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Steric and Electronic Factors Influencing the Reactivity of Tertiary Phosphines toward Platinum(II) Complexes

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The displacement of 5-aminoquinoline (5-AQ) from the complex *cis*-[$PtPh_2(CO)(5\text{-}AQ)$], by an extended series of phosphines (L) of widely different steric and electronic properties, takes place in toluene by way of a direct bimolecular attack of the ligand on the substrate. The sequence of reactivity observed is $PMe_2Ph > PEt_3 > PMePh_2 > P(n\text{-}Bu)_3 > P(p\text{-}MeOC_6H_4)_3 > P(m\text{-}MeC_6H_4)_3 > P(p\text{-}MeC_6H_4)_3 > PPh_3 > P(p\text{-}ClC_6H_4)_3 > P(m\text{-}ClC_6H_4)_3 > P(EtCN)_3 > PCy_3 > P(i\text{-}Pr)_3 > P(t\text{-}Bu)_3 > P(o\text{-}MeC_6H_4)_3$. The difference in reactivity between the first and the last members of the series spans at least 6 orders of magnitude. A series of nucleophilic reactivity constants ($n^{P}{}_{Pt}$), for phosphines reacting with platinum(II), has been derived from the second-order rate constants of the reaction. These $n^{P}{}_{Pt}$ correlate very well with the heats of reaction measured when the same phosphines react with *trans*-[$Pt(PPhMe_2)_2(Me)(THF)]^+$. The values of the rate constants can be resolved quantitatively into electronic and steric effects, by means of correlations with the pK_a values of the phosphines or with some internal parameters of the system such as ν_{CO}, ${}^1J_{Pt-P}$, or ${}^1J_{Pt-C(CO)}$ of the *cis*-[$PtPh_2(CO)(L)$] products. Electronic and steric profiles of the reaction were obtained showing that (i) the reactivity is only slightly affected by σ-inductive effects brought about by substituents on the phosphine ligands and (ii) steric effects are quite small for small substituents but they increase steadily as the size of the substituent increases.

Introduction

The observation that tertiary phosphines can bind easily to heavy metals dates back to the last century,[1] and since then, their use in the synthesis of coordination and organometallic compounds has been extensive.[2] Efforts have been made to take account of all the possible modes by which the phosphines influence a given physicochemical quantity of a compound. These eventually can be restricted to two factors of overriding importance: steric hindrance and σ-donor ability, as dictated by changes in the nature of the substituents on the phosphorus ligand. Ligand cone angles (θ) of space-filling CPK molecular models and A_1 carbonyl stretching frequencies (ν) in $Ni(CO)_3L$ complexes have been proposed as quantitative measures of steric and electronic effects.[3] The latter can be conveniently measured also by pK_a values (for HPR_3^+), as derived from half-wave neutralization potentials in nitromethane (ΔHNP),[4] or by values of enthalpies of protonation,[5] or even by an extended number of ^{13}C NMR chemical shifts of $Ni(CO)_3L$ complexes.[6]

Phosphines have been widely used as reagents in kinetic studies of CO substitution of metal carbonyls. In this context, the most interesting examples come from associative reactions, where it is possible to discriminate among different reacting phosphines and to measure their relative nucleophilic power. Basolo[7] pioneered this type of study and was able to show that an associative pathway is possible, without violating Tolman's 16,-18-electron rule,[8] when the substrate contains ligands capable of withdrawing a pair of electrons as the nucleophile approaches. Thus, the four-coordinate $Co(CO)_3NO$[9] and $Fe(CO)_2(NO)_2$ species,[10] isoelectronic and isostructural with $Ni(CO)_4$, react by an associative mechanism and the metal can avoid the unfavorable 20-electron configuration because the ligand NO^+ becomes NO^- as the metal–nucleophile bond is formed. Other five- and six-coordinate nitrosyl complexes behave likewise. A ring slippage from a $(\eta^5\text{-}C_5H_5)^-$ form to a $(\eta^3\text{-}C_5H_5)^-$ form accounts for the associative mechanism found for cyclopentadienylmetal carbonyl complexes.[11] Nice correlations of the rate data with the basicity of the entering phosphines were found for a number of mononuclear metal carbonyls.[7] The kinetic studies have been extended to metal carbonyl clusters, and quite recently[12] it was suggested that the reaction rates can be correlated through a three-parameter equation:

$$\log k_2 = \alpha + \beta pK_a + \chi\theta \qquad (1)$$

where pK_a and θ have the meanings given above, β and χ are regression coefficients that measure the relative importance of electronic and steric factors in the process, and α refers to the intrinsic reactivity of the substrate. The kinetics and mechanism of substitution reactions of mononuclear and cluster metal carbonyls were reviewed recently.[13,14]

Surprisingly, kinetic studies on square planar coordination and organometallic complexes of phosphines are scarce, especially

