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Electrophilic Attack upon *trans*-Bis(triethylphosphine)diphenylplatinum

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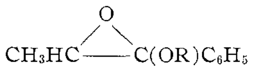
This paper reports kinetic measurements on the reaction of *trans*-[Pt(P(C_2H_5)$_3$)$_2$(C_6H_5)$_2$] with acids in methanol in the presence of chloride ion as nucleophilic agent. The rates are first order in substrate and proton concentration. The activation enthalpy is 10.6 kcal/mole and the activation entropy is −24 eu. A mechanism is suggested involving a rapid preequilibrium between the starting material and H^+ leading to a Pt(IV) six-coordinated hydrido complex, followed by a slow elimination reaction with loss of benzene, and rearrangement to *trans*-[Pt(P(C_2H_5)$_3$)$_2$(C_6H_5)Cl].

Introduction

No information is available dealing with the general subject of the selectivity of a given reagent when various, alternative reactions with different centers in a metal complex are possible. On the other hand, investigations of this type have been extensively carried out upon organic substrates, as illustrated for example by the various nucleophilic displacements which are possible for α-halo ketones. Thus, the compound $CH_3CHXCOC_6H_5$ is attacked by RS^- which displaces X^- by an S$_N$2 process, whereas RO^- attacks the carbonyl group, the products being, respectively, $CH_3CH(SR)COC_6H_5$ and



Investigations extended to other appropriate organic substrates lead to the general conclusion that strong bases tend to react at the more electron-deficient centers, whereas large polarizable ions tend to react at the centers with higher electron density.[1]

There are relatively little discussion and limited data concerning the role played by electrophilic agents in substitution reactions of four-coordinate d^8 metal ion complexes. The aim of the present work is to throw some light on the factors which determine whether the electrophilic attack takes place directly at the metal–ligand bond or whether the unshared d electrons of the metal become materially involved, leading to the formation of a transient intermediate, complex-electrophilic species, followed by a facilitated nucleophilic addition and rearrangement as the rate-determining step. We report here the reactions of some electrophilic agents, such as H^+, $C(CH_3)_3^+$, and silver ion, on *trans*-[Pt(C_2H_5)$_3$)$_2$(C_6H_5)$_2$] in methanol.

Experimental Section

The complexes *trans*-[Pt(P(C_2H_5)$_3$)$_2$(C_6H_5)$_2$] and *trans*-[Pt(P(C_2H_5)$_3$)$_2$(C_6H_5)Cl)] were prepared and purified following the methods reported in the literature. Each compound was characterized by elemental analysis.[2]

Methanol was purified by distillation after refluxing over Mg(OCH_3)$_2$ to remove water.

Other chemical products were all reagent grade commercial materials and were used without further purification. Anhydrous *p*-toluenesulfonic acid was obtained by heating the commercial product at 50° under vacuum for 24 hr.

Kinetics.—Fresh solutions of the complex *trans*-[Pt(P(C_2H_5)$_3$)$_2$(C_6H_5)$_2$] ($\sim 10^{-5}$ *M*) and of the acid HA (A^- = Cl^-, ClO_4^-, *p*-toluenesulfonate) (10^{-3}–10^{-2} *M*) in the presence of lithium chloride ($\sim 10^{-2}$ *M*) and/or lithium perchlorate were prepared and stored separately in a thermostat. The reaction was started by mixing known volumes of the two solutions in a 1-cm quartz cell placed in a thermostated cell compartment of a Beckman DK-2A recording spectrophotometer. In almost all of the runs the ionic strength was kept constant (5×10^{-2} *M*) by adding lithium perchlorate. However no significant ionic strength effect was found for a 10-fold change of the molar concentration of lithium perchlorate. The reactions were followed by recording from time to time the spectral changes in optical density in the ultraviolet region of the reaction mixture. The reference cell contained the reagent blank. In each series of kinetic runs the acid concentration was changed at least fivefold. All the reactions were followed in the presence of a large excess of acid in order to provide pseudo-first-order conditions and to force the reactions to go to completion. This was checked by the comparison of the final spectra with that of the known product independently prepared. Pseudo-first-order rate constants were determined graphically by plotting $\log (A_t - A_\infty)$ *vs.* time. A_t and A_∞ are the optical densities of the reaction mixture at *t* seconds and after 10 half-lives, at some wavelength where the absorbance of the product is considerably lower than that of the starting material. The spectral changes during the reaction showed well-defined isosbetic points which are indicative of only two absorbing species, the substrate and the product. From linear plots of k_{obsd} *vs.* the concentration of acid (Figure 1), the second-order rate constants, *k* (M^{-1} sec^{-1}), were obtained as the slopes. The characterization of the final product, *trans*-[Pt(P(C_2H_5)$_3$)$_2$(C_6H_5)Cl)], formed during the reaction was made by spectral analysis. The identification of the benzene has been performed as follows. A solution of *trans*-[Pt(P(C_2H_5)$_3$)$_2$(C_6H_5)$_2$] (10^{-3} *M*) was allowed to react with *p*-toluenesulfonic acid (10^{-2} *M*) in methanol in the presence of LiCl (10^{-2} *M*) for 3 hr at 30°. From the reaction mixture the liquid was recovered in a liquid air cooled trap by molecular distillation. The benzene was identified by spectrophotometric analysis in the ultraviolet region.

