despite the great chemical interest in understanding the way in which such species undergo geometrical isomerization, very few mechanistic studies have been devoted to date to this subject.[2] During the last few years our interest was drawn to the uncatalyzed cis to trans isomerization of complexes of the type [$Pt(PEt_3)_2$(R)X] (PEt_3 = triethylphosphine, R = alkyls or substituted aryl groups; X = halide ions).[3] The main features of the reaction mechanism involve dissociative loss of the coordinated halide group and interconversion of two geometrically distinct 3-coordinate T-shaped cationic intermediates. In protic solvents, whose role is crucial in promoting the dissociation of the halide ion from the metal,[4] the process is somewhat complicated by a possible solvolytic pre-equilibrium between the halide species and a *cis*-[PtL_2(R)S]$^+$ solvento species. In a recent report Yamamoto[5] has claimed that "no cationic organoplatinum solvento complexes with monodentate tertiary phosphines that have *cis* geometry have been reported so far". We discovered that these elusive compounds can be formed "in situ" easily by protonolysis of precursor dialkyls or mixed alkyl−aryl platinum complexes and that the reason for their instability in solution is an easy spontaneous conversion into the trans isomers.[6] The process is extremely simple and clean, it can be monitored by a variety of spectroscopic techniques, and proceeds through the same dissociative mechanism mentioned above. The *trans* solvento products have been known for many years, and their reactivity

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has been investigated in detail in reactions of olefin insertion or of β-hydrogen elimination.[7]

There are many interesting features in these processes: (i) Dissociative pathways in platinum(II) chemistry are rare.[8] (ii) We are far from a complete understanding of the factors that promote the formation and stabilization of 3-coordinate 14-electron species, as well as of the efficiency with which they can interconvert, as in uncatalyzed isomerization, undergo intramolecular processes, as in some β-hydride elimination reactions,[9] or be intercepted in solution by the solvent, nucleophiles, or other chemical species. (iii) These coordinatively unsaturated species offer favorable low-energy reaction routes to catalytic processes as an alternative to 4- and 5-coordinate species. (iv) Our understanding of substituent effects of phosphine ligands is still small, despite their crucial role in coordination and organometallic chemistry.[10]

In this study, we were interested in 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*-$[PtL_2Me_2]$ (L = an extended series of phosphines of widely different steric and electronic properties) were synthesized and used as precursors for the formation of *cis*-$[PtL_2(R)(MeOH)]^+$ in methanol. The rates of the ensuing uncatalyzed isomerization were measured at various temperatures. The results are discussed within the framework of a dissociative mechanism. The application of QALE (quantitative analysis of ligand effects)[11] to the rate data provided a means of ascertaining the relative importance of electronic and steric properties of the "spectator" ligands in governing the lability of the substrates. A clear structure−reactivity correlation was obtained. The way in which the size and the electron-releasing ability of the substituents on the phosphorus atoms influence the spectroscopic properties of the dialkyl and solvento complexes complexes is also discussed.

Experimental Section

Materials. Solvents used in the synthetic procedures were distilled under nitrogen from appropriate drying agents (diethyl ether from sodium benzophenone; dichloromethane from barium oxide; methanol from magnesium methoxide; dimethyl sulfoxide, at a low pressure, from CaH_2, after preliminary filtration through an alumina column) and then stored in dried, N_2-filled flasks over activated 4 Å molecular sieves. Methanol for use in kinetic runs was obtained by purification of spectrophotometric grade methanol (Aldrich). Deuterated solvents for NMR measurements were used as received from Aldrich Chemical Co.

Solid phosphines were recrystallyzed from EtOH, by dissolving in the hot solvent, filtering, and cooling the filtrate to 0 °C. The crystals were stored under N_2. The phosphines PEt_3 and $PMePh_2$ (Aldrich) were distilled prior to use. The remaining phosphines were used as received from Strem. All the other chemicals were the highest grade commercially available and were used as received or purified by distillation or crystallization when needed.

Instrumentation. ^{1}H and ^{31}P NMR spectra were obtained on a Bruker AMX R-300 spectrometer equipped with a broad-band probe operating at 300.13 and 121.49 MHz, respectively. ^{1}H chemical shifts are measured relative to the residual solvent peak and are reported in δ units downfield from Me_4Si. ^{31}P chemical shifts, in parts per million, are relative to external phosphoric acid. The temperature within the probe was checked using the methanol or ethylene glycol method.[12] Microanalysis were performed by Redox Analytical Laboratories, Milan, Italy.

Synthesis of Complexes. All the complexes were synthesized under a dry oxygen-free nitrogen atmosphere using standard Schlenk-tube techniques. The reaction products were handled under nitrogen in the refrigerator. Elemental analyses were consistent with the theoretical formulas. ^{1}H and ^{31}P NMR spectra were taken in a 3:1 (v:v) CD_2Cl_2/CD_3OD mixture at 253 K.

***cis*-[Pt(Me$_2$SO)$_2$(CH$_3$)$_2$]** was prepared according to a published method[13] and was crystallized several times from a 1:1 dichloromethane/diethyl ether mixture.

Dialkyl Substrates. Some of the complexes *cis*-$[PtL_2(CH_3)_2]$ are well-known and were prepared with a variety of synthetic procedures, L (reference number): PEt_3 (14); PPh_3 (14); PMe_3 (15); PMe_2Ph (16); $PMePh_2$ (16); $P(4\text{-}MeC_6H_4)_3$ (17). The known compounds and the new ones (L = $P(Pr^n)_3$, $P(Pr^i)_3$, $P(4\text{-}ClC_6H_4)_3$, $P(3\text{-}ClC_6H_4)_3$, $P(4\text{-}MeOC_6H_4)_3$, $P(2\text{-}MeOC_6H_4)_3$, $P(3\text{-}MeC_6H_4)_3$) were prepared by using essentially the following general procedure. A weighed amount of *cis*-$[Pt(Me_2SO)_2(Me)_2]$ was reacted in degassed dichloromethane with the stoichiometric amount of phosphine. In the case of the least reactive phosphines, the reaction mixture was set aside overnight. After evaporation of most of the solvent, the complex separated out as oil or solid on adding light petroleum (bp 60−80 °C) and cooling. The residue was crystallized from a suitable solvent. The identity of known complexes was checked by their NMR spectra. The identity and purity of the new compounds were established by elemental analysis and by ^{1}H and ^{31}P NMR.

***cis*-[Pt(PMe$_3$)$_2$(Me)$_2$] (1):** crystallized from light petroleum. ^{1}H NMR: δ 1.44 (d, $^2J_{PH}$ = 8.1 Hz, $^3J_{PtH}$ = 19.8 Hz, 18H, PCH_3), 0.37 (m, $^2J_{PtH}$ = 65.5 Hz, 6H, PtCH_3). ^{31}PNMR: δ −23.1 ($^1J_{PtP}$ = 1761 Hz).

***cis*-[Pt(PMe$_2$Ph)$_2$(Me)$_2$] (2):** crystallized from methanol. ^{1}H NMR: δ 7.5−7.3 (m, 10H, PPh); 1.47 (d, $^2J_{PH}$ = 7.3 Hz, $^3J_{PtH}$ = 21.3 Hz, 12H, PCH_3), 0.44 (m, $^2J_{PtH}$ = 66.9 Hz, 6H, PtCH_3). ^{31}P NMR: δ −10.0 ($^1J_{PtP}$ = 1794 Hz).

