Reactivity of Aliphatic Amines toward Platinum(II) Complexes

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The rates of displacement of 5-aminoquinoline (5-Aq) and diethyl sulfide (SEt_2) from cis-[$PtPh_2$(CO)(L)] (L = 5-Aq or SEt_2) by an extended series of aliphatic amines of comparable basicity (pK_a = 10.6 ± 0.4) and of widely different steric properties have been measured in dichloromethane solution. The reaction products *cis*-[$PtPh_2$(CO)(am)] (**1–15**) were characterized either as solids or in solution by their IR and ^1H and ^{13}C NMR spectra. Crystals of cis-diphenyl(pyridine)carbonyl platinum(II) (**12**) belong to the monoclinic space group $P2_1/n$ with lattice constants a = 11.756(2) Å, b = 9.853(2) Å, c = 13.552(2) Å, β = 100.27(2)°, and Z = 4. *cis*-diphenyl(diisopropylamine)carbonyl platinum(II) **13** crystallizes in the monoclinic space group $P2_1/n$ with lattice constants a = 8.926(2) Å, b = 14.439(2) Å, c = 14.468(2) Å, β = 92.88(2)°, and Z = 4. Least-squares refinement of the structures led to R factors of 1.93% and 3.08%, respectively. The substitution reactions take place by way of a direct bimolecular attack of the ligand on the substrate. The sulfide group is 100 times more labile than 5-Aq, but both complexes exhibit the same discrimination ability toward the entering amines. The sequence of reactivity observed is $NH_2{}^nPr \approx NH_2{}^nPent \approx NH_2{}^nHex > NH_2Cy \approx NH_2{}^nBu > NH_2{}^iBu > NH_2Bz \approx$ pip $\approx$ py $> NH_2{}^tBu > NHEt_2 \approx NH^nBu_2 > NH^iPr_2$, and it is determined by the number and the encumbrance of the substituents on the nitrogen atom. The difference of reactivity between the first and the last members of the series spans 2 orders of magnitude. For the most sterically hindered amines, such as $NHCy_2$ or NEt_3, the bimolecular attack is prevented and the reaction proceeds only by way of a nucleophile independent pathway, which most likely involves dissociation of a ligand (5-Aq or SEt_2) from the coordination sphere of the metal. Different shapes of steric profiles for the two reactions were obtained by correlating the reactivity data with different sets of steric parameters such as the amine cone angles (θ) of space-filling CPK molecular models or the van der Waals steric repulsion (E_R) as derived from molecular mechanics calculations. Limits and significance of such relationships are discussed in order to account for apparently conflicting interpretations.

Introduction

The main feature of nucleophilic substitution reactions on square planar complexes, apart from a few documented exceptions,[1] is the associative nature of the activation process, which is usually revealed by a strong dependence of the rates on the nature of the entering nucleophile.[2] When a process is characterized by an associative mode of activation, it is interesting to see to what extent the reactivity, measured by a second-order rate constant k_2 ($M^{-1} s^{-1}$), depends on some of the characteristics of the nucleophile, such as the nature of the donor atom, the σ- and π-donor or -acceptor properties, the hardness, the redox characteristics, etc. The difficulty of relating quantitatively the rates to the parameters mentioned above led to a somewhat different approach for reactions of square planar platinum(II) complexes. Thus, a scale of nucleophilic reactivity constants was derived from the kinetic parameters of nucleophiles Y reacting with a standard substrate *trans*-[$Pt(py)_2Cl_2$] in methanol at 25 °C. Values of $n°_{Pt}$ were defined 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.[3] The sequence of the $n°_{Pt}$ values in the derived nucleophilicity scale reflects roughly the characteristics of softness of the d^8 metal center, and therefore ligands with light donor atoms such as N, O, or F are found to be much less reactive than their analogues in the second period. This nucleophilicity scale makes it possible to compare the kinetic behavior of different substrates in terms of nucleophilic discrimination ability and intrinsic reactivity. There are however several severe limitations. For instance some nucleophiles, such as NO_2^-, $SeCN^-$, or $SC(NH_2)_2$, because of their π acceptor properties, deviate significantly from their position in the nucleophilicity scale when the π basicity of the substrate is greater or less than that of the standard substrate.[4] Electrostatic interactions also play a significant role and it was shown that it is useful to use a different reactivity scale for monocationic[5] substrates and yet another one for dicationic complexes of platinum(II).[6] Apart from the limits mentioned above, the principal defect of the procedure used to derive the $n°_{Pt}$ values is that no account is taken of a steric contribution to the reactivity, even though steric effects can strongly influence the values of the derived parameters. For instance the $n°_{Pt}$ values listed for Ph_3P, $^nBu_3P$, and Et_3P are almost identical (8.93, 8.96, and 8.99, respectively)[3] and can lead to the wrong conclusion that phosphines

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are all strongly reactive regardless of the nature of the substituents on the phosphorous atom.

In a recent study of the substitution of 5-aminoquinoline (5-Aq) from the complex cis-[$PtPh_2(CO)$(5-Aq)] by an extended series of phosphines of widely different steric and electronic properties, we found that the difference in reactivity between the first (Me_2PhP) and the last ((o-$MeC_6H_4)_3P$) members of the series spans at least 6 orders of magnitude.[7] The values of the rate constants were resolved quantitatively into electronic and steric effects, by means of correlations with the cone angles and pK_a 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*-[$PtPh_2(CO)$-(phosphine)] products. Electronic and steric profiles of the reaction were obtained showing that the reactivity is only slightly affected by σ-inductive effects brought about by substituents on the phosphine ligands while steric effects are dominant.

We thought it of interest to extend the study of this reaction to amines as entering groups. Quantitative information on the relative importance of steric and electronic factors in determining the reactivity of amines can guide the synthesis and design of new platinum(II) antitumor compounds[8] and can lead to a better understanding of the role of this important class of ligands in coordination and organometallic chemistry and in bioinorganic systems. We report here a kinetic study of the substitution of 5-aminoquinoline (hereafter referred to as 5-Aq) and diethyl sulfide from the complexes *cis*-[$PtPh_2(CO)(L)$] (L = 5-Aq and SEt_2) by an extended series of aliphatic amines of comparable basicity (pK_a = 10.6 ± 0.4) and of different steric hindrance. The steric profiles obtained will be discussed in connection with those obtained for the reactions of the same substrates with phosphines. Crystal structure analyses for two amine complexes (am = py and NH^iPr_2) were determined to provide information on the effect of changing the nature of the amine on the structural properties of *cis*-[$PtPh_2(CO)$(am)] products.

Experimental Section

All reactions were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk-tube techniques and the products were worked up in air, unless otherwise stated.

The amines were purchased from Aldrich Chemical Co. and distilled over KOH under reduced pressure. Diethyl ether was dried with sodium/benzophenone under a nitrogen atmosphere and distilled before use. Dichloromethane was distilled from barium oxide. All the other chemicals were of the best commercial grade available and were used without further purification.

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 made up in dichloromethane. ^1H, ^{13}C, and ^{195}Pt NMR spectra were recorded on a Bruker AMX R-300 spectrometer operating at 300.13, 76.46, and 64.22 MHz, respectively. ^1H and ^{13}C chemical shifts are measured relative to the residual solvent peak and are reported in δ units (δ(TMS) = 0). ^{13}C NMR spectra of the *cis*-[$PtPh_2(CO)$(am)] products were obtained by adding amine to a CD_2Cl_2 solution of a ^{13}CO-enriched sample of *cis*-[$PtPh_2(CO)SEt_2$]. The ^{195}Pt NMR spectra were recorded using a $\pi/2$ pulse of 7 μs and a relaxation delay of 1 s. Typically the spectral width was set at 62.5 kHz with 16 k data points. ^{195}Pt chemical shifts were referenced to the absolute frequency scale by setting the TMS resonance exactly to 100 MHz.[9] ^{195}Pt chemical shifts were converted to the Na_2PtCl_6 scale by using the following expression: $\delta(Na_2PtCl_6)$ = δ(frequency scale) − 4533.[10] Microanalysis were performed by Analytical Laboratories, Engelskirchen, Germany.

Preparation of Complexes. *cis*-[$Pt(Ph)_2(CO)(SEt_2)$][11] and *cis*-[$Pt(Ph)_2(CO)$(5-Aq)][12] were prepared by methods reported elsewhere. *cis*-[$Pt(Ph)_2(CO)$(am)] (am = *n*-propylamine ($NH_2{}^nPr$), **1**, *sec*-butylamine ($NH_2{}^sBu$), **3**, *tert*-butylamine ($NH_2{}^tBu$), **4**, cyclohexylamine (NH_2Cy), **7**, pyridine (py), **12**, diisopropyl amine (NH^iPr_2), **13**, dicyclohexylamine ($NHCy_2$), **14**) are new compounds and were prepared by using essentially the following procedure. A weighed amount of *cis*-[$Pt(Ph)_2(CO)(SEt_2)$] (0.150 g, 0.321 mmol) was reacted in dichloromethane (50 mL) with an excess of amine (in a 1:3 ratio for **1**, **3**, **4**, **7**, and **12** and in a 1:10 ratio for **13** and **14**). After the mixture was stirred for 12 h, most of the solvent was removed under vacuum, and *n*-hexane was added to the concentrated solution in a 1:1 ratio. The solid compounds that separated out upon crystallization were washed with diethyl ether and dried under vacuum.