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those directed toward the search for an extended correlation between characteristics of the phosphines and reactivity. Thus, in the range of nucleophilic reactivities n°_{Pt},[15] we find only three very similar values for phosphines (PPh_3, 8.91; PEt_3, 8.96; $P(n\text{-}Bu)_3$, 8.99). In the reactions of *trans*-$[NiL_2(NCS)_2]$ (L = PEt_3, PEt_2Cy, $PEtCy_2$, PCy_3, $P(n\text{-}Pr)_3$, $P(n\text{-}Bu)_3$) with bipyridine, the labilities of the phosphines seem to depend linearly on their basicities.[16] The cis effect of phosphines and phosphites in the reactions of the cationic complexes $[Pt(en)(L)Cl]^+$ (L = PMe_3, PEt_3, $P(n\text{-}Bu)_3$) with various nucleophiles seems to be mainly steric in origin,[17] although the differences in reactivity observed are very low. Still lower appear to be the differences in the trans effect of the same phosphines, when the rate data for the reactions of $[PtLCl_3]^-$ with some amines are compared.[18]

We report here a kinetic study of the displacement of 5-aminoquinoline (hereafter referred to as 5-AQ) from the complex *cis*-$[PtPh_2(CO)(5\text{-}AQ)]$ by an extended series of phosphines of widely different steric and electronic properties. The observed sequence of reactivity gives the first extended scale of nucleophilic reactivity of phosphines toward platinum(II). The values of the rate constants can be resolved quantitatively into electronic and steric effects, by means of correlations with the pK_a values of the phosphines or with some internal parameters of the system such as ν_{CO}, $^1J_{Pt-P}$ or $^1J_{Pt-CO}$ of the *cis*-$[PtPh_2(CO)(phosphine)]$ products. The steric profile obtained shows that steric effects are quite small for small substituents but they increase steadily as the size of the substituent increases.

Experimental Section

Preparation of Complexes. ***cis*-$[Pt(C_6H_5)_2(CO)(SEt_2)]$** was prepared by carbonylation from $[Pt_2(C_6H_5)_4(\mu\text{-}SEt_2)_2]$ following essentially the procedure described by Vrieze et al.[19]

***cis*-$[Pt(C_6H_5)_2(CO)(5\text{-}AQ\text{-}N1)]$ (1).** 5-Aminoquinoline (87 mg, 0.60 mmol) was added to a solution of *cis*-$[Pt(C_6H_5)_2(CO)(SEt_2)]$ (280 mg, 0.60 mmol) in dichloromethane (60 mL). The solution was stirred for 48 h in the dark at room temperature and then concentrated under reduced pressure, and finally hexane was added. The precipitated crude product was recrystallized from a dichloromethane/hexane mixture. The elemental analysis was consistent with the theoretical formula. IR: $\nu_{C=O}$ 2065 cm^{-1}. ^1H NMR spectral data (only for the 5-AQ protons): δ 9.29 (d, ^3J = 4.98 Hz, 1 H), 8.95 (d, ^3J = 8.53 Hz, 1 H), 8.82 (d, ^3J = 8.48 Hz, 1 H), 7.94 (t, av ^3J = 7.97 Hz, 1 H), 7.65 (q, ^3J = 4.98 Hz, ^3J = 8.53 Hz, 1 H), 7.16 ppm (d, ^3J = 7.72 Hz, 1 H). ^{13}C NMR ($CDCl_3$): ^{13}CO δ 181 ppm.

Purification of Reagents. Some solid phosphines (PPh_3, $P(p\text{-}MeC_6H_4)_3$, $P(o\text{-}MeC_6H_4)_3$, PCy_3) were recrystallized 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 best commercially available.

Purification of Solvents. Diethyl ether was dried by distillation from sodium benzophenone. Methylene chloride was distilled from barium oxide under nitrogen. Toluene for use in kinetic runs was obtained by purification of spectrophotometric grade toluene (Aldrich). The solvent, after refluxing over sodium, was distilled under a nitrogen atmosphere, treated with a series of freezing–pumping cycles, and eventually stored in a Schlenk tube.

Kinetics. The rates of reaction were followed spectrophotometrically by repetitive scanning of the spectrum at suitable times in the range 450–340 nm or at a fixed wavelength, where the difference of absorbance was largest. The reactions were carried out in a special 10-mm silica cell (Helma), divided into two compartments by a transparent silica septum, in the thermostated cell compartment of a Cary 219 or a Perkin-Elmer Lambda 3 spectrophotometer, with a temperature accuracy of ±0.02 °C. Faster reactions required the use of a rapid-scanning Hewlett-Packard Model 8452 A spectrophotometer. Standard solutions of reagent and complex in the degassed solvent were prepared and manipulated in a glovebox with a continuous slow purge of N_2 gas.[20] Using the vacuum technique, aliquots of these solutions were transferred to the silica cell placed at the bottom of a wide-necked Schlenk tube and held in place by a suitable plastic ring. Once the two separated compartments were filled with the solutions of reagent and complex, respectively, under nitrogen atmosphere, the cuvette was sealed with a gastight rubber serum cap and eventually transferred to the thermostated cell compartment of the spectrophotometer, where it was left for the time necessary to reach the reaction temperature. The reaction was started by overturning the cell and shaking it vigorously until the mixing of the two solutions was complete. The use of at least a 10-fold excess of nucleophile over complex ensured pseudo-first-order kinetics in any run. All the reactions obeyed a first-order rate law until well over 90% of the reaction, and the rate constants k_{obsd} (s^{-1}) were obtained either by means of graphs or from a nonlinear least-squares fit of the experimental data to $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obsd}t)$ with A_0, A_∞, and k_{obsd} as the parameters to be optimized (A_0 = absorbance after mixing of reagents; A_∞ = absorbance at completion of reaction).