***cis*-[Pt(PEt$_3$)$_2$(Me)$_2$] (3):** crystallized first from light petroleum and then from methanol. ^{1}H NMR: δ 1.75 (m, 12H, PCH_2−), 1.05 (m, 18H, PCCH_3), 0.30 (m, $^2J_{PtH}$ = 64.7 Hz, 6H, PtCH_3). ^{31}P NMR: δ 9.3 ($^1J_{PtP}$ = 1843 Hz).

***cis*-[Pt(P(Pr^n)$_3$)$_2$(Me)$_2$] (4):** oil, crystallized several times from acetone/light petroleum and finally from acetone. ^{1}H NMR: δ 1.75 (m, 12H, PCH_2−), 1.45 (m, 12H, PCCH_2−), 1.01 (t, $^3J_{HH}$ = 7.3, 18H, PCCCH_3), 0.31 (m, $^2J_{PtH}$ = 64.7 Hz, 6H, PtCH_3). ^{31}P NMR: δ −0.1 ($^1J_{PtP}$ = 1828 Hz).

***cis*-[Pt(PMePh$_2$)$_2$(Me)$_2$] (5):** crystallized from acetone/light petroleum. ^{1}H NMR: δ 7.41−7.27 (m, 20 H, PPh), 1.63 (d, $^2J_{PH}$ = 6.6 Hz, $^3J_{PtH}$ = 20.6 Hz, 6H, PCH_3), 0.29 (m, $^2J_{PtH}$ = 68.4 Hz, 6H, PtCH_3). ^{31}P NMR: δ 7.6 ($^1J_{PtP}$ = 1851 Hz).

***cis*-[Pt(PPh$_3$)$_2$(Me)$_2$] (6):** crystallized from benzene. ^{1}H NMR: δ 7.4−7.1 (m, 30 H, PPh), 0.29 (m, $^2J_{PtH}$ = 69.9 Hz, 6H, PtCH_3). ^{31}P NMR: δ 28.0 ($^1J_{PtP}$ = 1910 Hz).

***cis*-[Pt(P(4-MeC$_6$H$_4$)$_3$)$_2$(Me)$_2$] (7):** crystallized from dichloromethane/

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light petroleum. ^{1}H NMR: δ 7.3−7.0 (m, 24H, PPh), 2.33 (s, 18H, CCH_3), 0.24 (m, $^2J_{PtH}$ = 67.8 Hz, 6H, PtCH_3). ^{31}P NMR: δ 26.0 ($^1J_{PtP}$ = 1924 Hz).

***cis*-[Pt(P(4-ClC$_6$H$_4$)$_3$)$_2$(Me)$_2$] (8):** crystallized from dichloromethane/ methanol. ^{1}H NMR: δ 7.3−7.2 (m, 24H, PPh), 0.35 (m, $^2J_{PtH}$ = 69.8 Hz, 6H, PtCH_3). ^{31}P NMR: δ 26.7 ($^1J_{PtP}$ = 1887 Hz).

***cis*-[Pt(P(4-MeOC$_6$H$_4$)$_3$)$_2$(Me)$_2$] (9):** crystallized from dichloromethane/ methanol. ^{1}H NMR: δ 7.3−7.0 (m, 24H, PPh), 3.79 (s, 18H, O−CH_3), 0.27 (m, $^2J_{PtH}$ = 68.4 Hz, 6H, PtCH_3). ^{31}P NMR: δ 24.7 ($^1J_{PtP}$ =1930 Hz).

***cis*-[Pt(P(Pr^i)$_3$)$_2$(Me)$_2$] (10):** crystallized from light petroleum/ acetone. ^{1}H NMR: δ 2.43 (m, 6H, PCH−), 1.22 (m, 36H, PCCH_3), 0.34 (m, $^2J_{PtH}$ = 66.0 Hz, 6H, PtCH_3). ^{31}P NMR: δ 29.8 ($^1J_{PtP}$ = 1866 Hz).

***cis*-[Pt(P(3-MeC$_6$H$_4$)$_3$)$_2$(Me)$_2$] (11):** crystallized from dichloromethane/ methanol. ^{1}H NMR: δ 7.3−7.1 (m, 24H, PPh), 2.15 (s, 18H, CCH_3), 0.27 (m, $^2J_{PtH}$ = 69.1 Hz, 6H, PtCH_3). ^{31}P NMR: δ 28.1 ($^1J_{PtP}$ = 1923 Hz).

***cis*-[Pt(P(3-ClC$_6$H$_4$)$_3$)$_2$(Me)$_2$] (12):** crystallized from dichloromethane/ methanol. ^{1}H NMR: δ 7.4−7.1 (m, 24H, PPh), 0.39 (m, $^2J_{PtH}$ = 70.6 Hz, 6H, PtCH_3). ^{31}P NMR: δ 29.5 ($^1J_{PtP}$ = 1876 Hz).

***cis*-[Pt(PCy$_3$)$_2$(Me)$_2$] (13):** crystallized from dichloromethane/ acetone. ^{1}H NMR: δ 2.3−1.1 (m, 66H, Cy), 0.31 (m, $^2J_{PtH}$ = 64.4 Hz, 6H, PtCH_3). ^{31}P NMR: δ 20.1 ($^1J_{PtP}$ = 1828 Hz).

***cis*-[Pt(P(2-MeOC$_6$H$_4$)$_3$)$_2$(Me)$_2$] (14):** crystallized from chloroform/ methanol. ^{1}H NMR: δ 7.5−6.6 (m, 24H, PPh), 3.3 (s, 18H, O−CH_3), −0.30 (m, $^2J_{PtH}$ = 70.6 Hz, 6H, PtCH_3). ^{31}P NMR: δ 9.5 ($^1J_{PtP}$ = 1839 Hz).

Kinetics. The kinetics of isomerization of *cis*-[PtL$_2$(Me)(MeOH)]$^+$ (L = alkyl, aryl, and mixed alkyl−aryl phosphines) complexes were followed spectrophotometrically by the traditional method, at constant temperature (CTK) and by a non-isothermal method (VTK).[18,19]

(a) CTK Method. The kinetics were followed by repetitive scanning of the spectrum at suitable times in the range 320−220 nm or at a fixed wavelength, where the difference of absorbance with the *trans* product was largest. The reactions were carried out in a silica cell, in the thermostated cell compartment of a Cary 219 or of a rapid-scanning Hewlett-Packard Model 8452 A spectrophotometer, with a temperature accuracy of ±0.05 °C. The reactions were started by adding with a syringe a prethermostated solution of *cis*-[PtL$_2$(Me)$_2$] in methanol to a thermostated methanol solution of $H^+BF_4^-$. In all cases the concentration of acid was sufficient to produce a fast cleavage of the first Pt−CH_3 bond. All the reactions obeyed a first-order rate law until well over 90% of the reaction and the rate constants k_i (s^{-1}) were obtained from a nonlinear least-squares fit of the experimental data to $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_i t)$ with D_0, D_∞, and k_i as the parameters to be optimized (D_0 = absorbance after mixing of reagents, D_∞ = absorbance at completion of reaction). Activation parameters were derived from a linear least-square analysis of $\ln(k_i/T)$ *vs* T^{-1} data.