Results and Discussion

Kinetic measurements on the reaction of *trans*-[Pt(P(C_2H_5)$_3$)$_2$(C_6H_5)$_2$] with Cl^- have been carried out in methanol in the presence of the acid HA (A^- = Cl^-, ClO_4^-, *p*-toluenesulfonate ion). The complex *trans*-[Pt(P(C_2H_5)$_3$)$_2$(C_6H_5)Cl] and benzene are formed as the reaction products, so that the reaction is

$$trans\text{-}[Pt(P(C_2H_5)_3)_2(C_6H_5)_2] + Cl^- + H^+ \longrightarrow trans\text{-}[Pt(P(C_2H_5)_3)_2(C_6H_5)Cl] + C_6H_6 \quad (1)$$

No reaction occurs with LiCl in the absence of acid. Somewhat analogous to reaction 1 is the preparation

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(1) R. F. Hudson, *Chimia* (Aarau), **16**, 173 (1962), and in "Structure and Bonding," Springer-Verlag, Heidelberg, 1966, p 221.

(2) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 4020 (1959).

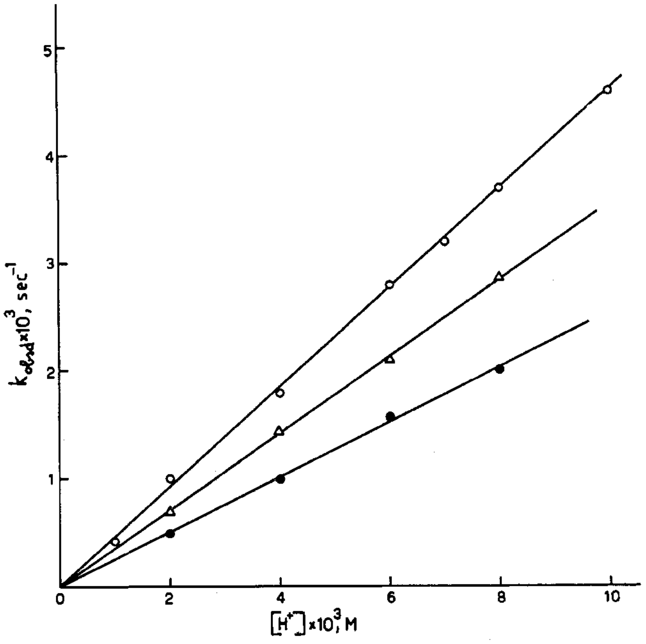

Figure 1.—Plots of the experimental rate constants, k_{obsd} (sec^{-1}) *vs.* the proton concentration at different temperatures.

of *cis*-$[Pt(P(C_2H_5)_3)_2(CH_3)Cl]$ obtained by treating *cis*-$[Pt(P(C_2H_5)_3)_2(CH_3)_2]$ with HCl in dry ether; cleavage of the methyl group from the platinum center results in the formation of methane.

The rates of reaction 1 in methanol are reported in Table I.