The reaction products *cis*-$[PtPh_2(CO)(L)]$ were characterized in solution by their IR and ^1H, ^{13}C, and ^{31}P NMR spectra. Generally, these species were obtained quite easily from *cis*-$[PtPh_2(CO)(SEt_2)]$, by adding the stoichiometric amount of phosphine to a solution of the complex, using standard techniques for handling air-sensitive compounds as described above. The thioether proved to be by far a better leaving group than 5-AQ. Only in the case of the less reactive phosphines was it necessary to add an excess of reagent or to gently warm the reaction mixture to allow the reaction to go to completion. When an excess of the most reactive phosphines was used (PEt_3 or PMe_2Ph, for example), the IR spectra showed that also the carbonyl group could be removed after the displacement of the sulfide. This aspect of the reaction has not been further investigated in detail.

Infrared spectra were recorded with KBr cells in the range 4000–400 cm^{-1} using a Perkin-Elmer FT-IR Model 1730 spectrometer. The samples for IR measurements were prepared in toluene. One- and two-dimensional correlated (COSY) ^1H NMR spectra of the starting complex *cis*-$[PtPh_2(CO)(5\text{-}AQ)]$ were recorded on a Bruker AMX-600 spectrometer operating at 600 MHz. Chemical shifts are reported in ppm (δ) from TMS as internal reference. ^{13}C NMR spectra of the *cis*-$[PtPh_2(CO)(L)]$ products were obtained on a Varian Gemini 300 spectrometer, operating at 75.5 MHz. These species were obtained by adding phosphine to a C_6D_6 solution of a ^{13}CO-enriched sample of *cis*-$[PtPh_2(CO)(SEt_2)]$. ^{13}C NMR chemical shifts are referred to the solvent peak and are reported versus TMS. ^{31}P NMR spectra were recorded at 230 K, on a Bruker WP 80 SY operating at 32.442 MHz, using $CDCl_3$ as solvent. The chemical shifts, in parts per million, are relative to external phosphoric acid. Microanalyses were performed by Analytical Laboratories, Engelskirchen, Germany.

Results

The reactions

$$cis\text{-}[PtPh_2(CO)(5\text{-}AQ)] + L \rightarrow cis\text{-}[PtPh_2(CO)(L)] + 5\text{-}AQ \qquad (2)$$

(L = PMe_2Ph, $P(EtCN)_3$, PEt_3, $P(n\text{-}Bu)_3$, $PMePh_2$, PPh_3, $P(p\text{-}MeC_6H_4)_3$, $P(p\text{-}ClC_6H_4)_3$, $P(p\text{-}MeOC_6H_4)_3$, $P(i\text{-}Pr)_3$, $P(m\text{-}CH_3C_6H_4)_3$, $P(m\text{-}ClC_6H_4)_3$, PCy_3, $P(t\text{-}Bu)_3$, $P(o\text{-}MeC_6H_4)_3$) were carried out in toluene as solvent. The analysis of the changes of the IR and ^1H, ^{13}C, and ^{31}P NMR spectra during the course of the reaction showed that the process under study was indeed the simple substitution of the bound 5-AQ by L.

The systematic kinetics of this reaction were studied at different ligand concentrations and were followed spectrophotometrically. The spectral changes occur in the near-visible region between 440 and 340 nm with an isosbestic point at 353 nm, and since they are due essentially to the difference in optical density between coordinated and uncoordinated 5-aminoquinoline, their shapes

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Table I. Ligand Properties of Phosphorus(III) Compounds and Rate Constants for the Reaction

$$cis\text{-}[PtPh_2(CO)(5\text{-}AQ\text{-}N1)] + L \rightarrow cis\text{-}[PtPh_2(CO)(L)] + 5\text{-}AQ$$

	phosphine	pK_a [a]	θ,[b] deg	k_2,[c] $M^{-1}\ s^{-1}$	n^{P}_{Pt} [d]	$-\Delta H$,[e] kcal mol^{-1}
1	PMe_2Ph	6.50	122	47.4	5.91	25.0
2	$P(EtCN)_3$	1.36	132	0.117	3.36	17.6
3	PEt_3	8.69	132	16.2	5.45	24.3
4	$P(n\text{-}Bu)_3$	8.43	132	7.22	5.09	
5	$PMePh_2$	4.57	136	9.58	5.22	22.1
6	PPh_3	2.73	145	1.02	4.25	19.5
7	$P(p\text{-}MeC_6H_4)_3$	3.84	145	2.06	4.56	
8	$P(p\text{-}ClC_6H_4)_3$	1.03	145	0.681	4.08	
9	$P(p\text{-}MeOC_6H_4)_3$	4.59	145	2.56	4.65	
10	$P(i\text{-}Pr)_3$	(9.60)	160	0.046	2.90	12.7
11	$P(m\text{-}MeC_6H_4)_3$	3.30	165	2.17	4.58	
12	$P(m\text{-}ClC_6H_4)_3$	1.03	165	0.447	3.89	
13	PCy_3	9.70	170	0.083	3.16	15.9
14	$P(t\text{-}Bu)_3$	11.40	182	0.0003	0.73	4.8
15	$P(o\text{-}MeC_6H_4)_3$	3.08	194	0.000058	0.00	1.9

[a] pK_a values for PR_3H^+ as taken from ref 4. [b] Cone angle data taken from ref 3. [c] Second-order rate constants for reaction 2 in toluene at 298.16 K. [d] n^{P}_{Pt} values (see text). [e] Enthalpies of Pt–P bond formation in *trans*-$[PtCH_3(PMe_2Ph)_2(L)]^+$, as measured for the reaction of phosphines with *trans*-$[PtCH_3(PMe_2Ph)_2(THF)]^+$, from ref 24.