(b) VTK Method. Kinetic runs were carried out using a Perkin-Elmer Lambda 3 spectrophotometer, connected to a 486/DX IBM microcomputer and equipped with a cell compartment thermostated by a Perkin-Elmer PTP (Peltier temperature programmer), which allows a controlled change of the temperature with time with an accuracy of ±0.05 °C. The temperature was checked by a platinum resistor inserted into the spectrophotometric cell and connected to the computer. The reactions were started as described above for the CTK method, the only difference being that the starting temperature (T_0) was made sufficiently low to slow down the initial rate of reaction. This procedure makes negligible the dead-time before reaching the linear part of the temperature program of the PTP device. The reactions were followed at a fixed wavelength, and the absorbance−time data were automatically acquired by using the Perkin-Elmer PECSS program. The processing of the stored data was performed by use of the MicroMath SCIENTIST program[20] with a Powell modified Marquadt algorithm[21] for the fitting and the Eulero method[21] for solving the differential equation

$$-\frac{d(D_t - D_\infty)}{dt} = \frac{k(T_0 + \alpha t)}{h}\exp\left[\frac{\Delta S^{\ddagger}}{R}\right]\exp\left[-\frac{\Delta H^{\ddagger}}{R(T_0 + \alpha t)}\right](D_t - D_\infty) \quad (1)$$

where α is the temperature gradient and D_∞, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are the parameters to be optimized. For a detailed description of the VTK method see ref 18 and the Supporting Information, including Figure SI1.

Results

Organometallic complexes of the type *cis*-[PtL$_2$(Me)$_2$] (L = PEt_3, PMe_3, PPh_3) can be prepared starting from *cis*-[PtL$_2$Cl$_2$] and methylating agents[14−16] or using other synthetic procedures such as the reaction of [Pt(COD)(Me)$_2$] with phosphines (PPh_3 and P(4-MeC$_6$H$_4$)$_3$),[17,22] the reaction of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] with phosphines (PPh_3, PEt_3, PMe_3, PMe_2Ph, $PMePh_2$),[23] and, eventually, the reaction of *cis*-[Pt(Me$_2$SO)$_2$(Me)$_2$] with phosphines (PPh_3).[13] In our hands, this latter method proved to be very useful, and therefore, an extended series of phosphine complexes was synthesized, according to eq 2

$$cis\text{-}[Pt(Me_2SO)_2(Me)_2] + 2L \rightarrow cis\text{-}[PtL_2(Me)_2] + 2Me_2SO \quad (2)$$

The removal of both molecules of sulfoxide from the starting material by the phosphines (L) is fast and easy, the reactions go to completion, and the desired products were obtained in high yield and purity. Complications arise only with the most sterically demanding phosphines. Thus, for P(2-MeC$_6$H$_4$)$_3$ and P(2-MeOC$_6$H$_4$)$_3$, the reaction mixture showed the contemporary presence of mono- and bis-substituted phosphine products, and this latter product was obtained in a satisfactory pure solid form only in the case of P(2-MeOPh)$_3$. Attempts to synthesize the compound with P(Bu^t)$_3$ failed. The new compounds, therefore, are those containing P(Pr^n)$_3$ (**4**), P(4-ClC$_6$H$_4$)$_3$ (**8**), P(4-MeOC$_6$H$_4$)$_3$ (**9**), P(Pr^i)$_3$ (**10**), P(3-MeC$_6$H$_4$)$_3$ (**11**), P(3-ClC$_6$H$_4$)$_3$ (**12**), PCy_3 (**13**), and P(2-MeOC$_6$H$_4$)$_3$ (**14**). Traces of dimethyl sulfoxide incorporated in the products were eliminated by crystallization. The complexes were characterized by ^{1}H and ^{31}P NMR in a 3:1 CD_2Cl_2/CD_3OD mixture, cooled at 253 K, and selected resonances are listed in Table 1.

Spectral Characteristics of the Complexes. The methyl part of the ^{1}H NMR spectrum of all the *cis*-[PtL$_2$(Me)$_2$] complexes is similar to that described in detail for L = PPh_3,[24] PEt_3,[25] PMe_2Ph,[16] and PMe_3.[26] The ^{31}P NMR spectrum shows a single resonance with low values of $^1J_{PtP}$ coupling constants, typical of phosphorus atoms *trans* to carbon in platinum complexes.[25,47]

A solution of a weighed amount of *cis*-[PtL$_2$(Me)$_2$] in a 3:1 CD_2Cl_2/CD_3OD mixture was frozen in the NMR tube and then added with the stoichiometric amount of an ethereal solution of HBF_4. The temperature was slowly increased to 253 K, and the ^{1}H and ^{31}P NMR spectra of the ensuing cis-monoalkyl

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Table 1. Selected ^{1}H and ^{31}P NMR Data for Dialkyl Phosphine Complexes of Platinum(II) and for the Cis and Trans Monalkyl Solvento Species Obtained upon Protonolysis and Subsequent Isomerization[a]

		complexes						
		cis-[$PtL_2(Me)_2$]		*cis*-[$PtL_2Me(MeOH)]^+$			*trans*-[$PtL_2Me(MeOH)]^+$	
no.	phosphine (L)	$\delta(^1H)(PtCH_3)$	$\delta(^{31}P)$	$\delta(^1H)(PtCH_3)$	$\delta(^{31}P_A)$[b]	$\delta(^{31}P_B)$[c]	$\delta(^1H)(PtCH_3)$	$\delta(^{31}P)$
1	PMe_3	0.37 (65.5)	−23.1 (1761)	0.56 (41.2)	−4.0 (1780)	−29.6 (4367)	0.58 (89.0)	−6.4 (2789)
2	$PPhMe_2$	0.44 (66.9)	−10.0 (1794)	0.66 (37.5)	7.4 (1820)	−16.7 (4500)	0.51 (85.3)	5.4 (2919)
3	PEt_3	0.30 (64.7)	9.3 (1843)	0.52 (43.4)	25.5 (1827)	8.9 (4427)	0.48 (86.8)	25.9 (2817)
4	$P(Pr^n)_3$	0.31 (64.7)	−0.1 (1828)	0.59 (45.0)	16.7 (1801)	−2.7 (4424)	0.48 (89.0)	15.2 (2793)
5	PPh_2Me	0.29 (68.4)	7.6 (1851)	0.57 (41.3)	20.3 (1846)	−2.2 (4655)	0.40 (86.7)	18.4 (3021)
6	PPh_3	0.29 (69.9)	28.0 (1910)	0.62 (41.2)	35.8 (1903)	15.3 (4823)	0.30 (82.4)	32.7 (3139)
7	$P(4\text{-}MeC_6H_4)_3$	0.24 (67.8)	26.0 (1924)	0.55 (43.5)	34.3 (1924)	12.3 (4807)	0.25 (86.8)	30.9 (3108)
8	$P(4\text{-}ClC_6H_4)_3$	0.35 (69.8)	26.7 (1887)	0.67 (48.1)	35.5 (1897)	13.3 (4854)	0.26 (80.7)	31.3 (3178)
9	$P(4\text{-}MeOC_6H_4)_3$	0.27 (68.4)	24.7 (1930)	0.58 (48.6)	33.5 (1945)	10.1 (4798)	0.29 (80.1)	29.3 (3085)
10	$P(Pr^i)_3$	0.34 (66.0)	29.8 (1866)				0.57 (88.2)	38.6 (2841)
11	$P(\mathbf{3}\text{-}MeC_6H_4))_3$	0.27 (69.1)	28.1 (1923)	0.58 (41.0)	35.2 (1890)	14.3 (4836)	0.25 (79.4)	32.8 (3128)
12	$P(3\text{-}ClC_6H_4)_3$	0.39 (70.6)	29.5 (1876)	0.72 (47.1)	37.4 (1860)	15.1 (4876)	0.25 (86.8)	33.4 (3214)
13	PCy_3	0.31 (64.4)	20.1 (1828)				0.25	27.9 (2807)
14	$P(2\text{-}MeOC_6H_4)_3$	−0.30 (70.6)	9.5 (1839)				0.46 (96.0)	24.1 (3274)