Plots of the experimental rate constants, k_{obsd} (sec^{-1}) *vs.* the concentration of hydrogen ion at three different temperatures are shown in Figure 1. The activation parameters for reaction 1 are: $\Delta H^{\ddagger} = 10.6$ kcal/mole (± 1 kcal/mole, estimated) and $\Delta S^{\ddagger} = -24 \pm 3$ eu.

The general rate law for reaction 1 is

$$-\frac{d[\text{complex}]}{dt} = k[H^+][\text{complex}] \qquad (2)$$

The value of k at 30.5° is 0.46 M^{-1} sec^{-1}.

No real evidence has been found for a path which involves A^-, since the reaction rate is independent of the concentration of A^-, within a wide range of concentration. It is pertinent to note that the rate of reaction 1 with HCl decreases drastically on going from methanol to the less dissociating anhydrous ether, whereas it increases very slightly with the water content of the methanol.

TABLE I

RATES OF THE REACTION

$$trans\text{-}[Pt(P(C_2H_5)_3)_2(C_6H_5)_2] + H^+ + Cl^- \longrightarrow trans\text{-}[Pt(P(C_2H_5)_3)_2(C_6H_5)Cl] + C_6H_6$$

IN METHANOL AT DIFFERENT TEMPERATURES AND COMPLEX CONCENTRATION OF 10^{-5} M

$10^3[H^+]$, N	$10^3[Cl^-]$,[a] N	$10^3[ClO_4^-]$, N	$10^3 \times p$-toluenesulfonate ion concn, N[b]	10^3k_{obsd}, sec^{-1}
		20.5°		
2	20	28	2	0.5
4	20	26	4	1.0
6	20	24	6	1.6
6	10	...	6	1.6
6	10	144	6	1.65
6.8	50	...	...	1.78
6.3	44	6.3	...	1.65
8	20	22	8	2.0
		25.5°		
2	20	28	2	0.7
4	20	26	4	1.45
6	20	24	6	2.1
8	20	22	8	2.85
		30.5°		
1	20	29	1	0.4
2	20	28	2	1.0
4	20	26	4	1.85
6	20	24	6	2.8
7	20	23	7	3.2
8	20	22	8	3.7
10	20	20	10	4.6

[a] Lithium and acid form. [b] As *p*-toluenesulfonic acid. The acid added is assumed to be completely dissociated.

Electrophilic catalysis in substitution reactions of some platinum(II) complexes has been already reported.[3] As an example, the rate of the reaction of *trans*-$[Pt(pip)_2Cl_2]$ (pip = piperidine) with NO_2^- and $^{36}Cl^-$ as entering groups strongly increases in the presence of nitrous acid or boric acid. Nitrous acid exhibits an accelerating effect on the nitrite ion substitution of some other Pt(II) complexes. For the catalyzed step, a mechanism has been proposed involving the formation of a transient intermediate between the complex and HNO_2 or H_3BO_3 (acting as electrophilic agents) followed by nucleophilic attack and rearrangement of the intermediate as the rate-determining step. The assumed role of nitrous or boric acid is therefore to withdraw π electrons from platinum. This in turn would make it easier for the metal to accept electrons from the entering group. Accordingly, no HNO_2 acceleration was observed with complexes containing coordinated π-electron-withdrawing ligands, such as $P(C_2H_5)_3$ and $As(C_2H_5)_3$, which can to some extent explicate the role played by electrophilic agents. Whereas π bonding in the ground state may be small, the addition of the nucleophile will produce an excess of electronic charge on the metal which these ligands can remove by increased π bonding. No HNO_2 acceleration was observed with $[Pt(Et_4dien)Cl]^+$ (Et_4dien = 1,1,7,7-tetraethyldiethylenetriamine). This has been explained assuming that in this complex the Pt(II) is shielded by the four ethyl groups which prevent it from interacting with HNO_2 along the z axis. Reactions of the analogous $[Pt(dien)Cl]^+$ complex, where Pt(II) is accessible, are catalyzed by nitrous acid. This supports the view that an interaction with Pt(II) is involved rather than an electrophilic attack on the departing Cl^-. Considering reaction 1, it is reasonable to assume that the most probable reaction centers involving the protonation of the substrate in the activated complex are the coordinated phenyl group and