Table II. Spectroscopic Properties of *cis*-$[PtPh_2(CO)(L)]$ Compounds

	phosphine	ν_{CO} [a]	$\delta(^{13}C(CO))$ [b]	$^1J_{Pt-C}$ [c]	$^2J_{P-C}$ [d]	$\delta(^{31}P)$ [e]	$^1J_{Pt-P}$ [f]
1	PMe_2Ph	2060	181.4	986.4	5.5	−14.9	1745.6
2	$P(EtCN)_3$	2069					
3	PEt_3	2055	182.0	987.9	5.6	3.3	1781.9
4	$P(n\text{-}Bu)_3$	2055	182.1	990.5	5.8	−3.6	1779.5
5	$PMePh_2$	2063	181.4	984.7	5.7	1.3	1780.4
6	PPh_3	2064	181.6	975.7	5.3	15.6	1645.0
7	$P(p\text{-}MeC_6H_4)_3$	2064	181.8	978.4	5.4	13.3	1662.1
8	$P(p\text{-}ClC_6H_4)_3$	2066	181.1	973.1	5.1	14.4	1616.5
9	$P(p\text{-}MeOC_6H_4)_3$	2062	181.8	979.2	5.5	11.7	1674.5
10	$P(i\text{-}Pr)_3$	2055	182.5	986.4	5.8		
11	$P(m\text{-}MeC_6H_4)_3$	2064	181.8	978.1	5.5	15.6	1659.4
12	$P(m\text{-}ClC_6H_4)_3$	2068	181.0	971.4	5.3	16.7	1610.7
13	PCy_3	2050	182.5	984.1	6.0	21.3	1637.7
14	$P(t\text{-}Bu)_3$	2059	185.1	1000.9	5.8	69.8	1589.3
15	$P(o\text{-}MeC_6H_4)_3$	2059	180.8	988.3	4.6	11.9	1597.0

[a] Carbonyl stretching frequencies, in cm^{-1}. [b] Carbonyl chemical shifts, in ppm relative to TMS. [c] ^{195}Pt–^{13}C coupling constants, in Hz. [d] ^{31}P–^{13}C coupling constants, in Hz. [e] Chemical shifts, in ppm ($CDCl_3$, H_3PO_4 external reference). [f] ^{195}Pt–^{31}P coupling constants, in Hz.

do not depend on the nature of the entering phosphine. The pseudo-first-order rate constants, k_{obsd}, are listed in Table SI (supplementary material). These pseudo-first-order rate constants, when plotted against the concentration of the entering phosphine, give straight lines with a zero intercept (Figure S1 (supplementary material)), indicating that in the usual two-term rate equation

$$k_{obsd} = k_1 + k_2[L] \qquad (3)$$

the k_1 term in making little if any contribution to the reactivity (k_1 arises from the solvolytic path, and k_2 is the second-order rate constant for bimolecular attack of L on the substrate). The values of k_2, from linear regression analysis of the rate law, are collected in Table I. The relevant spectroscopic properties of the reaction products *cis*-$[PtPh_2(CO)(L)]$, obtained as described above, are given in Table II.

Discussion

Yellow crystals of the starting complex *cis*-$[Pt(C_6H_5)_2(CO)(5\text{-}AQ)]$ were prepared by easy displacement of the sulfide from the complex *cis*-$[Pt(C_6H_5)_2(CO)(SEt_2)]$. The compound exhibits luminescence properties that, together with those of other platinum(II) complexes, have been described elsewhere.[21] 5-Aminoquinoline binds to platinum(II) through the endocyclic nitrogen N1, as shown by the large high-frequency shifts of the resonances of both the H2 and H8 protons (+0.40 and +1.31 ppm, respectively) and by the coupling constant (δ = 9.29 ppm, $^3J_{Pt-H}$ = 25.2 Hz) of the H2 proton due to the 33.8% abundant ^{195}Pt isotope with $I = {}^1/_2$. The remaining proton resonances of the quinoline and of the phenyl rings were assigned on the basis of their chemical shifts, ^{195}Pt coupling constants, and the connectivity in the COSY spectrum. The substrate under study was particularly designed to have the following characteristics: (i) it must be uncharged and soluble in nonpolar solvents, (ii) three of four groups must remain firmly bonded to the metal and only one (the 5-aminoquinoline) may undergo the substitution process, (iii) the lability of the leaving group may not be too high or too low, in order to avoid the use of techniques for fast reactions or to give inconveniently long reaction times, (iv) the changes in the electronic spectra must occur in the near-visible region, where the interference of the absorbing phosphines is greatly reduced or vanishes, and (v) one of the coordinated ligands, CO in this case, must be a good probe of the changes of electronic density or of the steric repulsions induced by the entering phosphine in the reaction products *cis*-$[Pt(C_6H_5)_2(CO)(L)]$. The latter were characterized by their IR and ^{13}C and ^{31}P NMR spectra (Table II).

