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$_6$H$_5$ from the reaction of *trans*-[Pt(P(C$_2$H$_5$)$_3$)$_2$(C$_6$H$_5$)$_2$] 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$_2$H$_5$)$_3$)$_2$(C$_6$H$_5$)$_2$] by interacting with the unshared d electrons of the platinum, whereas Ag$^+$ is believed to attack the leaving group.

Acknowledgment.—The Italian Consiglio Nazionale delle Ricerche (CNR, Rome) is gratefully acknowledged for the financial support of this work.

(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).

(3) U. Belluco, M. Martelli, and A. Orio, *ibid.*, **5**, 582 (1966); **5**, 1370 (1966); see also R. Ettorre, M. Graziani, and P. Rigo, *Gazz. Chim. Ital.*, in press.

(4) A. J. Parker, *Quart Rev.* (London), **16**, 163 (1962).

(5) R. F. Hudson in "Structure and Bonding," Vol. I, Springer-Verlag, Heidelberg, 1966, p 221, and references therein; see also J. F. Bunnett in *Ann. Rev. Phys. Chem.*, 271 (1963).

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

TABLE I[a]

SECOND-ORDER RATE CONSTANTS, 10^3k_2 M^{-1} SEC^{-1}, FOR THE REACTIONS
trans-$[Pt(pip)_2(NO_2)X] + Y^- \rightarrow$ *trans*-$[Pt(pip)_2(NO_2)Y] + X^-$

Entering group	*trans*-$[Pt(pip)_2(NO_2)Cl]$			*trans*-$[Pt(pip)_2(NO_2)_2]$			*trans*-$[Pt(pip)_2(NO_2)N_3]$	*trans*-$[Pt(pip)_2(NO_2)Br]$
	CH_3OH	$HCON(CH_3)_2$	$(CH_3)_2SO$	CH_3OH	$HCON(CH_3)_2$	$(CH_3)_2SO$	CH_3OH	CH_3OH
Solvent[b]	10	200	100	<0.5	25	~6	1	20
Cl^-				0.2[c]	43	8.5		
NO_2^-	5.7[d]		16				0.75	15.5[c]
Br^-	9.4[e]	75	24	1[c]	35	5.5	2.2	
N_3^-	45[c]	250		5.2[c]	78			83
I^-	140		85					
SCN^-	550			25			32	
$SeCN^-$	4200							
Thiourea	2200	~700	275	80	18	8	160	4100

[a] Supplementary material (specific kinetic data used to estimate values in this table) has been deposited as Document No. 9246 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints, or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress. [b] Values of 10^5k_1, sec^{-1}. [c] Data from M. Martelli, A. Orio, and M. Graziani, *Ric. Sci.*, **8**, 361 (1965). [d] U. Belluco, L. Cattalini, and A. Turco, *J. Am. Chem. Soc.*, **86**, 3257 (1964). [e] L. Cattalini, U. Belluco, R. Ettorre, and M. Martelli, *Gazz. Chim. Ital.*, **94**, 356 (1964).

spectra of all of these complexes corresponded exactly with those of the previously described and analyzed samples.

Absolute methanol was dried and purified by distillation after refluxing over $Mg(OCH_3)_2$. Dimethylformamide and dimethyl sulfoxide were fractionated under reduced pressure in a nitrogen atmosphere.[7]

Kinetics.—The reactions were followed spectrophotometrically using a Beckman DK-2A recording spectrophotometer. The changes of optical density in the ultraviolet region with time were recorded. All solutions were kept at 30° prior to mixing. The reactions were carried out in 1-cm quartz cells in the thermostatically controlled cell compartment of the spectrophotometer. The reference cell contained the reagent blank. The solution of the entering reagent was added with a syringe; in the case of fast reactions, less than 10 sec elapsed between mixing and the start of the recording of absorbance *vs.* time. All of the kinetic runs were carried out under psuedo-first-order conditions, using at least a tenfold excess of reagent ligand (within the range 2×10^{-3}–2×10^{-1} M) with respect to the complex ($\sim 5 \times 10^{-4}$ M). In each sequence of kinetic runs, the reagent concentration was changed by at least tenfold. Almost all the reactions proceed to completion and the final spectra were in good agreement with those of the known available products that were prepared independently. Allowance was made for the reactions in which an equilibrium was reached. The pseudo-first-order rate constants, k_{obsd}, were obtained from the slope of the plot of log $(A_\infty - A_t)$ against time. A_t and A_∞ are the optical densities of the reaction mixture at the wavelength of maximum change at t seconds and after 7–10 half-lives, respectively. The values of the observed rate constants were reproducible to better than 5–10%.