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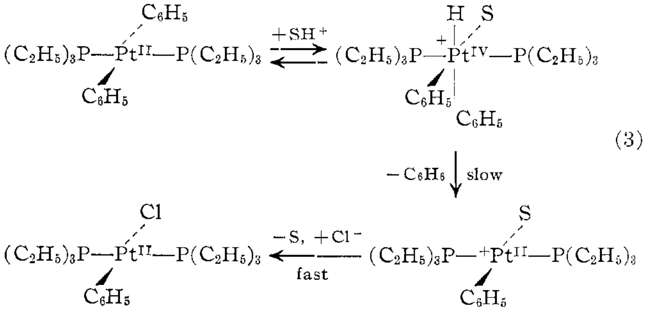
[3] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **4**, 925 (1965).

the platinum. A possible reaction mechanism consistent with the experimental results is that shown by



(3)

(Notice that perchlorate and *p*-toluenesulfonate ions have a very poor coordinating power toward platinum center. The oxidation number of -1 is generally assigned to the hydride ligand coordinated to d^n transition metal ions. S is the solvent and SH^+ is its conjugate acid.) The proposed mechanism suggests a rapid formation of a six-coordinated hydrido species (arbitrarily chosen *cis* configuration) as an active intermediate, followed by an elimination and rearrangement as the rate-determining step. The first equilibrium reaction formally represents an insertion reaction (redox) of the four-coordinate molecule into a single bond ($S-H^+$) and reflects a rather common property of d^8 transition metal ion complexes. The postulated transient intermediate of mechanism 3 was not detected. Both the *trans*- and *cis*-diphenyl structures may indeed account for the fact that the *trans* configuration is retained in reaction 1. No isomerization has been observed, in fact, as shown by the spectral analysis of the final reaction product. However, the *cis*-diphenyl configuration for the six-coordinated intermediate has been chosen merely by analogy with similar reactions of other d^8 metal ion complexes. Thus, for the complex $[IrClH_2(CO)(P(C_6H_5)_3)_2]$ obtained by addition of hydrogen to *trans*-$[IrCl(CO)(P(C_6H_5)_3)_2]$, it has been claimed that infrared and nmr evidence favors a *cis*-dihydride *trans*-diphosphine configuration.[4] Furthermore, treating Vaska's compound with hydrogen halides, octahedral complexes of *cis*-hydrogen halide have been obtained, as confirmed by infrared spectra.[5]

Generally speaking, mechanism 3 cannot be *a priori* extended to include the proton cleavage of other platinum–ligand bonds such as Pt–N, Pt–S, etc., since the difference of electronegativity between the two linked atoms may determine which of the two reaction centers is preferred.

On the basis of the available kinetic data, it is difficult to discard the alternative possibility of a direct electrophilic attack of the proton upon the aryl carbon attached to the platinum atom. However, nonkinetic considerations provide some evidence to support mechanism 3. For example, the formation of metal hydrides by the protonation of complexes having π-bonded ligands appears to be a general reaction. The first example of protonation of the central metal atom in a neutral transition metal complex was that of hydridodi-π-cyclopentadienylrhenium(I) which formed the corresponding $[(\pi\text{-}C_5H_5)_2Re^{III}H_2]^+$.[6] By protonation involving a redox process, Sacco and Ugo[7] obtained $[Rh^{III}HCl((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]Cl$ by adding HCl to $[Rh^{I}((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]Cl$. Moreover, Vaska and DiLuzio[8] have described the addition of HCl to $[IrCl(CO)(P(C_6H_5)_3)_2]$. Cramer[9] has recently reported evidence for the addition of HCl to $[Cl_2Rh^{I}(C_2H_4)_2]^-$ yielding an unstable intermediate which is supposed to be the rhodium hydride $[Cl_3Rh^{III}(C_2H_4)_2H]^-$. As far as Pt(II) is concerned, Chatt and Shaw[10] have reported the preparation of the compound $[Pt^{IV}(P(C_2H_5)_3)_2H_2Cl_2]$ by adding HCl to *trans*-$[Pt^{II}(P(C_2H_5)_3)_2(H)Cl]$ in dry ether. The dihydrido complex decomposes by loss of HCl on heating or by reaction with water. We have shown that this compound decomposes rapidly enough in methanol for it to be an acceptable transient intermediate.