***cis*-Diphenyl(*n*-propylamine)carbonylplatinum(II), 1.** ν(C=O): 2060 cm^{-1}. ^1H NMR: δ 7.34 (dd, 2H, $^3J_{PtH}$ = 79.2 Hz), 7.18 (dd, 2H, $^3J_{PtH}$ = 58.2 Hz), 7.09 (m, 2H), 6.96–6.91 (m, 4H), 3.03 (m, 2H), 2.85 (br s, 2H, NH_2), 1.66 (m, 2H), 0.96 (t, 3H). ^{13}C NMR: $\delta(C_1)$ 162.9, 132.8; $\delta(C_2)$ 138.2 ($^2J_{PtC_2}$ = 49.0 Hz), 135.8 ($^2J_{PtC_2}$ = 32.9 Hz); $\delta(C_3)$ 127.7 ($^3J_{PtC_3}$ = 64.0 Hz), 127.4 ($^3J_{PtC_3}$ = 77.6 Hz); $\delta(C_4)$ 124.4, 123.2; 50.2, 25.7, 11.1; δ(CO) 180.4 ($^1J_{PtC}$ = 1022.2 Hz). Anal. Calcd for $C_{16}H_{19}$-NOPt: C, 44.03; H, 4.39; N, 3.21. Found: C, 44.12; H, 4.20; N, 3.29.

***cis*-Diphenyl(*sec*-butylamine)carbonylplatinum(II), 3.** ν(C=O): 2062 cm^{-1}. ^1H NMR: δ 7.35 (dd, 2H, $^3J_{PtH}$ = 78.6 Hz), 7.19 (dd, 2H, $^3J_{PtH}$ = 57.2 Hz), 7.09 (m, 2H), 6.97–6.92 (m, 4H), 3.03 (m, 1H), 2.80 (br s, 2H, NH_2), 1.72 (m, 2H), 1.33 (d, 3H), 0.96 (t, 3H). ^{13}C NMR: $\delta(C_1)$ 163.2, 132.9; $\delta(C_2)$ 138.1 ($^2J_{PtC_2}$ = 48.5 Hz), 136.0 ($^2J_{PtC_2}$ = 33.1 Hz); $\delta(C_3)$ 127.7 ($^3J_{PtC_3}$ = 64.2 Hz), 127.4 ($^3J_{PtC_3}$ = 78.0 Hz); $\delta(C_4)$ 124.2, 123.2; 55.3, 31.8, 22.9, 10.1; δ(CO) 180.5 ($^1J_{PtC}$ = 1024.7 Hz). Anal. Calcd for $C_{17}H_{21}$NOPt: C, 45.33; H, 4.70; N, 3.11. Found: C, 45.42; H, 4.78; N, 3.20.

***cis*-Diphenyl(*tert*-butylamine)carbonylplatinum(II), 4.** ν(C=O): 2061 cm^{-1}. ^1H NMR: δ 7.35 (dd, 2H, $^3J_{PtH}$ = 79.6 Hz), 7.17 (dd, 2H, $^3J_{PtH}$ = 57.2 Hz), 7.08 (m, 2H), 6.96–6.88 (m, 4H), 3.03 (br s, 2H, NH_2, $^2J_{PtH}$ = 34.2 Hz), 1.32 (s, 9H). ^{13}C NMR: $\delta(C_1)$ 164.2, 132.8; $\delta(C_2)$ 137.9 ($^2J_{PtC_2}$ = 49.1 Hz), 135.9 ($^2J_{PtC_2}$ = 32.9 Hz); $\delta(C_3)$ 127.7 ($^3J_{PtC_3}$ = 64.4 Hz), 127.5 ($^3J_{PtC_3}$ = 78.9 Hz); $\delta(C_4)$ 124.1, 123.1; 53.7; 32.5; δ(CO) 180.9 ($^1J_{PtC}$ = 1026.1 Hz). ^{195}Pt: δ −3932. Anal. Calcd for $C_{17}H_{21}$-NOPt: C, 45.33; H, 4.70; N, 3.11. Found: C, 45.39; H, 4.77; N, 3.04.

***cis*-Diphenyl(cyclohexylamine)carbonylplatinum(II), 7.** ν(C=O): 2061 cm^{-1}. ^1H NMR: δ 7.33 (dd, 2H, $^3J_{PtH}$ = 79.2 Hz), 7.17 (dd, 2H, $^3J_{PtH}$ = 57.6 Hz), 7.07 (m, 2H), 6.95–6.90 (m, 4H), 2.88 (br s, 2H, NH_2), 2.61 (m, 1H) 2.18 (br m, 4H), 1.81–1.69–1.06 (m, 6H). ^{13}C NMR: $\delta(C_1)$ 163.2, 133.2; $\delta(C_2)$ 138.1 ($^2J_{PtC_2}$ = 48.2 Hz), 136.0 ($^2J_{PtC_2}$ = 33.2 Hz); $\delta(C_3)$ 127.7 ($^3J_{PtC_3}$ = 64.5 Hz), 127.4 ($^3J_{PtC_3}$ = 77.0 Hz); $\delta(C_4)$ 124.2, 123.1; 57.0; 35.8; 25.4; 24.7; δ(CO) 180.5 ($^1J_{PtC}$ = 1024.7 Hz). Anal. Calcd for $C_{19}H_{23}$NOPt: C, 47.89; H, 4.87; N, 2.94. Found: C, 47.97; H, 4.75; N, 3.03.

***cis*-Diphenyl(pyridine)carbonylplatinum(II), 12.** ν(C=O): 2058 cm^{-1}. ^1H NMR: δ 8.70 (dd, 2H, $^3J_{PtH}$ = 22 Hz, py), 7.84 (m, 1H, py), 7.40 (m, 4H), 7.03–6.96 (m, 8H). ^{13}C NMR: $\delta(C_1)$ 163.8, 131.1; $\delta(C_2)$ 138.4 ($^2J_{PtC_2}$ = 47.0 Hz), 136.5 ($^2J_{PtC_2}$ = 34.9 Hz); $\delta(C_3)$ 126.9 ($^3J_{PtC_3}$ = 66.7 Hz), 127.4 ($^3J_{PtC_3}$ = 77.9 Hz); $\delta(C_4)$ 124.0, 123.3; 152.5 ($^2J_{PtC}$ = 16.4 Hz); 136.3; 126.0; δ(CO) 180.7 ($^1J_{PtC}$ = 996.0 Hz). Anal. Calcd for $C_{18}H_{15}$NOPt: C, 47.37; H, 3.31; N, 3.07. Found: C, 47.44; H, 3.41; N, 3.03.

***cis*-Diphenyl(diisopropylamine)carbonylplatinum(II), 13.** ν(C=O): 2058 cm^{-1}. ^1H NMR: δ 7.36 (dd, 2H, $^3J_{PtH}$ = 79.2 Hz), 7.24 (dd, 2H, $^3J_{PtH}$ = 57.2 Hz), 7.05 (m, 2H), 6.94 (m, 4H), 3.36 (m, 2H), 2.87 (br t, 2H, NH_2, $^3J_{PtH}$ = 44 Hz), 1.60 (d, 6H), 1.24 (d, 6H). ^{13}C NMR: $\delta(C_1)$ 163.9; $\delta(C_2)$ 137.0 ($^2J_{PtC_2}$ = 49.3 Hz), 137.2 ($^2J_{PtC_2}$ = 30.5 Hz); $\delta(C_3)$ 127.7 ($^3J_{PtC_3}$ = 63.0 Hz), 127.5 ($^3J_{PtC_3}$ = 79.8 Hz); $\delta(C_4)$ 123.7, 123.1; 52.4; 23.6; 23.0; δ(CO) 181.0 ($^1J_{PtC}$ = 1051.7 Hz). ^{195}Pt: δ −3858. Anal. Calcd for $C_{19}H_{25}$NOPt: C, 47.69; H, 5.27; N, 2.93. Found: C, 47.76; H, 5.34; N, 3.02.

***cis*-Diphenyl(dicyclohexylamine)carbonylplatinum(II), 14.** ν(C=O): 2057 cm^{-1}. ^1H NMR: δ 7.36 (dd, 2H, $^3J_{PtH}$ = 79.2 Hz), 7.23 (dd, 2H, $^3J_{PtH}$ = 57.2 Hz), 7.05 (m, 2H), 6.95 (m, 4H), 3.00 (m, 3H), 2.75 (m, 2H), 1.56–1.73–1.25 (m, 18H). ^{13}C NMR: $\delta(C_1)$ 163.9, 132.9; $\delta(C_2)$ 138.1 ($^2J_{PtC2}$ = 51.6 Hz), 137.4 ($^2J_{PtC_2}$ = 30.5 Hz); $\delta(C_3)$ 127.6 ($^3J_{PtC_3}$ = 65.7 Hz), 127.5 ($^3J_{PtC_3}$ = 77.5 Hz); $\delta(C_4)$ 123.6, 123.1; 59.8; 34.3; 33.8; 25.8; 25.6; 25.5; δ(CO) 181.2 ($^1J_{PtC}$ = 1054.6 Hz). ^{195}Pt: δ −3858. Anal.

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Calcd for $C_{25}H_{33}NOPt$: C, 53.75; H, 5.95; N, 2.51 . Found: C, 53.88; H, 6.04; N, 2.46.