Rate data in Table I for the reactions of *trans*-$[Pt(pip)_2(NO_2)_2]$ with thiourea in dimethylformamide and in dimethyl sulfoxide were obtained by conductivity measurements from the linear plots of log $R_t/(R_t - R_\infty)$ *vs.* time. These values are significantly larger than those observed spectrophotometrically, due to the difficulty in obtaining the correct absorbance of the product.

Results and Discussion

In almost all cases the reactions involve two stages which can be resolved readily since the first stage of the reaction is essentially complete before the second stage has developed. Chemical identification and spectrophotometric evaluation confirm that the first stage is the replacement of the ligand in the *trans* position to the nitro group, *i.e.*

$$trans\text{-}[Pt(pip)_2(NO_2)X] + Y^- \longrightarrow trans\text{-}[Pt(pip)_2(NO_2)Y] + X^- \quad (1)$$

In some runs carried out in the presence of good entering groups ($Y^- = I^-$, SCN^-, $SeCN^-$), the final products were the disubstituted derivatives, *trans*-$[Pt(pip)_2Y_2]$. However, it was possible to detect the presence of the intermediate *trans*-$[Pt(pip)_2(NO_2)Y]$ by spectral analysis, since, in the earlier stages of the reaction, a "pseudo" isosbestic point was observed at a position corresponding to the crossing of the spectra of the starting complex and the intermediate; at later stages this disappeared and an isosbestic point appeared at the position consistent with the spectrum of the product. Here, as in all cases, the second stage was much slower than the first.

The kinetics of these substitutions follow the normal square-planar rate law: rate = $(k_1 + k_2[Y^-])$[complex]. In this expression k_1 is the pseudo-first-order rate constant associated with the bimolecular solvolysis of the complex and k_2 is a second-order rate constant for the direct reagent displacement path.[8,9] The values of k_1 and k_2 have been obtained from the intercept and slope of the linear plots of the pseudo-first-order rate constants, k_{obsd} (sec^{-1}), *vs.* the concentration of entering group. The rate data for reaction 1 in methanol, in dimethylformamide, and in dimethyl sulfoxide at 30° are summarized in Table I. In looking at these data, there are two important points to take into account in the discussion, *i.e.*, (i) the leveling effect exerted by the dipolar aprotic solvents upon the reactivities of the complexes under investigation and (ii) the small influence of the leaving group X upon the nucleophilic discrimination of *trans*-$[Pt(pip)_2(NO_2)X]$ complexes in methanol. We will examine these two arguments separately.

(i) **Effect of the Solvent upon the Reactivity Order.**—For comparison purposes, one can recall here some

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[7] A. Weissberger and E. S. Proskauer in "Organic Solvents," Vol. VII, Interscience Publishers, Inc., New York, N. Y., 1955.

[8] H. B. Gray and R. J. Olcott, *Inorg. Chem.*, **1**, 481 (1962).

[9] F. Basolo and R. G. Pearson in "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1967.

features about the effect of the solvent upon the reactivity of carbon aliphatic substrates.

It has been reported recently that for SN2 processes, other factors being equal, the effect of the solvent upon the reactivity of the alkyl halides depends upon the nature of the substrate.[10] This behavior has been rationalized assuming that the specific rate constant in methanol, k_m, is related to that in dimethylformamide, k_d, by the simplified equation[11]

$$k_m = k_d[\gamma^H(Y^-)\gamma^H(RX)/\gamma^H(YRX^-)]$$

The activity coefficient γ^H is a function of the change in free energy of each reactant species (RX and Y^-) and of the activated complex (YRX^-) due to hydrogen-bonding solvation by methanol (dimethylformamide is not a hydrogen-bond donor). In addition to this, an allowance has to be made for ion pairing in the transition state which affects the reaction rate as the hydrogen bonding does.[12] Thus, with small, negatively charged activated complexes in solvents of low dielectric constant there may be considerable ion pairing with positive ions; the ion-pairing activity coefficient of the transition state might be much less than 1.[10]