On the other hand, the facile oxidation of Pt(II) complexes to Pt(IV) intermediates is confirmed by the low activation energy usually found for the hydrogenolysis of such substrates.[11] Falk and Halpern have suggested that the acid-catalyzed deuterium–hydrogen exchange of *trans*-$[Pt(P(C_2H_5)_3)_2(H)Cl]$ involves the reversible addition of both D^+ and Cl^- to form the platinum(IV) intermediate *trans*-$[Pt(P(C_2H_5)_3)_2(H)(D)Cl_2]$, with the alternative loss of H^+ and Cl^- to give the exchange product.[12] Very recently it has been reported that the reactions of *cis*- and *trans*-$[Pt(P(C_2H_5)_3)_2(Ge(C_6H_5)_3)_2]$ with hydrochloric acid leads to the formation, *inter alia*, of $[(C_6H_5)_3GeH]$ and $[(C_6H_5)_3GeCl]$, suggesting that the HCl cleavage proceeds, at least in part, *via* octahedral intermediates.[13] The possibility of an oxidation–reduction catalysis involving some labile Pt(III) species has been ruled out by the lack of reaction between *trans*-$[Pt(P(C_2H_5)_3)_2(C_6H_5)_2]$ and LiCl in methanol in the presence of added Ce(IV) or Pt(IV).[14] The substitution reaction of *trans*-$[Pt(P(C_2H_5)_3)_2(C_6H_5)_2]$ with LiCl can be made to take place in acetonitrile in the presence of a polarizable electrophilic agent, such as $C(CH_3)_3^+$, which, in comparison to the proton, should be preferred in attacking the unshared d electrons of the polarizable platinum center,[15] provided that steric hindrance is not important. Finally, an Ag^+-promoted substitution reaction of *trans*-$[Pt(P(C_2H_5)_3)_2(C_6H_5)_2]$ in methanol was observed with $AgNO_3$ ($\sim 10^{-4}$ *M*) in the absence of acid. This reaction may be due to an electrophilic attack on the de-

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(4) L. Vaska and R. E. Rhodes, *J. Am. Chem. Soc.*, **87**, 4970 (1965).

(5) L. Vaska, personal communication.

(6) L. Friedman, A. P. Irsa, and G. Wilkinson, *J. Am. Chem. Soc.*, **77**, 3689 (1955); M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3916 (1958).

(7) A. Sacco and R. Ugo, *ibid.*, 3274 (1964).

(8) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961), **84**, 679 (1962); see also J. Chatt, *Proc. Chem. Soc.*, 318 (1962).

(9) R. Cramer, *J. Am. Chem. Soc.*, **87**, 4717 (1965).

(10) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

(11) R. J. Cross and F. Glockling, *ibid.*, 5422 (1965).

(12) J. Halpern and C. D. Falk, "Exchange Reactions," International Atomic Energy Agency, Vienna, 1965, p 191; *J. Am. Chem. Soc.*, **87**, 3523 (1965).

(13) F. Glockling in Proceedings of the Ninth International Conference on Coordination Chemistry, St. Moritz, Sept 5–9, 1966, p 443.

(14) L. R. Rich and H. Taube, *J. Am. Chem. Soc.*, **76**, 2608 (1954).

(15) R. G. Pearson, *ibid.*, **85**, 3533 (1963).

parting phenyl group rather than to an interaction of Ag^+ with the platinum ion, since cleavages of alkyl and/or aryl groups from a metal by transition metal ions of group Ib are fairly general. In particular, as far as Ag^+ is concerned, it is well known that alkyl or aryl silver organometallic compounds can be easily obtained by treating organometallic compounds of group IVb metals with silver salts.[16] We were able to isolate AgC_6H_5 from the reaction of *trans*-$[Pt(P(C_2H_5)_3)_2(C_6H_5)_2]$ with $AgNO_3$ in methanol at −78°. Thus, protonation and the addition of $C(CH_3)_3{}^+$ are supposed to promote the replacement of the aryl group in *trans*-$[Pt(P(C_2H_5)_3)_2(C_6H_5)_2]$ by interacting with the unshared d electrons of the platinum, whereas Ag^+ is believed to attack the leaving group.