The other reaction products *cis*-[$PtPh_2(CO)(am)$] (am = *n*-butylamine ($NH_2{}^nBu$) **2**, *n*-pentylamine ($NH_2{}^nPent$), **5**, *n*-hexylamine ($NH_2{}^nHex$), **6**, benzylamine (NH_2Bz), **8**, diethylamine ($NHEt_2$), **9**, di-*n*-butylamine ($NH{}^nBu_2$), **10**, piperidine (pip), **11**, and triethylamine (NEt_3), **15**) were obtained *in situ* by reacting *cis*-[$PtPh_2(CO)SEt_2$] (0.005 g, 0.011 mmol) with a sufficient excess of amine in 0.5 mL of $CDCl_3$ and were characterized in solution through their IR and ^{1}H, ^{13}C and ^{195}Pt NMR spectra. Generally these species were obtained quite easily, and only in the case of the less reactive amines was it necessary to gently warm the reaction mixture to allow the reaction to go to completion. In no case was there evidence for the removal of the carbonyl group after the displacement of the sulfide.

***cis*-Diphenyl(*n*-butylamine)carbonylplatinum(II), 2.** ν(C═O): 2065 cm^{-1}. ^{1}H NMR: δ 7.33 (dd, 2H, $^3J_{PtH}$ =79.3 Hz), 7.18–7.09–6.97 (m, 8H), 3.04 (m, 2H), 2.80 (br t, 2H, NH_2), 1.63 (m, 2H), 1.39 (m, 2H), 0.96 (t, 3H). ^{13}C NMR: $\delta(C_1)$ ...; $\delta(C_2)$ 138.2, 135.9; $\delta(C_3)$ 127.7,127.5; $\delta(C_4)$ 124.4, 123.2; 48.3; 34.6; 19.6; 13.6; δ(CO) 181.2 ($^1J_{PtC}$ = 1054.6 Hz). ^{195}Pt: δ −3858.

***cis*-Diphenyl(n-pentylamine)carbonylplatinum(II), 5.** ν(C═O): 2061 cm^{-1}. ^{1}H NMR: δ 7.33 (dd, 2H, $^3J_{PtH}$ = 78.2 Hz), 7.18 (dd, 2H), 7.09 (m, 2H), 6.96 (m, 4H), 3.03 (m, 2H), 2.87 (br s, 2H, NH_2), 1.64 (m, 2H), 1.32 (m, 4H), 0.92 (t, 3H). ^{13}C NMR: $\delta(C_1)$ ...; $\delta(C_2)$ 138.2, 135.7; $\delta(C_3)$ 127.7, 127.5; $\delta(C_4)$ 124.3, 123.2; 48.5; 32.2; 28.5; 22.2; 13.8; δ(CO) 180.4 ($^1J_{PtC}$ = 1023.5 Hz). ^{195}Pt: δ −3858.

***cis*-Diphenyl(*n*-hexylamine)carbonylplatinum(II), 6.** ν(C═O): 2062 cm^{-1}. ^{1}H NMR: δ 7.32 (dd, 2H, $^3J_{PtH}$ = 78.8 Hz), 7.17 (dd, 2H), 7.08 (m, 2H), 6.95 (m, 4H), 3.02 (m, 2H), 2.98 (br s, 2H, NH_2), 1.63 (m, 2H), 1.30 (m, 6H), 0.90 (t, 3H). ^{13}C NMR: $\delta(C_1)$ ...; $\delta(C_2)$ 138.2, 135.6; $\delta(C_3)$ 127.7,127.4; $\delta(C_4)$ 124.3, 123.1; 48.5; 32.5; 31.3; 26.1; 22.4; 14.0; δ(CO) 180.4 ($^1J_{PtC}$ = 1023.4 Hz); ^{195}Pt: δ −3858.

***cis*-Diphenyl(benzylamine)carbonylplatinum(II), 8.** ν(C═O): 2067 cm^{-1}. ^{1}H NMR: δ 7.40–7.30 (m, 7H), 7.2 (m, 2H), 7.1 (m, 2H), 6.96 (m, 4H), 4.07 (m, 2H), 3.28 (br t, NH_2; $^2J_{PtH}$ = 40 Hz). ^{13}C NMR: $\delta(C_1)$ ...; $\delta(C_2)$ 138.2 ($^2J_{PtC_2}$ = 47.2 Hz), 135.9 ($^2J_{PtC_2}$ = 32.7 Hz); $\delta(C_3)$ 127.8,127.5; $\delta(C_4)$ 124.4, 123.2; 129.3; 128.7; 128.1; 52.1; δ(CO) 181.0 ($^1J_{PtC}$ = 1051.7 Hz); ^{195}Pt: δ −3871.

***cis*-Diphenyl(diethylamine)carbonylplatinum(II), 9.** ν(C═O): 2058 cm^{-1}. ^{1}H NMR: δ 7.33 (dd, 2H, $^3J_{PtH}$ = 78.6 Hz), 7.23 (dd, 2H, $^3J_{PtH}$ = 57.2 Hz), 7.06 (m, 2H), 6.92 (m, 4H), 3.21 (m, 2H), 3.02 (m, 2H), 2.76 (br s, 1H, NH), 1.46 (t, 6H). ^{13}C NMR: $\delta(C_1)$ 163.4, 132.3; $\delta(C_2)$ 138.1 ($^2J_{PtC_2}$ = 49.1 Hz), 136.2 ($^2J_{PtC_2}$ = 31.2 Hz); $\delta(C_3)$ 127.6 ($^3J_{PtC_3}$ = 65.2 Hz), 127.3 ($^3J_{PtC_3}$ = 77.4 Hz); $\delta(C_4)$ 124.0, 123.1; 50.2; 14.8; δ(CO) 180.8 ($^1J_{PtC}$ = 1042.2 Hz).

***cis*-Diphenyl(di-*n*-butylamine)carbonylplatinum(II), 10.** ν(C═O): 2058 cm^{-1}. ^{1}H NMR: δ 7.32 (dd, 2H, $^3J_{PtH}$ = 78.2 Hz), 7.20 (dd, 2H, $^3J_{PtH}$ = 57.7 Hz), 7.04 (m, 2H), 6.91–6.85 (m, 4H), 3.09 (m, 2H), 2.98 (m, 2H), 2.85 (br s, 1H, NH), 2.03 (m, 4H), 1.76 (m, 4H), 0.92 (t, 6H). ^{13}C NMR: $\delta(C_1)$ 163.2, 132.0; $\delta(C_2)$ 138.2 ($^2J_{PtC_2}$ = 49.5 Hz), 136.1 ($^2J_{PtC_2}$ = 29.6 Hz); $\delta(C_3)$ 127.6 ($^3J_{PtC_3}$ = 66.2 Hz), 127.3 ($^3J_{PtC_3}$ = 76.5 Hz); 123.9, 123.0; 55.8; 31.2; 20.1; 13.6; δ(CO) 180.8 ($^1J_{PtC}$ = 1041.2 Hz).

***cis*-Diphenyl(piperidine)carbonylplatinum(II), 11.** ν(C═O): 2062 cm^{-1}. ^{1}H NMR: δ 7.29 (dd, 2H, $^3J_{PtH}$ = 75.8 Hz), 7.22 (dd, 2H, $^3J_{PtH}$ = 58.4 Hz), 7.10 (m, 2H), 6.96–6.88 (m, 4H), 3.49 (m, 2H), 2.80–1.75–1.54 (m, 8H). ^{13}C NMR: $\delta(C_1)$ 163.4, 131.6; $\delta(C_2)$ 138.4 ($^2J_{PtC_2}$ = 47.7 Hz), 135.5 ($^2J_{PtC_2}$ = 31.9 Hz); $\delta(C_3)$ 127.8 ($^3J_{PtC_3}$ = 65.1 Hz), 127.3 ($^3J_{PtC_3}$ = 75.8 Hz); $\delta(C_4)$ 124.4, 123.1; 54.2; 28.0; 23.7; δ(CO) 181.0 ($^1J_{PtC}$ = 1038.8 Hz).

***cis*-Diphenyl(triethylamine)carbonylplatinum(II), 15.** ν(C═O): 2061 cm^{-1}. ^{1}H NMR: δ 7.34 (dd, 2H, $^3J_{PtH}$ = 79.2 Hz), 7.30 (dd, 2H), 7.00 (m, 2H), 6.90–6.85 (m, 4H), 2.90 (q, 6H), 1.39 (t, 9H). ^{13}C NMR: 50.8; 10.6; δ(CO) 182.0 ($^1J_{PtC}$ = 1054.6 Hz).

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 started by mixing equal amounts of prethermostated solutions of both reagents in a silica cell, in the thermostated cell compartment of a Cary 219 or a Perkin-Elmer Lambda 3 spectrophotometer, with a temperature accuracy of ±0.02 °C. 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 graphically or from a non-linear 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).

Table 1. Crystallographic Data and Summary of Data Collection and Refinement for *cis*-[$PtPh_2(CO)(am)$] Complexes

	12[a]	**13**[b]
formula	$C_{18}H_{15}NOPt$	$C_{19}H_{25}NOPt$
fw	456.4	478.5
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	11.756(2)	8.926(2)
b, Å	9.853(2)	14.439(2)
c, Å	13.552(2)	14.468(2)
β, deg	100.27(2)	92.88(2)
V, Å^3	1544.7(4)	1862.4(3)
Z	4	4
d_{calcd}, g cm^{-3}	1.960	1.707
scan type	ω–2θ	ω–2θ
scan range (ω), deg	1.60 plus Kα-separation	
no of unique data	2723 (R_{int} = 1.72%)	4071 (R_{int} = 0.62%)
no of reflcns	2022 [$F \geq 5\sigma(F)$]	2226 [$F \geq 6\sigma(F)$]
no. of ref params	191	199
μ, mm^{-1}	9.081	7.54
R[c]	0.019	0.0331
R_w[d]	0.026	0.0327

[a] am = pyridine. [b] am = diisopropylamine. [c] $R = [\sum|F_o| - |F_c|]/\sum|F_o|$. [d] $R_w[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

X-ray Data Collection and Structure Refinement. Suitable transparent crystals of **12** and **13** were obtained by slow evaporation of the solvent from dichloromethane solutions.