The IR spectra of the reaction products exhibit a strong CO peak in the region 2050–2070 cm^{-1}. As expected, the stretching frequency νCO decreases with increasing the σ-donor power of the coordinated phosphine, and if the points for the most sterically hindered $P(o\text{-}MeC_6H_4)_3$, $P(t\text{-}Bu)_3$, and PCy_3 ligands are omitted, one obtains a good linear relationships between the pK_a values of the phosphines and the νCO values, according to the equation $\nu CO = 2069.4 - 1.58pK_a$ (12 data points, $R = 0.956$ by linear regression analysis).

Analysis of the ^{13}C NMR spectra has been limited to the resonance of the carbonyl ligand, which appears as a doublet centered at 181.9 ± 1.0 ppm ($^2J_{P-C}$ = 5.40 ± 0.35 Hz) with two ^{195}Pt satellites. The values of the ^{195}Pt coupling constants (values of $^1J_{Pt-C}$ in Table II) seem to depend significantly on the nature the coordinated phosphine and increase as its basicity increases. The overall difference of $^1J_{Pt-C}$ is not large, being 30 Hz between the first and the last members of the series. Setting apart the data for the highly hindered $P(o\text{-}MeC_6H_4)_3$, PCy_3, $P(t\text{-}Bu)_3$, and $P(i\text{-}Pr)_3$ ligands, one finds a linear correlation of the type $^1J_{Pt-C} = 970.2 + 2.30pK_a$ (11 data points, $R = 0.924$). The deviations observed for the bulky phosphines are not unexpected. Clark and Nicholas[22] have already found significant steric effects on the ^{195}Pt chemical shifts of *cis*-$[PtCl_2L_2]$ complexes containing bulky phosphines (a high-frequency shift of over 200 ppm was obtained for L = PCy_3). Likewise, in the complexes *trans*-$[Pt(PCy_3)_2(X)Cl]$, the deshielding of ^{195}Pt was found to increase with increasing size of the ligand X. These findings were rationalized in terms of lengthening of the Pt–P bond and deshielding of the Pt nucleus induced by steric congestion.

The complexes *cis*-$[Pt(C_6H_5)_2(CO)(L)]$ show also a ^{31}P resonance as a 1:4:1 triplet (C_6D_6, H_3PO_4 external reference) with values of δ between −15 and +21 ppm. The values of the coupling constants $^1J_{Pt-P}$ are within the range typical of a phosphorus atom trans to a carbon in platinum complexes.[23] These values encompass a difference of 200 Hz and increase with increasing basicity of the phosphine. Here again, for unhindered phosphines, we find a fairly good linear relationship of the type $^1J_{Pt-P} = 1584.2 + 22.8pK_a$ (9 data points, $R = 0.984$). These findings suggest that, in the absence of steric effects, the values

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of the stretching frequencies ν_{CO} and of the coupling constants $^1J_{Pt-C}$ or $^1J_{Pt-P}$ of the *cis*-[Pt(C$_6$H$_5$)$_2$(CO)(L)] products can be regarded as good measures of the inductive effects of the substituents bonded to the phosphorus atom.

As described previously, reaction 2 proceeds in a single step. The dependence of the pseudo-first-order rate constants on the concentrations of the entering phosphines is described by a family of straight lines with a zero intercept (Figure S1). Linear regression analysis of these plots gives the values of k_2, second-order rate constants for the bimolecular attack of L on the substrate. Thus, the displacement of 5-aminoquinoline by phosphines is perfectly in keeping with the associative mode of activation usually found for substitution reactions in square planar complexes.[24] The substitution is dominated by the direct attack of the nucleophile on the metal, and there is no evidence for the contribution to the reactivity of a concurrent solvolytic pathway. The complex *cis*-[PtPh$_2$(CO)(5-AQ)] shows a considerable discrimination toward the various entering phosphines, the difference in reactivity between the first and the last members of the series being greater than 6 orders of magnitude. The reactivity decreases in the order PMe$_2$Ph > PEt$_3$ > PMePh$_2$ > P(n-Bu)$_3$ > P(p-MeOC$_6$H$_4$)$_3$ > P(m-MeC$_6$H$_4$)$_3$ > P(p-MeC$_6$H$_4$)$_3$ > PPh$_3$ > P(p-ClC$_6$H$_4$)$_3$ > P(m-ClC$_6$H$_4$)$_3$ > P(EtCN)$_3$ > PCy$_3$ > P(i-Pr)$_3$ > P(t-Bu)$_3$ > P(o-MeC$_6$H$_4$)$_3$. It can be seen at a first sight that the more marked differences in reactivity are due to differences in steric hindrance. Actually, phosphines of comparable basicity such as P(p-MeC$_6$H$_4$)$_3$ and P(o-MeC$_6$H$_4$)$_3$ or P(n-Bu)$_3$ and P(t-Bu)$_3$ show differences in reactivity of 5 and 4 orders of magnitude, respectively, while PEt$_3$ reacts only 100 times faster than the isosteric P(EtCN)$_3$, despite the considerable difference in basicity.