As shown in Table I, for a given entering group the rate constants of Pt(II) reactions in methanol differ at a maximum of about 2 orders of magnitude from those in dimethylformamide or in dimethyl sulfoxide. A similar behavior has been observed for the displacement of one halide from *trans*-[PtL_2Cl_2] complexes (L = piperidine or $P(C_2H_5)_3$) in protic solvents (methanol, ethanol, and *t*-butyl alcohol)[13,14] and in five structurally different dipolar aprotic solvents (dimethylformamide, dimethyl sulfoxide, acetonitrile, acetone, and nitromethane).[3] For SN2 reactions of alkyl halides the nucleophilic reactivity increases from 4 to 6 orders of magnitude on changing from a hydroxylic solvent type to acetone or dimethylformamide.[4] In attempting to explain the peculiar influence that the solvent exerts upon the reactivities of carbon and platinum(II) reaction centers, solvation of the central atom in the ground and in the transition states also must be taken into account.

For platinum(II) complexes, it is presumed that the solvent occupies coordination sites above and below the plane of the complex, so that a considerable rearrangement of the positions of the solvent molecules around the reacting complex must accompany the substitution process. The π interaction between the central atom and the solvent should be particularly strong with dipolar aprotic solvents containing functional groups with multiple bonds, such as >CO, –CN, etc., owing to their capacity to accept electrons from the metal.[15] Thus, in discussing the effect of the solvent upon the specific rates of bimolecular substitution processes of transition metal ion complexes, the change of free energy of solvation of the central atom which occurs during the activation process must be considered, in addition to the solvation of the entering and of the coordinated ligands.[16] The change of free energy of solvation of the coordinated metal ion on going from the starting complex to the more crowded activated complex should depend on both steric and electronic factors. It must be pointed out that such a free energy variation is larger in dipolar aprotic than in protic solvents, since for a polarizable metal ion a dipolar aprotic is a more active solvating species than a protic solvent.[17] Therefore, it is likely that for the reactions of Pt(II) complexes in dimethylformamide and in dimethyl sulfoxide, the solvation of the metal ion markedly decreases on going from the four-coordinate planar complex to the appropriate transition state. The complex hence "releases" solvent molecules in the activation process and, as a consequence, the rate constant in these solvents is "lowered," becoming comparable to or smaller than that in the less solvating methanol.

The observation that the reactivity of complexes of the type *trans*-[PtL_2Cl_2] does not change markedly in five different dipolar aprotic solvents[3] may indicate that the reacting species is not a substrate–solvent adduct, but it may be also explained more adequately by assuming that the interaction between the solvent and the substrate does not differ sufficiently to differentiate the reactivity of the complexes in these solvents.

For platinum(II) reactions, the loss of free energy of solvation of the metal ion in dipolar aprotic solvents involved in the substitution reaction may be similar to the loss of free energy of solvation of the reagent anions in protic solvents, so that the specific rate constants remain of comparable magnitude in the two classes of solvents. The lack of a large differentiation in the specific rates of platinum(II) complexes on changing the solvent may therefore arise from a balance of opposing factors, including hydrogen-bonding solvation and ion pairing of the reactants and of the transition states[18] and π-interaction from the metal in the ground and in the activated states. In addition, the solvent may affect also the form of the transition state.

Thus, whereas for bimolecular substitutions at carbon centers only the hydrogen-bonding activity co-

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[10] A. J. Parker, *J. Chem. Soc., Sect. A*, 220 (1966); see also B. O. Coniglio, D. E. Giles, W. R. McDonald, and A. J. Parker, *J. Chem. Soc., Sect. B*, 152 (1966), and D. Cook, I. P. Evans, E. C. F. Ko, and A. J. Parker, *ibid.*, 404 (1966).

[11] Notice that methanol and dimethylformamide have similar bulk dielectric constants.

[12] E. D. Hughes, C. K. Ingold, and A. J. Parker, *J. Chem. Soc.*, 4400 (1960).

[13] G. Faraone, U. Belluco, V. Ricevuto, and R. Ettorre, *J. Inorg. Nucl. Chem.*, **28**, 863 (1966).

[14] G. Faraone, L. Cattalini, V. Ricevuto, R. Romeo, and M. Martelli, *Ann. Chim.* (Rome), **55**, 506 (1965).