Diffraction measurements were made on a Siemens-R3m/v four-circle diffractometer using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. Accurate unit-cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 2θ, ω, χ, and ψ values of 25 strong reflections in the range 15° < 2θ < 30° for both (**12** and **13**) compounds. Further information on the crystallographic data collection and refinement of the structure determination are reported in Table 1 and Table S4 of the supplementary material. The diffraction data were processed with the learnt-profile procedure[13] and then corrected for decay and Lorentz–polarization effects. No correction was made for the extinction. The absorption correction was applied by fitting a pseudoellipsoid to the azimuthal scan data of 20 suitable reflections with high χ angles.[14]

Both structures were solved by using standard Patterson methods, successive least-squares refinements, and difference Fourier maps. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Hydrogen atoms were added at calculated positions and included in the structure factor calculations with a common thermal parameter (U = 0.06 Å^2).

The weighting scheme used in the last refinement cycles was $w = 1.00/(\sigma^2(F_o) + 0.00018F_o^2)$ for **12** and $w = 1.00/(\sigma^2(F_o) + 0.00895F_o^2)$ for **13**, which showed reasonable consistency in a test of $\omega\Delta^2$ for data sectioned with respect to both F_o and $(\sin\theta)/\lambda$.

Neutral-atom scattering factors and anomalous dispersion corrections were taken into account.[15] Data reduction and structure solutions and drawings were performed with the SHELXTL-PLUS package,[16] while structure refinement and final geometrical calculations were carried out with the SHELXL-93[17] and PARST programs,[18] respectively, on a DEC MicroVax/3400 computer. Atomic coordinates and isotropic thermal parameters for **12** and **13** are listed in Table 2 and 3, respectively. A selection of bond lengths and angles is listed in Table 4. ORTEP drawings for **12** and **13**, showing 40% probability thermal ellipsoids and atom numbering, are shown in Figures 1 and 2, respectively. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, anisotropic temperature factors, and the remaining bond lengths and angles.

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Table 2. Atomic Coordinates (×10[4]) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for the Non-Hydrogen Atoms of Compound **12**

	x	*y*	*z*	U,[a] $Å^2$
Pt	3430(1)	701(1)	1084(1)	39(1)
C	3799(5)	−117(6)	2371(4)	52(2)
O	3993(5)	−654(4)	3114(3)	87(2)
C(7)	2622(5)	−1040(5)	538(4)	40(2)
C(12)	3129(5)	−2314(5)	777(4)	50(2)
C(11)	2531(6)	−3506(6)	462(4)	57(2)
C(10)	1428(6)	−3448(6)	−86(4)	60(2)
C(9)	931(5)	−2211(6)	−331(4)	58(2)
C(8)	1513(5)	−1030(5)	−35(4)	51(2)
C(1)	3010(4)	1497(5)	−321(3)	39(1)
C(2)	3489(5)	1014(5)	−1122(4)	53(2)
C(3)	3217(6)	1590(6)	−2070(4)	61(2)
C(4)	2458(6)	2654(6)	−2239(4)	62(2)
C(5)	1955(6)	3148(6)	−1472(5)	65(2)
C(6)	2246(5)	2575(5)	−525(4)	55(2)
N	4207(3)	2606(4)	1573(3)	41(1)
C(13)	4947(4)	3211(5)	1066(4)	50(2)
C(14)	5457(5)	4445(6)	1355(4)	57(2)
C(15)	5199(5)	5082(6)	2185(5)	59(2)
C(16)	4437(5)	4467(5)	2714(4)	59(2)
C(17)	3962(5)	3228(5)	2384(4)	52(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Atomic Coordinates (×10[4]) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for the non-hydrogen Atoms of Compound **13**

	x	*y*	*z*	U,[a] $Å^2$
Pt	1391(1)	1273(1)	2292(1)	51(1)
C	546(10)	571(8)	3240(7)	74(4)
O	−85(11)	142(8)	3733(7)	128(5)
C(1)	2089(8)	1932(6)	1135(5)	51(2)
C(2)	2449(10)	2850(7)	1094(7)	68(3)
C(3)	2927(12)	3262(8)	279(8)	82(4)
C(4)	3048(11)	2747(9)	−508(6)	73(4)
C(5)	2676(11)	1827(9)	−482(6)	76(4)
C(6)	2188(10)	1428(7)	321(6)	62(3)
C(7)	−719(8)	1509(6)	1742(5)	51(3)
C(8)	−1401(10)	863(8)	1102(6)	67(3)
C(9)	−2834(11)	1076(10)	721(8)	84(5)
C(10)	−3586(10)	1827(9)	959(7)	80(4)
C(11)	−2932(11)	2451(8)	1566(8)	79(4)
C(12)	−1478(9)	2268(7)	1942(7)	63(3)
N	3748(7)	1161(6)	2785(5)	51(2)
C(13)	4211(10)	1708(8)	3641(7)	74(3)
C(14)	3519(17)	1345(11)	4496(7)	109(6)
C(15)	3760(13)	2710(9)	3468(8)	97(5)
C(16)	4302(10)	162(7)	2828(6)	62(3)
C(17)	5999(12)	105(8)	3091(7)	77(4)
C(18)	3964(10)	−311(7)	1920(7)	69(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results

Spectrophotometric Kinetic Studies. The reactions

$$cis\text{-}[PtPh_2(CO)(SEt_2)] + am \rightarrow cis\text{-}[PtPh_2(CO)(am)] + SEt_2 \quad (1)$$

$$cis\text{-}[PtPh_2(CO)(5\text{-}Aq)] + am \rightarrow cis\text{-}[PtPh_2(CO)(am)] + 5\text{-}Aq \quad (2)$$

$$am = NH_2{}^nPr,\ NH_2{}^nBu,\ NH_2{}^sBu,\ NH_2{}^tBu,\ NH_2{}^nPent,\ Nh_2{}^nHex,\ NH_2Cy,\ NH_2Bz,\ NHEt_2,\ NH^nBu_2,\ pip$$

were carried out in dichloromethane as solvent. The analysis of the changes of the IR and ^1H and ^{13}C NMR spectra during the course of the reactions showed that the processes under study were indeed the simple substitution of the bound 5-Aq and SEt_2 with am. There was no evidence before or after this substitution of an amine attack to the carbon monoxide[19] or of a subsequent removal of CO or of the buildup in solution of any other intermediate species. The systematic kinetics of these reactions were studied at different ligand concentrations and were followed spectrophotometrically. The spectral changes observed for

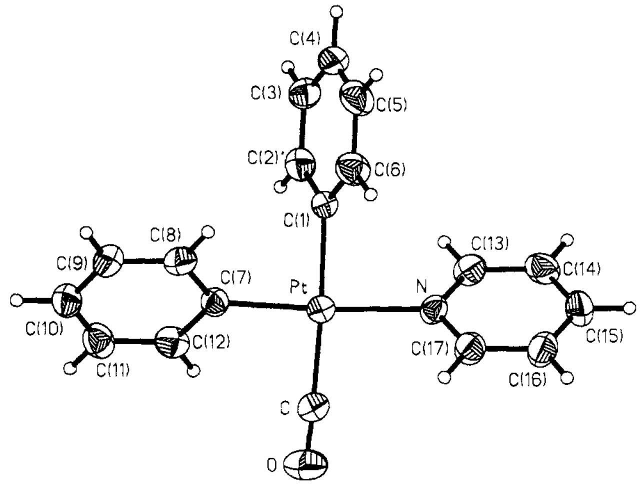

Figure 1. ORTEP drawing of compound **12**, showing the labelling of the non-H atoms. Thermal ellipsoids are drawn at the 40% probability level.

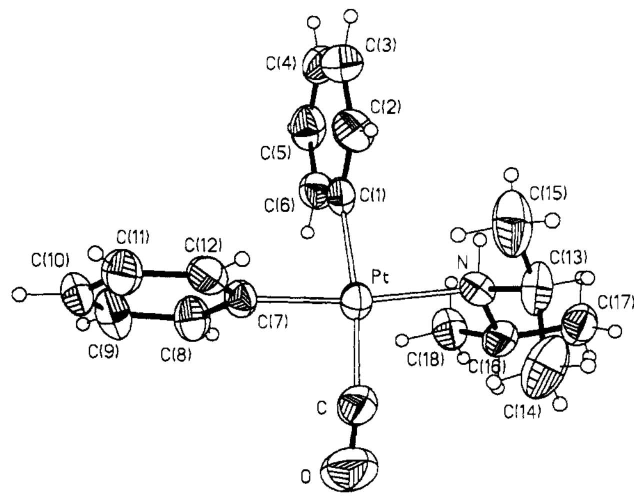

Figure 2. ORTEP drawing of compound **13**, showing the labelling of the non-H atoms. Thermal ellipsoids are drawn at the 40% probability level.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for *cis*-$[PtPh_2(CO)(am)]$