[a] Resonances in ppm from TMS and H_3PO_4 at 253 K; solvent = 3:1 CD_2Cl_2/ CD_3OD (v/v); $^2J_{PtH}$ in Hz for $PtCH_3$ and $^1J_{PtP}$ in Hz are given in parentheses. [b] P_A, phosphorus atom trans to the methyl group. [c] P_B, phosphorus atom trans to MeOH.

solvento species were recorded. As a typical example, in the case of *cis*-[$Pt(PMe_3)_2(Me)(MeOH)]^+$, the methylplatinum resonance appears at δ 0.56, as four lines of equal intensity due to the coupling with two nonequivalent ^{31}P atoms, with ^{195}Pt satellites ($^2J_{PtH}$ = 41.2 Hz). The two nonequivalent phosphine ligands give two ^{31}P resonances, $\delta(P_A) = -4.0$ ($^1J_{PtP}$ = 1780 Hz) and $\delta(P_B) = -29.6$ ($^1J_{PtP}$ = 4367 Hz). The low coupling constant $^1J_{PtPA}$ is indicative of a phosphorus atom trans to carbon, while the value $^1J_{PtPB}$ = 4367 Hz is consistent with the presence of a very weak trans donor ligand such as methanol. The low value of the $^2J_{PP}$ coupling constant (12 Hz) is typical of cis phosphines. Essentially the same pattern is observed when a moderate excess of acid is used and, therefore, *cis* configuration is retained at 253 K, as a result of Pt−CH_3 bond breaking. On increase of the temperature to 300 K, the isomerization can be monitored through the decrease in the ^{31}P signals associated with *cis*-[$Pt(PMe_3)Me(MeOH)]^+$ and the parallel and matching increase in the signal of the corresponding *trans* complex, which appears as a singlet with platinum satellites at δ −6.4 ($^1J_{PtP}$ = 2789 Hz). The rate of *cis* to *trans* conversion proved to be too fast to be followed for the complexes containing $P(Pr^i)_3$, PCy_3, and $P(2\text{-}MeOC_6H_4)_3$, and therefore, soon after the addition of acid, even at the lowest temperatures, only the ^{31}P signals due to the *trans* isomers were observed. A collection of ^{1}H and ^{31}P NMR data for the dialkyl complexes and for the monoalkyl *cis* and *trans* solvento isomers is reported in Table 1.

Spectrophotometric Kinetic Studies. ^{1}H and ^{31}P NMR spectra taken during the course of the reactions showed that the process under study was the simple uncatalyzed isomerization of the *cis* monoalkyl solvento complex. The amount or the nature of the acid used (provided the counteranion is not a nucleophile, as for HBF_4, $HClO_4$, or 4-toluenesulfonic acid) had no effect on the reaction. All isomerization reactions were followed spectrophotometrically using methanol as the solvent. The conversion was 100% complete, and the spectral changes showed isosbestic points (see Supporting Information Figure SI2). For the complexes containing $P(Pr^i)_3$, PCy_3, and $P(2\text{-}MeOC_6H_4)_3$ the two consecutive processes, protonolysis and isomerization, were complete soon after the mixing of the reagents. The isomerization follows a first-order rate law. Specific rate constants, k_i/s^{-1}, measured at different temperatures, were analyzed by least-squares regression of linear Eyring plots (primary kinetic data for isomerization at different temperatures are given as Supporting Information in Table SI1). The values of $\Delta H^{\ddagger}$ (kJ mol^{-1}) and $\Delta S^{\ddagger}$ (JK^{-1} mol^{-1}) are collected in Table 2, together with the values of the rate constant k_i/s^{-1} for the isomerization at 298.16 K. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained by the VTK method are collected in Table 2, where they can be compared with those obtained with the CTK method.

Discussion

Easy displacement of dimethyl sulfoxide by phosphines from the complex *cis*-[$PtMe_2(DMSO)_2$], according to eq 2, led to the synthesis of a wide series of complexes of the type *cis*-[PtL_2Me_2]. All attempts to obtain the compound with $P(Bu^t)_3$ failed, as a consequence of the strong steric congestion of the bulky phosphines occupying cis-positions. The compound with $P(2\text{-}MeC_6H_4)_3$ was detected in solution, but all efforts to isolate it were unsuccessful. The synthesis of the compound containing $P(2\text{-}MeOC_6H_4)_3$ came as a surprise because, on the basis of its encumbrance, we would have expected severe steric restriction to the formation of this molecule. Unfortunately, we were unable to grow suitable crystals for a crystallographic study, but it seems safe to conclude that a remarkable intermeshing and distortion of the two bulky phosphines must take place to minimize steric congestion at the metal center.[27−29]

The dialkyl complexes were used as precursors for the synthesis "in situ" of cationic *cis* solvento $[PtL_2(Me)(MeOH)]^+$ complexes. For the complexes containing the bulky $P(Pr^i)_3$, $P(Cy)_3$, and $P(2\text{-}MeOC_6H_4)_3$ phosphines the conversion of $[PtL_2(Me)(MeOH)]^+$ from the *cis* to the *trans* form was too fast to be followed, even at the lowest temperatures and, therefore, the spectral characteristics of these elusive *cis* species could not be detected. The ^{1}H and ^{31}P experiments indicate quite clearly that at 253 K the protonolysis of the dialkyls substrates is seen as a single-step conversion to the cis-monoalkyl products, with no evidence throughout of possible reaction intermediates such as platinum(IV) hydrido−alkyl species of the type recently reported in the literature.[30−32]