[15] Solvation of the coordinated platinum(II) by protic solvents (which mainly behave as σ donors) is believed to be weaker than with π acceptor solvents. See R. G. Pearson, H. B. Gray, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 787 (1960). For a general review see R. S. Drago and K. F. Purcell, *Progr. Inorg. Chem.*, **6**, 217 (1965); also see R. S. Drago, V. A. Mode, and J. G. Kay, *Inorg. Chem.*, **5**, 2050 (1966).

[16] Solvation of the activated complex is adequately accounted for by considering the transition state as a whole. In protic solvents, solvation of the entering and leaving groups in the transition state depends upon the electronic density localized on them, whereas in dipolar aprotic solvents, solvation mainly depends on the polarizability of the groups.

[17] Notice that for a given Pt(II) complex, the solvolytic rate constant, k_1, is usually consistently larger in dipolar than in protic solvents. See data in Table I and ref 1.

[18] For a discussion concerning the solvation of the leaving group in the transition state of Pt(II) reactions, see U. Belluco, P. Rigo, M. Graziani, and R. Ettorre, *Inorg. Chem.*, **5**, 1125 (1966).

efficients can be used to relate specific rates in protic and in dipolar aprotic solvents of similar bulk dielectric constants,[10] with transition metal ion centers one must also consider the σ- and particularly the π-bonding activity coefficients of the species participating in the reaction.

We will consider now the point concerning the relative reactivity sequence with respect to platinum(II) in different solvents. It is already known that a reactivity sequence (expressed in terms of an index of nucleophilicity, n^0_{Pt}, associated with the reactivity of each entering group toward the standard *trans*-[Pt(pyridine)$_2$Cl$_2$] in methanol) can be applied to correlate with reasonable approximation the rate data of different Pt(II) complexes in protic solvents.[19] One must expect, however, that the same reactivity order need not hold on changing from protic to the more solvating dipolar aprotic solvents. In fact, the free energy of solvation of the metal ion involved in the substitution process will be dependent upon the nature of the entering and coordinated ligands as well as upon the nature of the solvent. As a consequence, the entering group reactivity order also may be reversed. This hypothesis may therefore account for the important observation from Table I that in the reaction of *trans*-[Pt(pip)$_2$(NO$_2$)$_2$][20] with thiourea (which is generally a very effective reagent toward many platinum(II) complexes in hydroxylic solvents) this reagent loses a great deal of its extra reactivity in dipolar aprotic solvents.

(ii) **Effect of the Leaving Group upon the Nucleophilic Discrimination.**—As far as rate data in methanol are concerned, it can be seen from Table I that for a given entering group the ease of replacement of X^- in *trans*-[Pt(pip)$_2$(NO$_2$)X] depends upon the nature of the leaving group, the order being $Cl^- \sim Br^- > N_3^- > NO_2^-$. The same order was found for [Pt(dien)X]$^+$ complexes (dien = diethylenetriamine). This is consistent with an associative mechanism involving an unstable intermediate of increased coordination number.[1,2] The effect of X^- upon the discrimination power of platinum is however very small, suggesting that, whatever are the finer details of the mechanism, the nature of the leaving group should have only a small effect upon the extent of bond formation in the appropriate transition state.[21] In principle, a small influence of the leaving group upon the degree of bond making has to be expected if the bond formation can proceed by making use of an orbital that is not occupied by the leaving group, *i.e.*, when the leaving and the entering groups do not compete for the same orbital (or at least *not* to the same extent) in the activated complex.[22] All these observations are consistent with the hypothesis that in displacements on Pt(II) complexes there is an increased p character in the transition state bonding since, in terms of valence bond theory, the 6p$_z$ orbital becomes involved in bonding.[23] This assumption cannot be generally extended, *a priori*, to all of the reactions of the diamagnetic d^8 complexes. Generally speaking, there is a smaller p character in the bonding as the oxidation state increases on going from Pt(II) to the better electron acceptor Au(III). Thus, the behavior of Pt(II) complexes differs to some extent from that of the complexes of Au(III). As an example, in the replacement of the heterocyclic nitrogen base (am) in complexes of the type [AuCl$_3$(am)], both the discrimination ability of the central atom and the relative reactivities of the entering reagents are influenced by the nature of the leaving group. This has been attributed to the different way in which the entering group can interact with the metal ion in the transition state, in agreement with the observation that in the higher oxidation states of the d^8 isoelectronic series the electrostatic contributions to the bonding become more important.[24,25]