12		**13**	
	Bond Distances		
Pt–C	1.900(5)	Pt–C	1.89(1)
Pt–C(1)	2.037(4)	Pt–C(1)	2.048(8)
Pt–C(7)	2.035(5)	Pt–C(7)	2.036(7)
Pt–N	2.140(4)	Pt–N	2.193(6)
C–O	1.124(7)	C–O	1.12(1)
N–C(13)	1.340(7)	N–C(13)	1.51(1)
N–C(17)	1.335(7)	N–C(16)	1.52(1)
C(13)–C(14)	1.382(7)	C(13)–C(14)	1.50(2)
C(14)–C(15)	1.368(9)	C(13)–C(15)	1.52(2)
C(15)–C(16)	1.384(9)	C(16)–C(17)	1.54(1)
C(16)–C(17)	1.383(7)	C(16)–C(18)	1.50(1)
	Bond Angles		
C(7)–Pt–N	176.0(2)	C(7)–Pt–N	173.1(3)
C(1)–Pt–N	88.3(2)	C(1)–Pt–N	88.5(3)
C(1)–Pt–C(7)	88.0(2)	C(1)–Pt–C(7)	85.2(3)
C–Pt–N	94.2(2)	C–Pt–N	97.8(3)
C–Pt–C(7)	89.5(2)	C–Pt–C(7)	88.8(4)
C–Pt–C(1)	177.5(2)	C–Pt–C(1)	171.6(4)
Pt–C–O	176.9(5)	Pt–C–O	172.4(9)

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Table 5. Ligand Properties of Amine Compounds and Rate Constants for the Reactions[a]

cis-$[PtPh_2(CO)(L)]$ + am → *cis*-$[PtPh_2(CO)(am)]$ + L (L = 5-Aq; SEt_2)

compd	am	pK_a	θ,[b] deg	E_R,[c] kcal M^{-1}	10^3k_2,[d] s^{-1} M^{-1}	10^4k_1,[e] s^{-1}	10^3k_2,[f] s^{-1} M^{-1}	10^4k_1,[g] s^{-1}
1	$NH_2{}^nPr$	10.56[h]	106	31	83.9 ± 0.08	1.83 ± 0.2	1.56 ± 0.02	0.88 ± 0.10
2	$NH_{2n}Bu$	10.64[h]	106		66.0 ± 0.20	2.05 ± 0.2	1.15 ± 0.01	1.05 ± 0.05
3	$NH_2{}^sBu$	10.56[i]	113	43	46.6 ± 0.07	1.97 ± 0.1	1.04 ± 0.02	0.95 ± 0.05
4	$NH_2{}^tBu$	10.65[i]	123	53	21.8 ± 0.02	1.72 ± 0.03	0.401 ± 0.01	1.00 ± 0.03
5	NH_2Pent	10.60[h]	106[n]		82.6 ± 0.06	1.71 ± 0.1	1.38 ± 0.02	1.20 ± 0.08
6	NH_2Ex	10.63[h]	106[n]		80.5 ± 0.08	1.85 ± 0.2	1.33 ± 0.02	1.17 ± 0.06
7	NH_2Cy	10.62[i]	115	41	68.2 ± 0.05	1.64 ± 0.08	1.35 ± 0.08	0.98 ± 0.03
8	NH_2Bz	9.40[i]			39.5 ± 0.04	1.53 ± 0.08	1.02 ± 0.08	0.97 ± 0.09
9	$NHEt_2$	10.92[i]	125	73	6.69 ± 0.09	1.74 ± 0.2	0.152 ± 0.08	1.01 ± 0.03
10	NH^nBu_2	10.95			2.03 ± 0.01	1.76 ± 0.01	0.049 ± 0.01	1.01 ± 0.01
11	Pip	11.12[h]	121	61	32.6 ± 0.06	1.91 ± 0.02	0.654 ± 0.01	1.03 ± 0.04
12	py	5.24[i]			30.0 ± 0.10[m]	[l]		
13	$NH(^iPr)_2$	11.09[i]	137	105	0.385 ± 0.00	1.72 ± 0.04		
14	$NHCy_2$		133	113	[l]	1.71 ± 0.04		
15	NEt_3	10.76[i]	150	109	[l]	1.69 ± 0.03		

[a] In CH_2Cl_2 at 298.16 K. [b] Cone angle data of the amines taken from ref 27. [c] Values of the ligand repulsive energy taken from ref 33. [d] Second-order rate constants for reaction 1. [e] First-order rate constants for reaction 1. [f] Second-order rate constants for reaction 2. [g] First-order rate constants for reaction 2. [h] Values of pK_a for amH^+ taken from: Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1989; Vol. 6, 2nd supplement. [i] Values of pK_a for amH^+ taken from: Perrin, D. D. *Stability Constants of Metal-Ion Complexes*: *Part B- Organic Ligands*; -IUPAC Pergamon Press: London, 1979. [l] Not determined. [m] Data from ref 1a. [n] Estimated to be the same as *n*-butylamine.

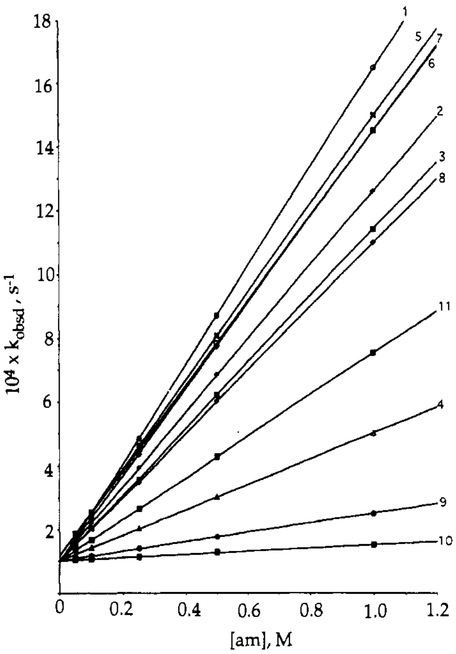

Figure 3. Dependence of the pseudo-first-order rate constants (k_{obsd}) on the reagent concentration for the reactions of *cis*-$[PtPh_2(CO)(5\text{-}Aq)]$ with various amines in dichloromethane at 298.16 K. (Numbers refer to the ligands as listed in Table 5.)

reaction 2 are due essentially to the difference of optical density between coordinated and uncoordinated 5-aminoquinoline, and their shapes do not depend on the nature of the entering amine. The pseudo-first-order rate constants, k_{obsd}, are listed in Tables S1 and S2 (supplementary material). These pseudo-first-order rate constants, when plotted against the concentration of the entering amine, give straight lines with a common nonzero intercept (Figure 3), indicating that the usual two-term rate equation

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

is obeyed. The values of k_1 and k_2, obtained from linear regression analysis of the rate law, are collected in Table 5. The relevant spectroscopic properties of the reaction products *cis*-$[PtPh_2(CO)L]$, obtained as described above, are given in Table 6.

Molecular Structures. The single-crystal X-ray diffraction analysis of **12** and **13** shows close similarities between the two complexes. As shown in Figures 1 and 2, the structures are made up of discrete molecules separated by ordinary van der Waals distances. The coordination around the platinum atom is square planar. The two phenyl rings are cis to each other and in **12** are tilted from the coordination plane by 47.7 and 114.1(1)° being rotated 101.7(2)° to each other, while in **13** they are tilted by 97.9(3) and 90.5(3)° with a rotation angle of 95.2(3)°. The least-squares plane through the four atoms of the coordination sphere show strong deviations from planarity for compound **13** {C, 0.126(11) Å; N, –0.040(8) Å; C(1), 0.068(8) Å; C(7), –0.055(8) Å}. Bond angle distortions away from 90° occur in the plane of the two molecules and are more relevant in the case of the compound containing the secondary aliphatic amine. The C(1)–Pt–C(CO) bond angle in **13** is 171.6(4)° and the Pt–C–O bond angle is 172.4(9)° while the corresponding values in **12** are 177.5(2) and 176.9(5)°, respectively. The strong deviation from linearity in **13** stems entirely from the steric congestion produced by the bulky secondary amine in the cis position, as clearly shown also in a molecular space-filling model (Figure S1). The two substituent isopropyl groups lie above and below the coordination plane and adopt different orientations with respect to the same plane. All the Pt–C bond lengths are in the range of values found for these distances in other aryl complexes of platinum(II)[20] and the C–C ring distances do not differ significantly from the expected values. The observed Pt–C(O) distances of 1.900(5) and 1.89(1) Å have almost the same value and are very near to the mean value of 1.865(10) calculated from the values reported in the CSD for other platinum carbonyl compounds. The Pt–N bond lengths of 2.193(6) and 2.140(4) Å are significantly longer than the sum of the single-bond radii as a consequence of the strong σ-donor power of the trans phenyl group.