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Table 2. Ligand Properties of Phosphorus(III) Compounds, Rate Constants, and Activation Parameters for the Spontaneous Cis to Trans Isomerization of the Solvento $[PtL_2(Me)MeOH]^+$ Species in Methanol

no.	phosphine (L)	χ^a	θ^b	$10^3k_1{}^c$	$\Delta H^{\ddagger}$(VTK)^d	$\Delta H^{\ddagger}$(CTK)^e	$\Delta S^{\ddagger}$(VTK)^f	$\Delta S^{\ddagger}$(CTK)^g
1	PMe_3	8.55	118	0.018	125 ± 1^h	127 ± 2	84 ± 1	92 ± 6
2	$PPhMe_2$	10.6	122	0.017		128 ± 3		92 ± 10
3	PEt_3	6.3	132	2.95	108 ± 1^h	106 ± 3	67 ± 1	63 ± 12
4	$P(Pr^n)_3$	5.4	132	9.26	119 ± 1^h	123 ± 2	116 ± 1	128 ± 4
5	PPh_2Me	12.1	136	0.071	125 ± 1^h	122 ± 2	94 ± 3	84 ± 4
					127 ± 1^i		103 ± 1	
6	PPh_3	13.2	145	5.31	121 ± 1^h	119 ± 1	120 ± 1	111 ± 2
					122 ± 1^i		121 ± 1	
7	$P(4\text{-}MeC_6H_4)_3$	11.5	145	17.9	119 ± 1^h	115 ± 5	119 ± 1	106 ± 15
					120 ± 1^i		123 ± 1	
8	$P(4\text{-}ClC_6H_4)_3$	16.8	145	0.543	129 ± 1^h	125 ± 2	124 ± 1	113 ± 5
					127 ± 1^i		117 ± 1	
9	$P(4\text{-}MeOC_6H_4)_3$	10.5	145	62.0	120 ± 1^h	117 ± 1	134 ± 1	124 ± 5
11	$P(3\text{-}MeC_6H_4)_3$		148	7.97	120 ± 1^h	120 ± 2	116 ± 1	117 ± 5
					120 ± 1^i		118 ± 1	
12	$P(3\text{-}ClC_6H_4)_3$	18.4	145	0.141	119 ± 1^h	116 ± 2	80 ± 1	69 ± 7
					124 ± 1^i		96 ± 1	

[a] Values in cm^{-1} taken from ref 34; for $P(Pr^i)_3$ and $P(Cy)_3$, $\chi = 3.45$ and 1.4, respectively. [b] Cone angle in deg data taken from ref 42; for $P(Pr^i)_3$ and $P(Cy)_3$, $\theta = 160$ and 170°, respectively. [c] First-order rate constants (s^{-1}) for isomerization at 298.16 K. [d] Enthalpies of activation (kJ mol^{-1}) from variable-temperature kinetics. [e] Enthalpies of activation (kJ mol^{-1}) from constant-temperature kinetics. [f] Entropies of activation (J K^{-1} mol^{-1}) from variable-temperature kinetics. [g] Entropies of activation (J K^{-1} mol^{-1}) from constant-temperature kinetics. [h] Temperature gradient $\alpha = 0.0166$ °C/s^{-1}. [i] Temperature gradient $\alpha = 0.0083$ °C/s^{-1}.

Quantitative Separation of Steric and Electronic Effects. To correlate electronic or steric effects with chemical and physical properties it is necessary to dissect the overall effect into its steric and electronic components. In the last few years, numerous papers by Giering, Prock, and co-workers[11a,b] and by Poë and co-workers[11c−g] 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[33]

$$\text{property} = a(\chi) + b(\theta) + b'(\theta - \theta_{st})\lambda + c(E_{ar}) + d \quad (3)$$

where χ is an infrared parameter[34] that measures the σ donicity of the ligand (the electron-donor ability decreases as χ increases), θ is Tolman's cone angle,[35] which 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 $\theta > \theta_{st}$, and E_{ar} is the aryl-effect parameter,[36] 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. a, b, b', and c 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 $(\theta - \theta_{st})\lambda$ 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.*[33] 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 Tables 1 and 2 we followed the protocol suggested by Giering.[33] Attempts to apply Drago's electrostatic/covalent model[37] were unsuccessful, since the properties being analyzed depend heavily upon steric effects and to a minor extent on aryl effects. The limits of Drago's E/C model in correlation analyses involving phosphines have been recently discussed.[38]

Stereoelectronic Analysis of $^1J_{PtP}$ Coupling Constants. The values of $^1J_{PtP}$ coupling constants of the *cis*-$[PtL_2(Me)_2]$ complexes in Table 1 are in the range typical of a phosphorus atom *trans* to carbon in platinum(II) compounds, and setting apart the rogue value for complex **14**, they encompass a range of 160 Hz. Values of χ, θ, and E_{ar} were used in the analysis as stereoelectronic parameters of the ligands, but in principle, other related parameters could be used, such as pK_a[39] or pK_a'[11c] values of PR_3H^+, Bodner's $\delta(^{13}CO)$ values,[40] Brown's E_R values,[41] or Coville's solid angle values,[42] but their use does not bring about any significant improvement in the analysis.

The results of a regression analysis of all data points ($n = 13$), performed using eq 3 and the MicroMath SCIENTIST program, were as follows: $a = -6.00 \pm 1$ Hz cm; $b = +4.0 \pm 0.4$ Hz deg^{-1}; $b' = -8.9 \pm 1$ Hz deg^{-1}; $c = 23.9 \pm 5$ Hz; $d = 1338 \pm 58$ Hz; $\theta_{st} = 149°$. The correlation coefficient of the linear plot of $^1J_{PtP(calc)}$ *vs* $^1J_{PtP(obs)}$ (where $^1J_{PtP(calc)}$ is obtained by applying eq 3 and $^1J_{PtP(obs)}$ is determined experimentally)

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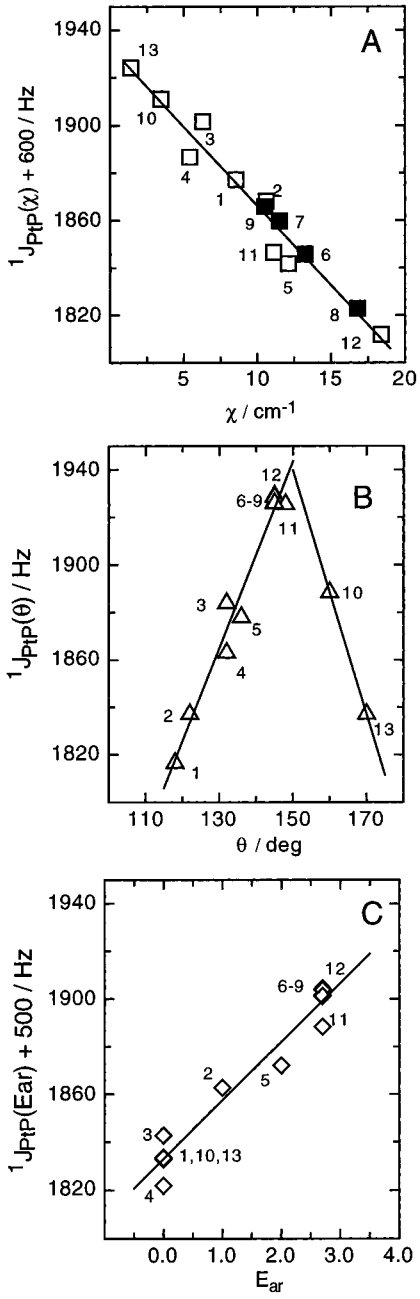