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(16) G. E. Coates in "Organo-metallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956.

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Reactivity and Solvation of Platinum(II) Complexes

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Kinetic data for the reactions between *trans*-$[Pt(pip)_2(NO_2)X]$ (pip = piperidine and $X^- = Cl^-, Br^-, N_3^-, NO_2^-$) and Cl^-, NO_2^-, Br^-, N_3^-, I^-, SCN^-, $SeCN^-$, and thiourea as entering groups in methanol, in dimethylformamide, and in dimethyl sulfoxide are reported. The dipolar aprotic solvents exert a strong leveling effect upon the reactivities of these substrates. The results are discussed by assuming that the activation process is accompanied by a change in the free energy of solvation of the coordinated metal ion which is larger in dipolar solvents than in methanol. A comparison of the solvent effects in the substitution reactions of platinum(II) complexes and bimolecular substitutions at aliphatic and aromatic carbons is presented. For the reactions in methanol, the discrimination power of the metal ion (*i.e.*, the changes in rate constants with the entering group) is affected only to a small extent by the nature of X^-, whereas the relative reactivities depend very much upon the leaving group. This is assumed to be indicative that the leaving group hardly affects the extent of bond formation in the transition state.

Introduction

Displacement reactions of four-coordinate planar Pt(II) complexes are believed to involve rather extensive bond formation in the transition state before the old bond is broken, so that the best model proposed to discuss these reactions is the associative mechanism.[1,2] Since the desolvation of the entering group which occurs during the substitution process is strictly related to the extent of bond formation developed in the transition state, the rate constants for displacements on Pt(II) complexes should be markedly affected by the nature of the solvent. In contrast to this, it has been found recently that the entering group reactivity toward the platinum(II) center does not change very much with the solvent.[3] In this connection, it is pertinent to note that rate constants for bimolecular substitutions of saturated aliphatic carbon substrates are usually greatly affected by the nature of the solvent,[4] although in these systems the extent of bond formation in the transition state is generally believed to be small.[5]

It was decided, therefore, to reinvestigate the question of the effect of the solvent upon displacements on platinum(II) complexes, using a set of rate data for reactions in methonol, in dimethylformamide, and in dimethyl sulfoxide of some complexes of the type *trans*-$[Pt(pip)_2(NO_2)X]$ with different leaving groups X^-.

Experimental Section

Materials.—*trans*-$[Pt(pip)_2(NO_2)_2]$ was obtained by the reaction of the dichloro compound with excess $NaNO_2$ for some days in methanol at room temperature. The solvent was evaporated under vacuum and the solid residue was washed with several portions of water and purified by recrystallization from boiling methanol. *trans*-$[Pt(pip)_2(NO_2)Cl]$ was obtained by the reaction of the dichloro compound with $NaNO_2$ in methanol in the presence of *p*-toluenesulfonic acid at 30° for 24 hr.[6] *trans*-$[Pt(pip)_2(NO_2)Cl)]$ was also prepared by treating *trans*-$[Pt(pip)_2(NO_2)_2]$ with an excess of LiCl in methanol at room temperature. In both cases the liquid was evaporated and the solid residue was washed with water and then repeatedly recrystallized from boiling methanol. The other halogen and psuedo-halogen complexes, *trans*-$[Pt(pip)_2(NO_2)Br]$ and *trans*-$[Pt(pip)_2(NO_2)N_3]$, were prepared by simple metathetical reactions of the chloro compound in methanol. *trans*-$[Pt(pip)_2(NO_2)N_3]$ was also prepared by the same procedure from the dinitro compound. The

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[1] C. H. Langford and H. B. Gray in "Ligand Substitution Processes," W. A. Benjamin Publishing Co., New York, N. Y., 1965, Chapter 2 and references therein.

[2] U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591, (1966).

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[6] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **4**, 495 (1965).