Discussion

The synthesis and the spectroscopic characteristics of the starting complexes *cis*-$[Pt(C_6H_5)_2(CO)(5\text{-}Aq)]$[12] and *cis*-$[Pt(C_6H_5)_2(CO)(SEt_2)]$[11] have been described elsewhere. In the first complex the 5-aminoquinoline binds to platinum(II) through the endocyclic nitrogen N_1, and the compound exhibits luminescence properties. This substrate proved to be very useful in the kinetic study of substitutions with phosphines in that it is uncharged and soluble in nonpolar solvents, three of four groups remain firmly bonded to the metal, and only one (the 5-aminoquinoline) undergoes the substitution process. The changes in

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Table 6. Selected Spectroscopic Data for *cis*-[Pt(Ph)$_2$(CO)(am)] Complexes[a]

		CO		phenyl group		
	am	ν^b	δ ($^1J_{PtC}$)^c	δ(C$_2$) ($^2J_{PtC}$)^c	δ(C$_{2'}$) ($^2J_{PtC}$)^c	δ(^{195}Pt)
1	NH$_2{}^n$Pr	2060	180.4 (1022.2)	138.2 (49.0)	135.8 (32.9)	
2	NH$_2{}^n$Bu	2065	180.4 (1023.2)	138.2	135.9	−3858
3	NH$_2{}^s$Bu	2062	180.5 (1024.7)	138.1 (48.5)	136.0 (33.1)	
4	NH$_2{}^t$Bu	2061	180.9 (1026.1)	137.9 (49.1)	135.9 (32.9)	−3932
5	NH$_2$Pent	2061	180.4 (1023.5)	138.2	135.9	−3858
6	NH$_2$Ex	2062	180.4 (1023.3)	138.2	135.9	−3858
7	NH$_2$Cy	2061	180.5 (1024.7)	138.1 (48.2)	136.0 (33.2)	
8	NH$_2$Bz	2067	180.1 (1022.2)	138.2	135.9	−3871
9	NHEt$_2$	2058	180.8 (1042.2)	138.1 (49.1)	136.2 (31.2)	
10	NH^{n}Bu$_2$	2058	180.8 (1041.2)	138.2 (47.0)	136.1 (29.6)	
11	pip	2062	181.0 (1038.8)	138.4 (47.7)	135.5 (31.9)	
12	py	2066	180.7 (996.0)	138.4 (47.0)	136.5 (34.9)	
13	NH^{i}Pr$_2$	2058	181.2 (1049.0)	138.0 (49.3)	137.2 (30.5)	−3858
14	NHCy$_2$	2057	181.2 (1051.7)	138.1 (51.6)	137.3 (30.5)	−3824
15	NEt$_3$	2061	182.0 (1054.6)			

[a] Recorded in CDCl$_3$ as solvent. [b] Carbonyl stretching frequencies, in cm^{-1}. [c] Chemical shifts (δ) in ppm relative to TMS. Coupling constants with ^{195}Pt in Hz are given in parentheses. C$_2$ and C$_{2'}$ are *ortho* carbons.

the electronic spectra occur in the visible region, and the spectroscopic properties of the coordinated carbon monoxide in the reaction products *cis*-[Pt(C$_6$H$_5$)$_2$(CO)(L)] were a good probe of the changes of electronic density or of the steric repulsions induced by the entering phosphine. The reactions with amines exhibit somewhat different characteristics. The rates are much slower than that with phosphines, and therefore, in order to collect reactivity data for the widest possible range of entering groups, we extended the study to the kinetics of substitution reactions to *cis*-[Pt(C$_6$H$_5$)$_2$(CO)(SEt$_2$)], taking advantage of the fact that SEt$_2$ is more labile than 5-Aq.

The previous study on the phosphines showed that, in the absence of steric effects, the values of the stretching frequencies ν(CO) and of the coupling constants $^1J_{PtC(CO)}$ or $^1J_{PtP}$ of the *cis*-[Pt(C$_6$H$_5$)$_2$(CO)(L)] (L = phosphine) complexes were all linearly dependent on the basicity of the phosphine and could be regarded as good parameters for the inductive effects of the substituents bonded to the phosphorus atom. This is no longer true for the corresponding amine complexes. The IR spectra of the reaction products *cis*-[Pt(C$_6$H$_5$)$_2$(CO)(am)] (**1–15** in Table 6) exhibit a strong CO peak centered at 2061 ± 2 cm^{-1}. The independence of this stretching frequency of the nature of the coordinated amine is not unexpected, since the amines used lie within a very restricted range of basicity (pK_a = 10.6 ± 0.4). Similar results were obtained[21] even for systems containing amines encompassing a wider range of basicity. Thus, for compounds of the type [M(CO)$_5$(am)] (M = Cr, Mo, W; pK_a of amH$^+$ within 11.0 and 5.0) no relation was found between the values of force constants calculated for CO with the basicity of the amine.

The ^{13}C NMR spectra show the expected signals for the aromatic and aliphatic carbons and a resonance for the carbonyl ligand centered at 180.7 ± 0.5 ppm with two ^{195}Pt satellites. The overall difference of $^1J_{PtC}$ is not large, being 30 Hz between the first and the last members of the series, and even though the values seem to increase with increasing encumbrance of the ligands, the relation with the steric properties of the amine is very poor. Likewise, both the values of the chemical shifts of the ortho-carbons of the aromatic rings and the ^{195}Pt resonances seem not to be depend significantly on the nature of the coordinated amine.

The electronic and ^{1}H and ^{13}C NMR evidence indicates that the changes that are observed and kinetically analysed correspond to the single stage reactions **1** and **2**. The dependence of the pseudo-first-order rate constants on the concentration of the entering amines is described by a family of straight lines with a nonzero intercept (Figure 3 and Figure S2) ($k_1 = 1.7 \times 10^{-4}$ s^{-1} for reaction **1** and $k_1 = 1.0 \times 10^{-4}$ s^{-1} for reaction **2**, respectively). The contribution from the nucleophile independent (k_1) term

Table 7. Temperature Effect on the Rate of Dissociation (k_1) of *cis*-[PtPh$_2$(CO)(SEt$_2$)] as Derived from the Reactions[a]

$$cis\text{-}[PtPh_2(CO)(SEt_2)] + Et_3N \rightarrow cis\text{-}[PtPh_2(CO)(Et_3N)] + SEt_2$$

T, K	$10^4\,k_1$, s^{-1}	T, K	$10^4\,k_1$, s^{-1}
288.16	0.309 ± 0.009	303.16	4.04 ± 0.087
293.16	0.761 ± 0.017	308.16	8.76 ± 0.002
298.16	1.66 ± 0.075		

$\Delta H^{\ddagger}$ = 120.9 ± 1.5 kJ mol^{-1}; $\Delta S^{\ddagger}$ = +88.8 ± 4.9 J K^{-1} mol^{-1}.

[a] In CH$_2$Cl$_2$. The values of k_1, at each temperature, are given by the statistical mean of at least five kinetic runs carried out under saturation conditions ([Et$_3$N] > 0.08 M).

was very small under the experimental conditions adopted to follow the kinetics of *cis*-[Pt(C$_6$H$_5$)$_2$(CO)(5-Aq)][7] with phosphines in toluene and of *cis*-[Pt(C$_6$H$_5$)$_2$(CO)(SEt$_2$)][1a] with heterocyclic amines in dichloromethane, so that the error in determining the intercepts (k_1) from plots with large slopes was too high to give reliable values. For reactions 1 and 2 the contribution of k_1 becomes more and more important as the values of k_2, the second-order rate constant for the bimolecular attack of the amine on the substrate, decrease. For the tertiary amine NEt$_3$ and for NHCy$_2$ the contribution of k_2 vanishes and the substitution is completely dominated by the reagent independent pathway.

The Reagent Independent Pathway. There are strong indications that this pathway refers to the dissociation of the leaving group rather than to a bimolecular solvolysis: **(i)** from the temperature dependence of k_1 (data in Table 7) the values of the activation parameters obtained for reaction 1 are as follows: $\Delta H^{\ddagger}$ = 120.9 ± 1.5 kJ mol^{-1} and $\Delta S^{\ddagger}$ = +88.8 ± 4.9 J K^{-1} mol^{-1}. The high value of the enthalpy of activation and the large positive value of the entropy of activation are consistent with a dissociative process. This is a case where the activation parameters assume particular reliability as a diagnostic tool of the mechanism, since solvational changes and electrostriction effects play a minor role in the exchange of neutral molecules in a nonpolar solvent.[22] **(ii)** The displacement of the thioether by the nitrogen-chelating ligand 2,2′-bipyridine to yield [PtPh$_2$(bpy)] takes place in a single stage, the act of ring closing being much faster than the displacement of the sulfide, and is retarded by the addition of the free leaving group. The values of k_{obsd} at various concentrations of bipy and SEt$_2$ are available as supplementary material (Table S3). At a constant concentration of sulfide, a curvilinear dependence on the concentration of the entering 2,2′-bipyridine is observed which tends to become linear and independent of [Et$_2$S] as [bpy] increases (Figure S2). All the rate data appear to fit the nonlinear

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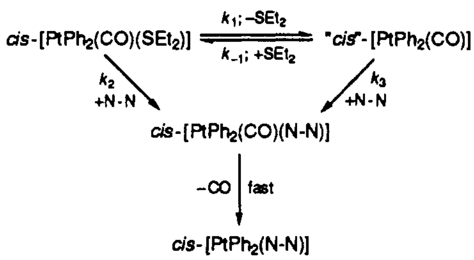
rate law

$$k_{obsd} = a[\text{bpy}]/(b[\text{Et}_2\text{S}] + [\text{bpy}]) + c[\text{bpy}] \quad (4)$$

The values of k_{obsd}, [bpy] and [Et_2S] were fitted to this expression by using a nonlinear least-squares curve-fitting program, and the best values of the constants *a*, *b*, and *c* were obtained together with their standard errors. The pattern of behavior is much the same as that found in our previous studies on strictly similar systems,[1] where an easy dissociation of thioethers or sulfoxides was shown to take place under the strong σ-donor power of a trans Pt–C bond. Thus, all these results can be explained by a stepwise mechanism involving dissociation of the starting complex (via k_1) to yield a 14-electron [$PtPh_2(CO)$] intermediate followed by the attachment (via k_3) of the chelating ligand bpy to form an open-ring species, also formed (via k_2) by a parallel associative attack of bpy on the starting substrate. There a fast ring closing follows to yield the observed products.