Figure 1. (A) Electronic profile, showing the dependence of the coupling constants $^1J_{PtP}$ upon the electronic parameter χ for *cis*-[Pt(PR$_n$Ar$_{3-n}$)$_2$(Me)$_2$] compounds. (B) Steric profile, showing the dependence of $^1J_{PtP}$ upon Tolman's cone angle. (c) E_{ar} plot. See text for the description of each plot. Numbers refer to the ligands as listed in Table 1. Filled squares refer to isosteric P(4-XC$_6$H$_4$)$_3$ ligands.

was $r^2 = 0.995$. A supplementary statistical criterion is given by the value of the root-mean-square deviation of $^1J_{PtP(calc)}$ from $^1J_{PtP(obs)}$ (rmsd = 6), which gives an estimate of the scatter of data. An appropriate index of goodness-of-fit is given also by the correspondence between the values of a (-6.00 ± 1 Hz cm) obtained from full regression analysis and the value of a (-6.89 ± 0.2 Hz cm) obtained from a plot of $^1J_{PtP(obs)}$ vs χ for the isosteric ligands P(4-XC$_6$H$_4$)$_3$, where θ and E_{ar} remain constant. These statistical criteria, r^2, rmsd, and correspondence of the a values, were used throughout to quantitatively assess the utility of the equations used in modeling the examined property.

The results of QALE analysis can be now displayed as electronic, steric, and aryl profiles. The electronic profile (Figure 1A) 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.* $a(\chi)$, from the $^1J_{PtP}$ experimental data, according to the following equation:

$$(^1J_{PtP})(\chi) = (^1J_{PtP})_{obs} - [b(\theta) + b'(\theta - \theta_{st})\lambda + c(E_{ar}) + d] \quad (4)$$

Likewise, the steric profile (Figure 1B) can be constructed using the equation

$$(^1J_{PtP})(\theta) = (^1J_{PtP})_{obs} - [a(\chi) + c(E_{ar}) + d] \quad (5)$$

and finally the aryl dependency (Figure 1C) can be obtained from the equation

$$(^1J_{PtP})(E_{ar}) = (^1J_{PtP})_{obs} - [a(\chi) + b(\theta) + b'(\theta - \theta_{st})\lambda + d] \quad (6)$$

In practice, for the sake of visual comparison of the plots, the term d has not been subtracted, and the figures are presented with the same absolute scale. The plots include all data points. The most relevant feature is that, before the steric threshold, 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.[29,43] The slope of the electronic profile in Figure 2D (-6.00 ± 1 Hz cm) is comparable to that found for isosteric ligands in *cis*-[PtPh$_2$(CO)(PR$_n$Ar$_{3-n}$)] compounds ($a = -8.2 \pm 0.9$ Hz cm)[44] indicating that inductive effects are transmitted primarily through the C−Pt−P bond axis and the nature of *cis* groups does not play a significant role.

The $^1J_{PtP}$ values of the *trans*-[PtL$_2$(Me)(MeOH)]$^+$ complexes encompass a range of 425 Hz, much wider than that for *cis*-[PtL$_2$(Me)$_2$]. The results of the QALE analysis, performed by using eq 3, were as follows: $a = 14.6 \pm 2$ Hz cm; $b = 3.6 \pm 0.6$ Hz deg^{-1}; $b' = -3.7 \pm 1$ Hz deg^{-1}; $c = 64 \pm 7$ Hz; $d = 2240 \pm 62$ Hz; $\theta_{st} = 151°$ ($r^2 = 0.998$, rmsd = 7, $n = 13$), in agreement with those obtained from the graphical analysis ($a = 14.4 \pm 1$ Hz cm, from the electronic plot for isosteric P(4-XC$_6$H$_4$)$_3$ ligands). The electronic and steric profiles are illustrated in Figure 2A,B, respectively. The most significant feature that emerges is that the values of $^1J_{PtP}$ decrease greatly with increasing the σ-donor power of the coordinated phosphines, in sharp contrast to the pattern of behavior observed for the *cis*-dialkyl complexes (the values of the slopes of the plots of the two electronic profiles are $a = -6.0 \pm 1$ Hz cm, Figure 1A, and $a = +14.6 \pm 2$ Hz cm, Figure 2A, respectively). Coupling constants $^1J_{PtP}$ of closely related planar platinum(II) complexes have been regarded as a good diagnostic probe of the extent of the covalence of the Pt−P bond, representing primarily the change in 6s character of the hybrid orbital of platinum used in bonding to the phosphorus atom.[25] Correlations with data available from other spectroscopic techniques and from X-ray diffraction studies have shown that smaller values of $^1J_{PtP}$ correspond to longer Pt−P bond distances and to higher trans influences of groups in trans position to the bond.[45−47] Thus, ligands of high trans influence increase the

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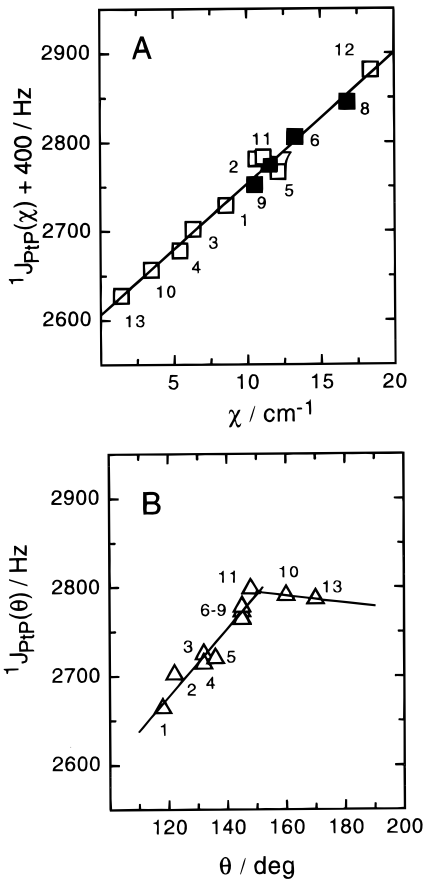
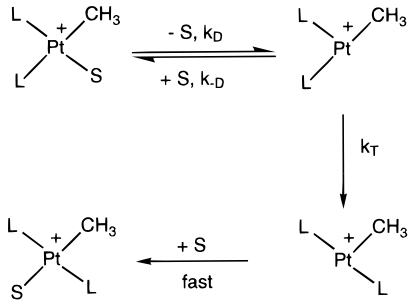


Figure 2. (A) Electronic profile, showing the dependence of the coupling constants $^1J_{PtP}$ upon the electronic parameter χ for *trans*-$[Pt(PR_nAr_{3-n})_2(Me)(MeOH)]^+$ compounds. (B) Steric profile. Numbers refer to the ligands as listed in Table 1.

Pt 6s character of their bond at the expense of the trans Pt−P bond which uses the same hybrid orbital. Our findings can be rationalized in terms of the competition of the two *trans* phosphines for the same orbital along the P−Pt−P bond axis and of the lengthening of the Pt−P bond. At the steric threshold ($\theta_{st} = 151°$), there is still an inversion in the direction of the steric effects. However, as expected for the less congested *trans* geometry, the negative steric effect ($b' = -3.7 \pm 1$ Hz deg^{-1}) is smaller than that for the *cis* compounds ($b' = -8.9 \pm 1$ Hz deg^{-1}).