In conclusion, assuming for the activated complex of Pt(II) reactions a trigonal-bipyramidal form with *trans* ligand, with leaving and entering groups in the trigonal plane, the bonds between these ligands and the central atom cannot be equivalent. The *trans* ligand, in fact, greatly affects the Pt–X and Pt–Y bonds (*trans effect*),[23] whereas the leaving group does not markedly affect the extent of bond formation. In other words, the reactivity of Pt(II) substrates arises mainly from a combined coupling of the *trans* group (strongly bonded *via* σ and/or π to the metal) with the entering and leaving groups (which may be both loosened to different extents) in the unsymmetrical trigonal-bipyramidal transition state.

It must be realized that this work deals with ligands leaving under the *trans* effect of the nitro group. A similar relationship has been found[2] for ligands leaving

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[19] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965); U. Belluco in "Coordination Chemistry Reviews," Elsevier Publishing Co., New York, N. Y., 1966, p 111.

[20] No evidence is available concerning the type of linkage between Pt(II) and the nitro group. The ^{19}F nmr spectra of both *m*- and *p*-*trans*-[Pt(P(C$_2$H$_5$)$_3$)$_2$(FC$_6$H$_4$)(NO$_2$)] in solution seem to indicate the existence of the equilibrium $PtNO_2 \rightleftarrows PtONO$, whereas the sole PtNO$_2$ form exists in the crystalline complex, as shown by infrared spectra: G. W. Parshall, personal communication. A similar behavior has been reported for the *trans*-[Pt(P(C$_2$H$_5$)$_3$)$_2$(NO$_2$)H] complex: J. Powell and B. L. Shaw, *J. Chem. Soc.*, 3879 (1965).

[21] The nucleophilic discrimination (s) can be approximately evaluated by making use of the linear free energy relationship: $\log k_2 = s n^0_{\mathrm{Pt}} + \log k_2^0$ (k_2^0 is the solvolytic rate constant; see ref 19). In relating the discrimination power of Pt(II) (*i.e.*, the dependence of the rate constant upon the nature of the entering group) to the degree of bond making in the transition state, it has been assumed that the difference in free energy of activation arising from solvation and bond breaking effects between each of the complexes considered and the standard *trans*-[Pt(py)$_2$Cl$_2$] (on which the n^0_{Pt} values have been estimated) should mainly affect the relative reactivities rather than discrimination. The use of the n^0_{Pt} values allows us to ignore, for any one complex, the dependence of bond formation upon the nature of the entering group. For a detailed discussion on the relationship between discrimination (or selectivity) and the degree of bond making in the transition state, see ref 5.

[22] Examples of competition for the same orbital are found in bimolecular reactions of saturated aliphatic compounds, where there is a single transition state that requires a change from sp^3 to sp^{2}p hybridization. See C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p 87.

[23] For a review and reference see: F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 388 (1962); H. B. Gray, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 102. See also ref 1.

[24] R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961); R. S. Nyholm and M. L. Tobe, *Experientia, Suppl.*, **9**, 112 (1965).

[25] L. Cattalini and M. L. Tobe, *Inorg. Chem.*, **5**, 1145 (1966).

under the *trans* effect of the amine group in [Pt(dien)X]$^+$, and it would be desirable to see to what extent this behavior is changed when a strong *trans*-effect ligand is present.

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Crystal Structure of *cis*-Pt[P(CH$_3$)$_3$]$_2$Cl$_2$

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The crystal structure of *cis*-Pt[P(CH$_3$)$_3$]$_2$Cl$_2$ has been determined from counter data by three-dimensional single-crystal X-ray diffraction techniques. Unit cell constants are: $a = 16.67 \pm 0.02$ A, $b = 11.93 \pm 0.02$ A, $c = 6.33 \pm 0.01$ A, $\beta = 91° 25' \pm 15'$. The space group is B2$_1$. The structure is made up of discrete molecular units with ordinary van der Waals separations. The asymmetric unit is one molecule with Pt–P distances of 2.256 and 2.239 A (both ±0.008 A) and Pt–Cl distances of 2.364 and 2.388 A (both ±0.008 A). The molecule is twisted toward a tetrahedral configuration with nearest neighbors of platinum displaced about 0.1 A out of the best least-squares plane defined by the platinum and its four nearest neighbors. These bond lengths are to be compared with Pt–P distances of 2.298 ± 0.018 and 2.315 ± 0.004 A and Pt–X distances of 2.294 ± 0.009 and 2.428 ± 0.002 A observed in *trans*-Pt[P(C$_2$H$_5$)$_3$]$_2$Cl$_2$ and *trans*-Pt[P(C$_2$H$_5$)$_3$]$_2$Br$_2$, respectively.