The rate constants are related to the empirical parameters *a*, *b*, and *c* by the expressions $a = k_1 = 1.7 \times 10^{-4}\ s^{-1}$, $b = k_{-1}/k_3 = 1.52$ and $c = k_2 = 2.85 \times 10^{-4}\ M^{-1}\ s^{-1}$. As expected, the rate of dissociation k_1 at 298.16 K is identical to that obtained for the k_1 term from eq 3. Summing up, mass-law retardation plots and a positive value of the entropy of activation are strongly indicative of a dissociatively activated pathway for the reagent independent term k_1. The contribution of this latter to the overall reactivity in *cis*-[$PtPh_2(CO)(SEt_2)$] is almost negligible for the less bulky entering groups, while it dominates the substitution of the most sterically demanding ligands.

The Reagent Dependent Pathway. Whatever the nature of the reagent independent path is, dissociation of a coordinated ligand or bimolecular solvolysis followed by fast anation, it is clear that its coming into play marks the onset of a type of steric threshold, discussed at length in the past in connection with the reactivity of sterically hindered square planar complexes.[23] When the steric repulsion between the entering ligand and the substrate becomes so high as to make the associatively activated process unfavorable, the k_1 pathway still offers a route for the formation of thermodynamically stable products. For most of the amines used in this study it is possible to obtain reliable values of k_2 either for the displacement of the thioether (eq 1) or of the 5-aminoquinoline (eq 2) and there is no reason to doubt that they refer to an associative mode of activation. The sequence of reactivity observed is $NH_2{}^nPr \approx NH_2{}^nPent \approx NH_2{}^nHex > NH_2Cy \approx NH_2{}^nBu > NH_2{}^sBu > NH_2Bz \approx$ pip $\approx$ py $> NH_2{}^tBu > NHEt_2 \approx NH_nBu_2 > NH^iPr_2$ and is the same for the two complexes . A plot of log k_2 for the reactions of [$PtPh_2(CO)$(5-Aq)] against log k_2 for the reactions of [$PtPh_2(CO)(SEt_2)$] in Figure 4 shows that there is a reasonably good linear relationship with a slope = 1.041 (11 data points, $r^2 = 0.988$). The value of the slope indicates that the two substrates have the same capacity of nucleophilic discrimination, the difference in reactivity arising only from the different lability of SEt_2 and 5-Aq. Such kinetic behavior is in keeping with an associatively activated process in which the Pt–N(ligand) bond formation is by far more important than bond breaking of the leaving group.

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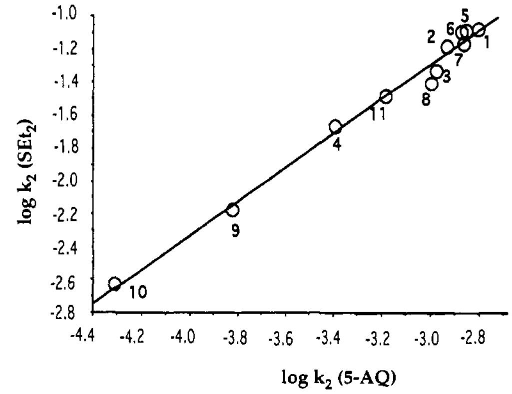

Figure 4. Correlation between the rates of reaction of *cis*-[$PtPh_2(CO)(SEt_2)$] and of *cis*-[$PtPh_2(CO)$(5-Aq)] with aliphatic amines. (Numbers refer to the ligands as listed in Table 5.)

The sequence of the k_2 values for the examined amines, all of comparable basicity and σ-donor power, indicates that the reactivity is dominated by the size of the substituents bonded to the nitrogen atom. Primary amines react significantly faster than secondary amines. For the most sterically demanding ligands, such as NEt_3 or $NHCy_2$, the bimolecular attack is prevented and substitution takes place only through the reagent independent pathway.

The most widely used method for evaluating the steric requirements of a ligand has been suggested by Tolman,[24] who measured the cone angles of space-filling CPK molecular models of phosphines. For phosphines having the same three organic substituents, the cone angle θ is defined as the apex angle of a cylindrical cone, centered along the 3-fold axis, with origin 2.28 Å from the center of the phosphorus atom, whose sides just touch the van der Waals surfaces of the outermost atoms of the substituents. Variants of the cone angle concept have been suggested based on mathematical models[25] and X-ray structural data.[26] Following Tolman's approach and fixing the metal–nitrogen bond distance at 2.20 Å, Seligson and Trogler[27] have determined values of cone angles for a wide series of amines. When the logarithms of the second-order rate constants (k_2) for reactions 1 and 2 are plotted against the cone angles of the amines the steric profiles obtained (Figure 5) are identical and consist of a plateau region of no steric effects for sufficiently small ligands followed by a sharp steric threshold at 117° after which the rate decreases linearly as function of θ. A similar pattern of behavior is considered to be quite common for nucleophile-dependent substitution reactions[28] and particularly for reactions of square planar complexes, as can be inferred from the QALE analysis carried out by Giering and Prock et al.[29] on Tolman's data of enthalpies of reaction of phosphines with *trans*-[$Pt(PMe_2Ph)_2(CH_3)(THF)]^+$ (THF = tetrahydrofurane), from the QALE analysis of the kinetic data of phosphines reacting with *cis*-[$PtPh_2(CO)$(5-AQ)][7] and more recently from the correlation of the equilibrium constants for the formation of [$Pd(dmpe)(CH_3)(amine)]^+$ (dmpe = 1,2-bis(dimethylphosphino)ethane) cations[27] with the cone angles of a series of amines of comparable basicity. The interpretation is rather straightforward. Steric effects are small for small entering groups but they increase steadily when

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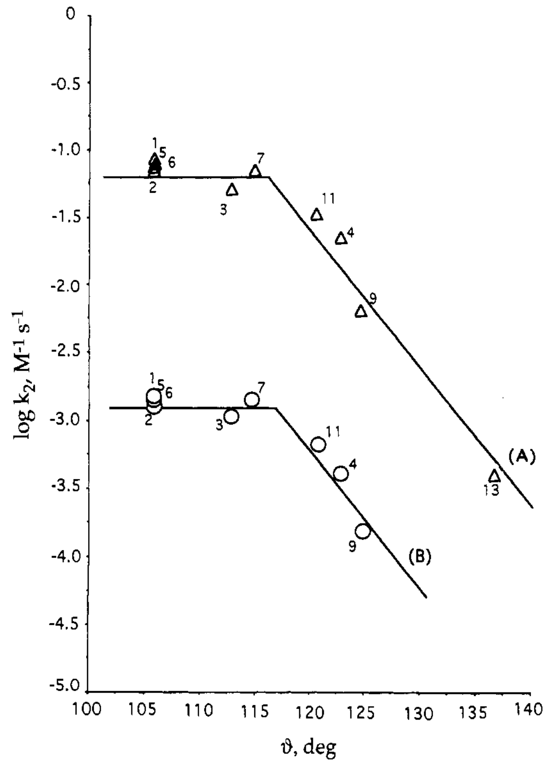

Figure 5. Steric profiles of reaction **1** (upper plot) and of reaction **2** (lower plot) with the cone angle as the steric parameter.

the size of the nucleophile increases. Additional considerations involve the value of the steric threshold (θ_{st}), which is thought to be a measure of the congestion about the metal in the transition state,[30] its sharpness, and the slope of the profile after the threshold which should both depend on the flexibility of the transition state; a flexible complex should show some curvature at the steric threshold[28,30] and a small slope of the subsequent linear region of the profile, while a rigid complex should show a sharper threshold and a greater sensitivity to steric effects.

Another method of estimating the steric requirements of ligands has been proposed, the ligand repulsive parameter E_R, based upon molecular mechanics calculations of the structures formed by a prototypical metal fragment $Cr(CO)_5$ with the various ligands.[31] The energy-minimised structure provides a starting point for computing E_R, which is expressed in units of kcal mol^{-1}, and represents a measure of the van der Waals repulsive force acting between ligand and metal complex. To date, E_R values have been computed for phosphines, phosphites, arsenic ligands,[32] and amines.[33] When the logarithms of the second-order rate constants (k_2) for reactions 1 and 2 are plotted against the values of E_R of the amines (Figure 6) one finds linear correlations of the type log $k_2(SEt_2) = 0.055 - 0.032E_R$ (six data points, $r^2 = 0.987$) and log k_2(5-Aq) = $-1.912 - 0.026$ ER (five data points, $r^2 = 0.955$). These steric profiles, at variance with what was discussed before, suggest that steric effects are continuously operative over the range of data without the onset of a steric threshold. This pattern of behavior is confirmed when the analysis using the E_R steric parameter is extended to other square planar systems. In the case of the entering ligand dependent substitution reaction between phosphines and $[PtPh_2(CO)(5\text{-}Aq)]$[7] a regular decrease of the reactivity is observed with increasing the encumbrance of the ligand according to the expression log $k_2 = 3.64 - 0.045E_R$ (14 data points, $r^2 = 0.952$) . Likewise, the heat of displacement of THF by phosphines from *trans*-$[Pt(PMe_2Ph)_2(CH_3)(THF)]^+$[34]

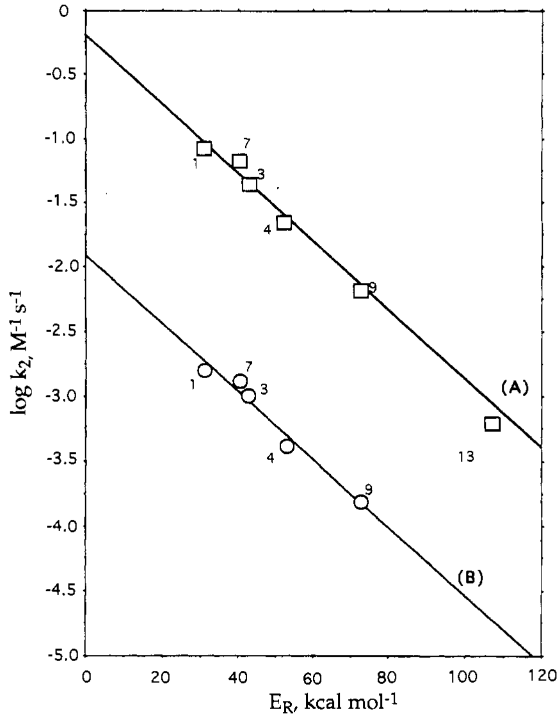

Figure 6. Steric profiles of reaction **1** (upper plot) and of reaction **2** (lower plot), with the ligand repulsion energy (E_R) as the steric parameter.

decreases according to the expression $\Delta H = 33.28 - 0.177E_R$ (eight data points, $r^2 = 0.952$).