Stereoelectronic Analysis of Kinetic Data. (a) Uncatalyzed Isomerization. The isomerization of *cis*-$[Pt(L)_2(Me)(MeOH)]^+$ complexes 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, and it can be considered approximately constant when one compares the kinetic behavior of compounds of strictly similar structural properties. Accordingly, the isomerization of *cis*-$[Pt(PEt_3)_2(R)(MeOH)]^+$ complexes[6] was found to proceed through the dissociative mechanism in the above reaction scheme, and is characterized by the following: (i) mass-law retardation by [MeOH] in diethyl ether−methanol mixtures; (ii) high values of $\Delta H^{\ddagger}$ and large positive values of $\Delta S^{\ddagger}$; (iii) small steric acceleration on going from R = methyl or phenyl to mesityl.[48]

The QALE analysis for the isomerization process has been performed according to the protocol described before. The regression analysis of all the kinetic data in Table 2 led to the following equation:

$$\log k_i = (-0.27 \pm 0.06 \text{ cm})(\chi) + (0.13 \pm 0.03 \text{ deg}^{-1})(\theta) + (0.066 \pm 0.3)(E_{ar}) - 17.8 \pm 4 \quad (7)$$

$$r^2 = 0.995 \qquad \text{rmsd} = 0.342 \quad 11 \text{ data points}$$

There is a good correspondence between the value of $a = -0.27 \pm 0.06$ cm and the slope of the line for isosteric ligands $P(4\text{-}XC_6H_4)_3$ with $\theta = 145°$ and $a = -0.32 \pm 0.04$ cm. It is worth remembering that this analysis does not include data points for highly reactive complexes, formed by the most sterically demanding ligands. Thus, the absence of a steric threshold could be due only to an insufficient variation of the steric parameter of the ligands. Assuming there is no steric threshold and eq 7 applies to the entire set of ligands, it is possible to predict the rates of isomerization of the complexes containing $P(Pr^i)_3$ ($k_{i,298} = 117$ s^{-1}) and PCy_3 ($k_{i,298} = 8300$ s^{-1}). The electronic profile (Figure 3A) and the steric profile (Figure 3B) for the overall set of ligands were constructed by using the parameters in eq 7 and the same absolute vertical scale for the two plots. As 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 process appears to be particularly sensitive in revealing electronic interactions between the metal and phosphine ligands. These findings are in keeping with the results of a study on the isomerization of *cis*-$[Pt(PEt_3)_2(YC_6H_4)X]$ complexes,[4a] where the rate constants k_i were correlated to the Hammett parameters of the substituents Y, in the meta or para position on the aromatic ring.

The linear plot of Figure 3B 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 the cone angle of the phosphines accounts for more than 1 order of magnitude increase in reactivity. The steric dependence is the result of the different response of the energy

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(48) In an associative process, the 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. See: Faraone, G.; Ricevuto, V.; Romeo, R. Trozzi, M. *J. Chem. Soc., Dalton Trans* **1974**, 1377.

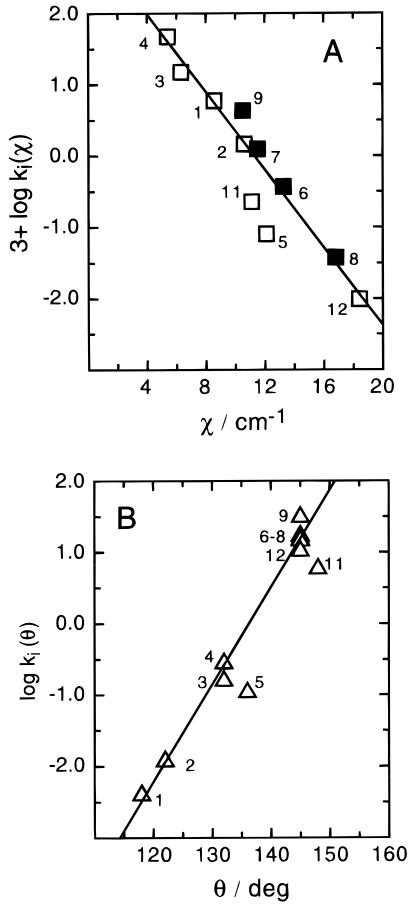

Figure 3. Stereoelectronic analysis of the rate constants k_i/s^{-1} for the uncatalyzed isomerization of *cis*-$[Pt(PR_nAr_{3-n})_2(Me)(MeOH)]^+$ compounds, at 298.16 K in methanol: (A) electronic profile; (B) steric profile. Numbers refer to the ligands as listed in Table 1.

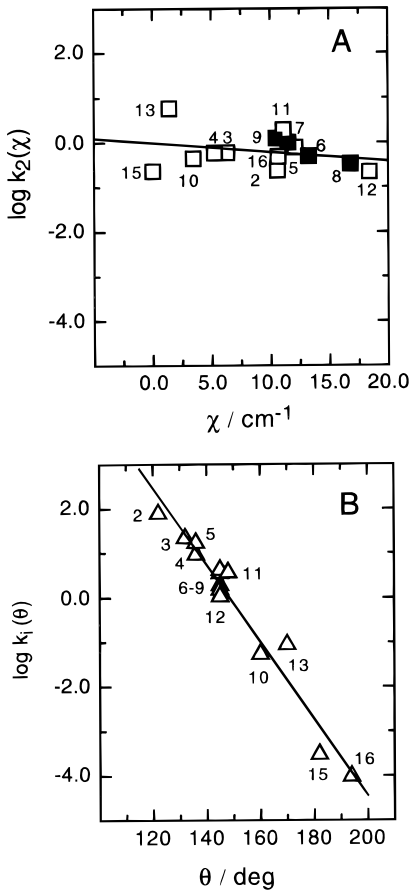

Figure 4. (A) Electronic profile for phosphines acting as entering groups in the nucleophilic substitution reaction of 5-Aq from the complex *cis*-$[PtPh_2(CO)(5\text{-Aq})]$ (5-Aq = 5-aminoquinoline; primary rate data taken from ref 44). (B) Steric profile for the same reaction. Numbers refer to the ligands as listed in Table 1. (15) refers to $P(Bu^t)_3$, and (16), to $P(2\text{-}MeC_6H_4)_3$.

of the ground and the transition states to changes in the size of the "spectator" ligands. For a purely dissociative process, the idealized steric profile is made up by lower and upper plateau regions, connected by a straight line with a positive slope.[49] The first horizontal lower part, for very small ligands, limits a region where steric effects are not operative both in the ground and in the transition state. A steric threshold marks the onset of steric destabilization of the ground state, and the rates increase with ligand size and steric congestion of the substrate. The second horizontal upper part, for the most sterically demanding ligands, reflects the case in which the energies of the ground state and of the more flexible transition state are sterically influenced to a comparable extent. Therefore, the plot of Figure 3B, found for ligands of intermediate size, where the rate increases with increasing steric destabilization of the ground state, is only a part of a more complicated steric profile. There are literature examples of a complete fitting of the experimental data to the expected profile, such as for the rates of dissociative substitution of CO from *mer*-$[Ru(CO)_3(SiCl_3)_2L]$ (L = phosphine),[50] analyzed by Giering *et al.* with the QALE method.[49] For a number of other dissociative processes of carbonyl compounds the steric profile is a straight line as shown in Figure 3B.[51] A reviewer has observed that the value of $b = 0.13 \pm 0.03$ deg^{-1} for isomerization is very large compared to the values reported for CO dissociation from a variety of carbonyl complexes, where it was claimed[51,52] that the steric effect decreased with the coordination number of the complexes. It could also increase as the transition state comes later, and since the electronic effect is much larger than in the CO dissociation reactions, this supports a very late transition state for the isomerization with MeOH being totally free. This is in contrast to CO dissociation reactions where the electronic and steric effects are both small and the extent of bond breaking is presumably much less.