These results show unambiguously that the reactivity of the phosphines toward platinum(II) is strongly affected by the nature of the substituents bonded to the phosphorus atom. A scale of nucleophilic reactivity constants can be derived from these second-order rate constants. For a nucleophile Y reacting with the standard substrate *trans*-[Pt(py)$_2$Cl$_2$] in methanol at 25 °C, the value of n°_{Pt} is defined[15] as the logarithm of the ratio k_Y/k_1(MeOH), where k_Y and k_1(MeOH) are second-order rate constants for the nucleophile and the solvent, respectively. Since in our reactions there is not a measurable solvolytic k_1 contribution and it is more convenient to deal with dimensionless values of reactivity constants, we could assume as reference the reactivity of the less reactive phosphine (P(o-MeC$_6$H$_4$)$_3$, $k_2 = 5.7 \times 10^{-5}$ M^{-1} s^{-1}). Thus, all the values of k_2 in Table I can be divided by 5.7×10^{-5} M^{-1} s^{-1} and the logarithms of these ratios can be called n^{P}_{Pt} (see Table I).

Before we attempt to separate the relative contributions of steric and electronic effects of substituents to the reactivity of the phosphines, it is worth mentioning a relationship which appears to be extremely significant. Manzer and Tolman[25] have measured the enthalpies of the reaction

$$\textit{trans}\text{-}[\mathrm{Pt(PMe_2Ph)_2(Me)(THF)}]^+ + \mathrm{L} \rightarrow \textit{trans}\text{-}[\mathrm{Pt(PMe_2Ph)_2(Me)(L)}]^+ + \mathrm{THF} \quad (4)$$

where L represents a series of phosphines, phosphites, arsines, and stibines. The main conclusion was that the energy of the platinum–ligand bond formed was dominated by the size of the ligand, even though electronic effects should be taken into account. Figure 1 shows that there is a perfectly linear relationship between the enthalpy data of the phosphines for reaction 4 and the reactivity data for reaction 2, according to the relationship $n^{P}_{Pt} = -0.519 + 0.249(-\Delta H)$ ($R = 0.991$, 9 data points). This relationship is maintained over a very large range of reactivity and enthalpy values (differences in reactivity of almost 6 orders of magnitude and in ΔH of 25 kcal mol^{-1}, respectively). The conclusion derived from this linear free energy relationship (LFER) is that the extent of platinum–phosphorus bond formation dictates the energy of either the square planar configuration or the five-coordinate trigonal bipyramidal transition state. In principle, the largest n^{P}_{Pt} means the smallest activation barrier, but this corresponds to the most exothermic phosphine formation and vice versa. Assuming that reactions 2 are all isoentropic, the simple relation $\Delta H^{\ddagger} + \alpha\Delta H$ = constant holds. A logical deduction is that the energy required to stretch the Pt–P bond to reach the transition state in the reverse reaction is not very sensitive to the nature of the phosphine. As a consequence, the lability of coordinated phosphines is expected to be much less dependent on changes in steric and electronic properties of phosphines than nucleophilicity.

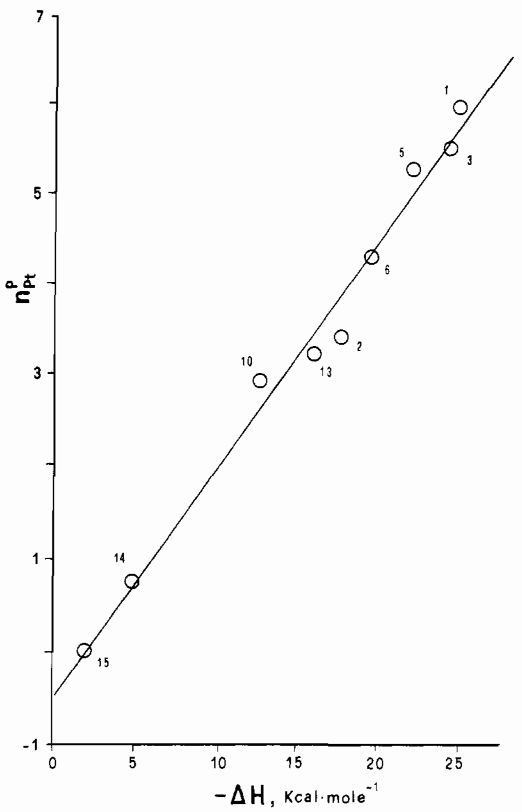

Figure 1. Correlation between the n^{P}_{Pt} values, as derived from the kinetic data for reaction 2, and the heats of Pt–P bond formation (eq 4, ref 24). Numbers refer to the ligands as listed in Table I.

Tolman's literature data for the heats of reaction of phosphines and phosphites with *trans*-[Pt(PMe$_2$Ph)$_2$(Me)(THF)]$^+$ (see reaction 4) were recently analyzed by Giering, Prock, et al.[26] according to their quantitative method (QALE) which allows the substituent effects to be dissected into their relative contributions of σ-bonding, π-bonding, and steric properties. We will perform the same analysis on the kinetic data of reaction 2, and since the phosphines used have no significant π-bonding characteristics, the rate data will be explained in terms of steric properties and σ-bonding alone. A regression analysis of a two-parameter equation to separate electronic and steric dependences of the data seems inappropriate, since the data are not continuous functions of the parameters. The σ-electronic contribution can be obtained from the dependence of the rate data on the pK_a