The use of different sets of parameters for estimating the steric requirements of ligands leads then to quite different steric profiles and to conflicting interpretations. E_R values are based on computations involving energies and forces while the cone angles are geometrical constructions. Despite the different origins the values of E_R and θ for phosphines and for amines correlate moderately well within a rather large range of values, but strong deviations for particular ligands are observed. Limits and advantages of E_R and θ have been discussed at length by Brown,[32] and 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.[26,35] The method based on molecular mechanics calculations seems to overcome such ambiguities. The E_R values are computed for each ligand in the conformation more appropriate for its binding to the metal center. This conformation can be significantly different from that assumed by the free ligand in the CPK model constructed to measure the cone angle. Although we are inclined to think that the molecular mechanics energy change depicted in the process of bond formation between the metal fragment and the ligand is, to some extent, reminiscent of the activation process along the reaction coordinate for a bimolecular substitution reaction, where then E_R values are to be preferred to θ at least for such a type of reaction, it is still possible that much of the difference observed is entirely due to a few uncertain values attributed cone angles, especially for those ligands whose values lie near the hypothized steric threshold. For instance, the cone angles for NH_2Me, NH_2Et, $NH_2(^n\text{-}Pr)$, $NH_2(^i\text{-}Pr)$, $NH_2(^t\text{-}Bu)$, and NH_2(neopentyl) were all reported[27] to have the same value (106°), while they could differ significantly. Thus, setting apart the data of cone angle for this group of reagents, one finds linear correlations of the type log $k_2 = 9.52 - 0.093\theta$ (six data points, $r^2 = 0.917$) and log $k_2 = 4.85 - 0.068\ \theta$ (five data points, $r^2 = 0.836$) for the reactions of amines with $[PtPh_2(CO)(SEt_2)]$ and $[PtPh_2(CO)(5\text{-}Aq)]$, respectively. Following the same reasoning, for the bimolecular displacement of 5-Aq by phosphines from $[PtPh_2(CO)(5\text{-}Aq)]$, the rate data for $P(EtCN)_3$, $P(m\text{-}MeC_6H_4)_3$,

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and $P(m\text{-}ClC_6H_4)_3$ were omitted, considering that the first ligand exhibits unusual electronic effects and for the latter the value of the Tolman cone angle (165°) greatly overstates the size of the groups. The reaction rates were analyzed using the equation[36]

$$\log k_2 = a(\chi_d) + b(\theta - \theta_{st})\,\lambda + c \qquad (5)$$

where χ_d is a measure of the σ donicity of the ligand, θ and θ_{st} have the meanings given above, λ is a switching function that equals 0 when $\theta < \theta_{st}$ and equals 1 when $\theta > \theta_{st}$, a and b are regression coefficients that measure the relative importance of electronic and steric factors in the process, and c refers to the intrinsic reactivity of the substrate. The multiple regression gives an r^2 of 0.956, but the electronic parameter makes a statistically insignificant contribution to the analysis. The reaction is dominated by steric factors and the analysis based on θ alone gives an r^2 of 0.956 for the relationship $\log k_2 = 12.12 - 0.094\theta$ (12 data points) with a steric threshold $\theta_{st} < 122°$. In other words, the steric threshold is less than the cone angle of the smallest ligand. The same reasoning applies for the heats of reaction of phosphines with *trans*-$[Pt(dmpe)(CH_3)(THF)]^+$,[34] which show a nice linear correlation only with θ ($r^2 = 0.944$) with $\theta_{st} < 118°$. Summing up, a cautious selection of the values of the cone angles used leads to the same pattern of behavior and to a unique mechanistic interpretation. Steric effects appear to be continuously operative over the range of ligands examined, the only clear-cut steric threshold being that associated with a changeover of reaction pathway, dissociation of a coordinated ligand or associatively activated solvolysis, when an excess of encumbrance of the ligand prevents a bimolecular attack on the metal.

Pyridine does not correlate well with the rate data for the other amines and it appears to react more effectively than expected from its pK_a value. Several studies of the way in which the rate of entry of amines into a variety of d^8 substrates depends upon the proton basicity showed that in many cases there is a linear dependence of the type $\log k_2 = \alpha(pK_a) + b$.[37] For platinum substrates the values of α are rather small, in agreement with the small sensitivity of the soft metal center to inductive effects brought about by the substituents on the amine ligand. In some cases,[38] for the entry of heterocyclic nitrogen bases, the least basic nucleophiles exhibit the greatest reactivity (α is negative), and it has been suggested that back-donation from filled orbitals on the metal into empty antibonding orbitals on the ligand can assist bond formation. An increased binding ability of pyridines as compared to saturated amines was observed for Ru(II)–pyridine complexes,[39] for $[Pd(dmpe)(Me)(pyridine)]^+$,[27] and for some pentacarbonyl complexes[21] and was attributed to π back-bonding from the metal center. The angle of 49.5(2)° formed by the pyridine plane in **12** with the coordination plane would suggest that the pyridine ligand is attempting to find the best orientation for π bonding. The values of the torsion angles for other platinum–pyridine complexes, all within the range 45–62°,[39,45] show that pyridine avoids lying perpendicular to the coordination plane and are consistent with the suggestion of π bonding interactions. The Pt–N distance of 2.140(4) Å approaches the upper end of the range known for pyridine nitrogen coordinated to platinum(II), as a consequence of the strong trans activating power of the aryl group. Smaller Pt–N separations were found when the trans activating group is chloride (2.01(1) Å),[40] pyridine (1.98(1)[40] and 2.017 Å),[41] dimethyl sulfoxide (2.056(6) Å),[42] and styrene (2.083(8) Å),[43] while the Pt–N separation increases to 2.160(2) Å when the trans activating group is triethylphosphine and the nitrogen base is a bulky quinoline.[44] The Pt–N bond distance between the metal and the diisopropyl amine in **13**, to the best of our knowledge, is the longest reported so far for a secondary amine bonded to platinum, being comparable only with the Pt–N bond length of 2.193(4) Å of a dimethylamine group in the trans position to a carbon bonded naphthyl group.[46]

Concluding Remarks

The replacement of 5-aminoquinoline or diethyl sulfide from *cis*-$[PtPh_2(CO)(L)]$ (L = 5-Aq or SEt_2) by a series of amines of comparable basicity and of different size takes place by way of a bimolecular attack of the ligand on the substrate. Linear plots, obtained correlating the rates with the set of steric repulsion parameters (E_R) or with selected values of cone angles (θ), indicate that steric effects come into play very soon, even for nucleophiles of relatively small size, and are continuously operative increasing with increasing encumbrance of the entering ligand. However, a linear plot is only a part of a more complicated steric profile which consists of upper and lower plateau regions connected by a straight line. The first horizontal upper part with no steric effects for very small ligands is not seen here since, as for other planar systems, the first steric threshold (θ_{st}) is less than the cone angle of the smallest ligand used. This first steric threshold marks the onset of steric destabilization in the 5-coordinate transition state which increases along the downward sloping part of the plot. A second steric threshold, for the most sterically demanding ligands, marks the beginning of the lower horizontal part of the steric profile and is associated with the point where steric saturation at the 5-coordinated transition state is at its peak. Under these circumstances a reagent independent reaction pathway of lower energy, such as dissociation of a coordinated ligand or associative solvolysis, becomes operative for substitution.

The steric properties of the entering amines do not produce significant variations in the spectroscopic characteristics of the final *cis*-$[PtPh_2(CO)(am)]$ products. The molecular structure of the pyridine compound confirms π-bonding interactions with d orbitals of the metal, already inferred from the reactivity data. The lengthening of the platinum–nitrogen bond distance in the pyridine compound stems entirely from the strong σ-donor power of the Ph group while in the diisopropyl amine compound a concurrent effect of the steric congestion of the ligand itself cannot be ruled out.

Acknowledgment. We wish to thank the CNR and MURST for financial support.

Supplementary Material Available: Tables giving primary kinetic data and complete crystallographic data, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates for **12** and **13** and figures showing the dependence of k_{obsd} on ligand concentration and a space filling model for **13** (15 pages). Ordering information is given on any current masthead page.

(36) We wish to thank Prof. W. Giering of Boston University for sending us the latest version of the computer code for doing linear regression with a steric threshold.

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