(b) Associative Substitutions. The different roles of electronic effects and steric hindrance in dissociative and associative processes can be seen clearly by comparing the pattern of behavior illustrated above with that found for the bimolecular displacement of 5-aminoquinoline (5-Aq) from $[PtPh_2(CO)(5\text{-Aq})]$. Our previously reported QALE analysis[44] of these rate data, proposed as a series of nucleophilic reactivity constants n_{Pt}^{P} for phosphines reacting with platinum(II), can be improved by omitting data points for ligands of unusual electronic effects, such as $P(C_2H_4CN)_3$, or considering that the value of cone angle (165°) originally used for $P(3\text{-}MeC_6H_4)_3$ and $P(3\text{-}ClC_6H_4)_3$ greatly overstates the size of these groups. With these corrections no steric threshold was observed. The reaction rates can be correlated through a three-parameter equation:

$$\log k_2 = a(\chi) + b(\theta) + c \qquad (8)$$

where $a = -0.021 \pm 0.02$ cm, $b = -0.087 \pm 0.05$ deg^{-1}, and $c = 12.8 \pm 1$ ($r^2 = 0.979$, rmsd = 0.354, $n = 14$). The negative

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sign of the *a* coefficient indicates that the transition state is electron-demanding relative to the ground state. The negative sign of the *b* coefficient indicates that increasing steric requirement of the ligand impedes the reaction. By using these parameters the electronic profile (in Figure 4A) and the steric profile (in Figure 4B) were constructed, which give a visual comparison of the relative importance of the two parameters. On the basis of eq 8,[53] log k_2 has a 94% steric contribution and only 6% electronic contribution. The main conclusions are when phosphines are used as entering groups in a bimolecular substitution on [$PtPh_2$(CO)(5-Aq)], (i) the contribution to the rates of changes in the σ-inductive ability of the attacking P-donor ligands is negligible and (ii) the reaction is dominated by steric factors. The generality of this pattern of behavior for phosphines needs to be confirmed. Shi and Elding[54] have recently reported that the rates of substitution of some square planar platinum(II) complexes with thioethers show a significant dependence on changes in the electronic properties of the entering ligands. As discussed previously,[55] the linear steric profile in Figure 4B is only a part of a more complicated hypothetical steric profile which consists of upper and lower plateau regions connected by a straight line with a negative slope. Along this downward sloping part of the plot, steric effects are operative through a continuous increasing destabilization of the five-coordinate transition state.

Activation Parameters. The activation parameters for the isomerization of the *cis*-[PtL_2(Me)(MeOH)]$^+$ solvento complexes were calculated from the temperature dependence of the reaction, using both the traditional isothermal (CTK) method and a non-isothermal (VTK) method. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained with the two methods, listed in Table 2, appear to be in excellent agreement. The advantages offered by the VTK 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 $k(T)$ 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 large values of enthalpy of activation and the positive entropies of activation associated with isomerization give a further indication that the reaction proceeds through the dissociative mechanism shown in the earlier scheme. Setting apart the complex with triethylphosphine, which appears as a rogue point, the values of $\Delta H^{\ddagger}$ encompass a difference of 10 kJ mol^{-1} between the highest and the lowest value, with a mean value of $\Delta H^{\ddagger} = 122 \pm 3$ kJ mol^{-1}. For the entropy of activation the mean value is $\Delta S^{\ddagger} = 111 \pm 15$ J K^{-1} mol^{-1}, the lowest value being 84 ± 1 J K^{-1} mol^{-1} and the highest 134 ± 2 J K^{-1}mol^{-1}. Therefore, the contribution of $T\Delta S^{\ddagger}$ to $\Delta G^{\ddagger}$, at 298 K, varies by $\sim$15 kJ mol^{-1}. These findings are in agreement with a mechanistic picture in which the relief of steric strain on going from the congested square planar substrate to the more flexible T-shaped 3-coordinate transition state makes a significant contribution to the dissociation of the bonded group from the substrate.

Conclusions

The overall structure−reactivity correlation for some organo−phosphine platinum(II) compounds has been rationalized. The QALE analysis has proved to be a useful method for evaluating the effects of ligand basicity and steric hindrance on the NMR parameters and the reactivity. For the complexes *cis*-[$Pt(PR_nAr_{3-n})_2Me_2$] the values of the coupling constants $^1J_{PtP}$ were found to increase linearly with the electron releasing ability of the substituents on the phosphorus atoms. However, the opposite trend was observed when the two phosphines occupy *trans* positions as in the *trans* [$Pt(PR_nAr_{3-n})_2$(Me)(MeOH)]$^+$ solvento complexes. These experimental findings are in agreement with theoretical predictions. The steric profile for $^1J_{PtP}$ has an inverted V shape, increasing with ligands of intermediate size and then decreasing, after the steric threshold. The decrease is sharp, for the *cis* complexes, and less dramatic for the *trans* compounds, as a consequence of the overload of steric congestion at the central metal.

The rates of the isomerization of the solvento complexes *cis*-[$Pt(PR_nAr_{3-n})_2(CH_3)$(MeOH)]$^+$ are accelerated both by electron donation and steric hindrance brought about by substituents on the "spectator" ligands. The rate-determining step is the *dissociation* of the weakly bonded molecule of MeOH from the metal. Inductive effects stabilize a flexible 3-coordinate T-shaped 14-electron transition state, and steric effects destabilize the rigid 4-coordinate square-planar ground state. High values of the enthalpy of activation and large positive entropies of activation are associated with isomerization. The release of steric strain on going from the ground state to the transition state significantly affects the rates. A plot of log $k_{i(\theta)}$ *vs* Tolman's cone angle of the phosphines is a straight line with a positive slope. This plot is only a part of the expected shape for the steric profile of a purely dissociative process and reflects the continuous increase of steric congestion at the metal. In contrast, when the phosphines are used as entering groups in associative substitution processes, the steric profile is a straight line with a negative slope.

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. Two factors, (i) ligand steric congestion and (ii) strong σ-electron donation by the 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-hydrogens on a alkyl chain is concerned. This will be the subject of a forthcoming paper.[56]

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Supporting Information Available: Text providing a detailed description of the non-isothermal method, including Figure SI1, Figure SI2, showing spectral changes for isomerization of cis-[$Pt(CH_3)(PPh_3)_2$-(MeOH)]$^+$ at 295 K, and Table SI1, reporting the temperature dependence of the rates of isomerization, k_i (s^{-1}) (7 pages). Ordering information is given on any current masthead page.

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