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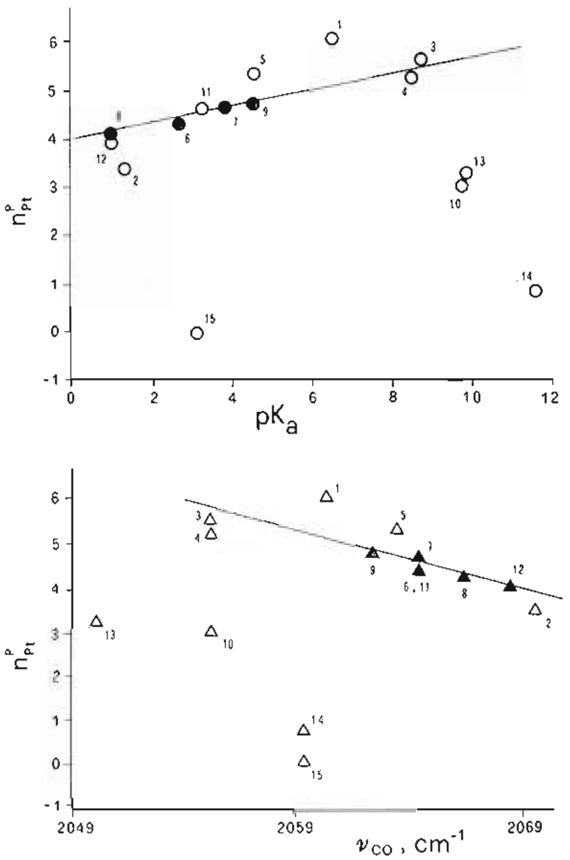

Figure 2. Correlation of the rates of reaction 2 (n^P_{Pt} values) with the pK_a of the phosphorus ligands (upper plot) and with the carbonyl stretching frequencies of the [$PtPh_2(CO)(L)$] reaction products (lower plot).

values of PR_3H^+ or, as shown in the Figure 2 and Figure 3, from the dependence of the rate data on some internal parameters of the system such as ν_{CO}, $^1J_{Pt-P}$, or $^1J_{Pt-C}$ of the *cis*-[$PtPh_2(CO)(L)$] products. The choice of one or another of these parameters, all internally correlated as discussed under Results, does not appreciably change the final conclusions. Therefore, we will use the more popular pK_a scale, which spans a wide range of pK_a values, comprises all the kinetic data points, and permits useful comparisons with the behavior of other classes of nucleophiles, such as amines or imines, reacting with square planar systems. Accordingly, in the plot of n^P_{Pt} against pK_a (Figure 2), a straight line has been drawn through the points for the isosteric ligands $P(p\text{-}MeOC_6H_4)_3$, $P(p\text{-}MeC_6H_4)_3$, PPh_3, and $P(p\text{-}ClC_6H_4)_3$. The linear regression analysis of this plot gives the equation $n^P_{Pt} = 3.87 \pm 0.08 + (0.17 \pm 0.02)\mathrm{p}K_a$. This linear plot can be defined as the σ-electronic profile of the reaction and represents the sensitivity of the reaction to the inductive effects brought about by the substituents on the phosphine ligands. As can be seen from the slope of the plot, the sensitivity of the reaction rates to changes in the electronic properties of the entering ligands is not large (on going from the least basic to the most basic phosphine, the reactivity is expected to increase only 100 times). This is hardly surprising for a soft reaction center such as platinum(II). Similar results were found many years ago by Cattalini[27] for reactions of square planar Pt(II) or Pd(II) complexes with various nitrogen ligands or thioethers. Electronic profiles such as that in Figure 2 (upper plot) can be obtained also by using some spectroscopic properties of the *cis*-[$PtPh_2(CO)(L)$] products such as the values of the stretching frequency of the carbonyl (Figure 2, lower plot) or the coupling constants for ^{195}Pt–P or ^{195}Pt–C(CO) (Figure 3). In all cases, strong deviations for phosphines having a large cone angle were found.

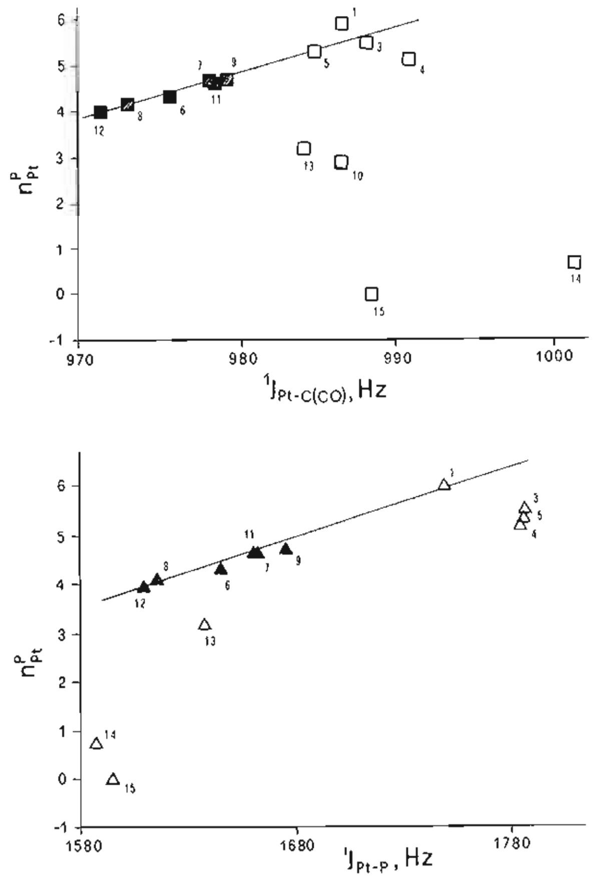

Figure 3. Correlation of the n^P_{Pt} values with the ^{195}Pt coupling constants of the carbon atom of the carbonyl ($^1J_{Pt-CO}$) (upper plot) and of the phosphorus atom ($^1J_{Pt-P}$) (lower plot) in the reaction products *cis*-[$PtPh_2(CO)(L)$].

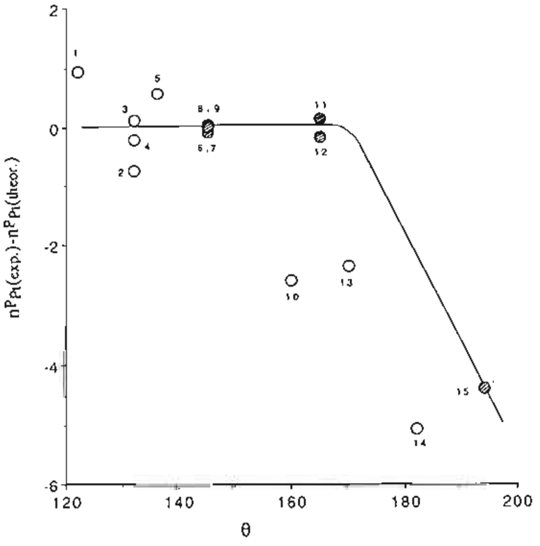

Figure 4. Steric profile of reaction 2.

The differences between the theoretical values expected on the basis of the electronic profile (n^P_{Pt} vs pK_a) and those found experimentally were plotted against the values of Tolman's cone angles (Figure 4). Once again, a line has been drawn through the points for the phenylphosphines. The steric profile so obtained shows a sharp steric threshold for cone angles greater than 170°. In other words, steric effects seems to be quite small for small substituents, but they increase steadily as the size of the substituents increases. This steric profile is identical to that obtained by Giering, Prock, et al.[26] applying the QALE method to the enthalpies of reaction 4, the only difference being that these authors have included enthalpy data for some crowded

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(27) Cattalini, L. *Prog. Inorg. Chem.* **1970**, *13*, 263–327.

phosphites ($P(O\text{-}t\text{-}Bu)_3$, $P(O\text{-}o\text{-}t\text{-}BuC_6H_4)_3$, $P(O\text{-}2,6\text{-}Me_2C_6H_4)_3$) which lie just on the inclined line after the steric threshold and have omitted the enthalpy data for some alkylphosphines, such as PCy_3 (**13**), $P(i\text{-}Pr)_3$ (**10**), and $P(t\text{-}Bu)_3$ (**14**), which should deviate significantly from this steric profile as they do in Figure 4. Points for other alkylphosphines (**1, 2, 5**) lie outside the steric profile shown in Figure 4, even though the deviations observed are very much less pronounced than those found for the most sterically hindered ligands.

We do not have a definite explanation for the deviations from the steric profile observed for the alkylphosphines. However, it is worth mentioning that often the values of Tolman's cone angles have been challenged, especially in those cases in which the ligand can assume several conformations. It has been pointed out that bulky phosphines, even though symmetrically substituted, such as PCy_3 (**13**), $P(i\text{-}Pr)_3$ (**10**), or $P(t\text{-}Bu)_3$ (**14**), may adopt unsymmetrical conformations[28] and, as a consequence, the circular "solid cone" approach can be improved by designing a "steric ligand profile" which takes into account the dependence of the ligand angular encumbrance on the orientation of the ligand itself about the metal–phosphorus bond. This leads to some uncertainty in assigning precise values of cone angles to flexible alkylphosphines, while the "solid cone" approach seems perfectly valid for the more rigid phenylphosphines.

To sum up, this work suggests that the replacement of 5-aminoquinoline from *cis*-$[Pt(C_6H_5)_2(CO)(5\text{-}AQ)]$ by tertiary phosphines takes place only by way of a bimolecular attack of the ligand on the substrate, according to the well-established mechanistic pattern of square planar complexes. Electronic (σ-donor) and steric properties of the nucleophile influence in the same way the energy and the extent of Pt–P bond formation either in the trigonal bipyramidal five-coordinate transition state or in the square planar four-coordinate phosphine products. The shape of the steric profile indicates that steric effects do not come into play for nucleophiles of relatively small size (horizontal part of the plot). In this region, either the rates of reaction or the heats of Pt–P bond formation are dominated by electronic effects. The kinetic or thermodynamic electronic discrimination of the soft reaction center appears to be significant but not particularly high. The sharp change from the horizontal to the downward sloping part of the plot marks the onset of steric destabilization in the transition state. This steric saturation is associated with the degree of flexibility and compressibility of the ancillary ligands of the square planar substrate relative to the steric demand of the incoming nucleophile. As for other systems,[12–14] the significance of measuring the intrinsic reactivity of a square planar complex in associative substitutions and its relative sensitivity to steric and electronic factors will be appreciated more when a larger body of data for other substrates is available.

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Supplementary Material Available: Table SI, giving primary kinetic data, and Figure S1, showing the dependence of k_{obsd} on phosphine concentration (2 pages). Ordering information is given on any current masthead page.

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