Introduction

We have completed crystal structure determinations of *trans*-Pt[P(C$_2$H$_5$)$_3$]$_2$X$_2$, X = Cl and Br, and found substantially shorter Pt–P bond lengths than would be predicted from a sum of covalent radii.[3,4] However, the Pt–X bonds were found to be normal single bonds, equal to the sum of the single-bond covalent radii. Hence, Pt–X (X = Cl, Br) and Pt–P distances have been carefully determined in the X–Pt–X and P–Pt–P atomic arrangements. To substantiate the thermodynamic results of Chatt and Wilkens[5] in terms of bond lengths, we undertook to solve the crystal structure of *cis*-Pt[P(CH$_3$)$_3$]$_2$Cl$_2$.

Experimental Section

Crystals of *cis*-Pt[P(C$_2$H$_5$)$_3$]$_2$Cl$_2$ and *cis*-Pt[P(CH$_3$)$_3$]$_2$Cl$_2$ were kindly provided to us by Professor J. Chatt. *cis*-Pt[P(C$_2$H$_5$)$_3$]$_2$Cl$_2$ was found to have a large triclinic cell, and this structure determination was abandoned. Crystals of *cis*-Pt[P(CH$_3$)$_3$]$_2$Cl$_2$ were found to be monoclinic with unit cell constants from calibrated precession photographs: $a = 16.67 \pm 0.02$ A, $b = 11.93 \pm 0.02$ A, $c = 6.33 \pm 0.01$ A, and $\beta = 91° 25' \pm 15'$ (Mo Kα, λ 0.7107 A). The systematic extinctions observed were: for hkl, $h + l = 2n + 1$; for $0k0$, $k = 2n + 1$. The possible space groups with these extinctions are B2$_1$ or B2$_1$/m. With a reorientation of the a and c axes, these would correspond to the more common P2$_1$ or P2$_1$/m.[6] The structure analysis established the correct space group as B2$_1$ or P2$_1$ (*vide infra*). We retained the use of the B-centered cell for the structure analysis because the crystals were most easily aligned about the c axis of the B-centered cell. All our intensity data were collected with this axis vertical on the diffractometer, and this orientation facilitated comparison with our previous photographic structure determination.[7] Further, the β angle for the B-centered cell is approximately 90°. With four molecular entities in the B-centered cell, the calculated density was found to be 2.16 g cm^{-3} compared with the observed of 2.18 g cm^{-3} obtained by flotation in carbon tetrachloride–bromoform mixtures. (This corresponds to two molecules in the primitive cell.)

A single crystal, 0.20 × 0.15 × 0.15 mm, mounted on a GE single-crystal orienter with a Picker diffractometer using Zr-filtered Mo Kα radiation was used to measure 2433 independent hkl intensity data by a scanning technique at room temperature. Background was estimated by stationary counting at $\pm 0.8° \ 2\theta$ from the peak maxima for 10 sec. The peak was then scanned for 40 sec with a 2θ scan. The integrated intensity was obtained by subtracting the background scaled to 20 sec from the 2θ scan. The value of the linear absorption coefficient (μ) for Mo Kα radiation is 132 cm^{-1}. No corrections were made for absorption and, consequently, no detailed physical interpretation should be made of the anisotropic temperature factors. Recently Srivastava and Lingafelter[8] have shown that absorption effects with $\mu = 191$ cm^{-1} do not appreciably affect atomic coordinates; hence, we feel our estimates of error in atomic coordinates are realistic. Corrections were made for anomalous dispersion (see below).

Structure Determination

In space group B2$_1$ with four molecules per unit cell, all atoms would be in the general positions: $(0, 0, 0;\ ^1/_2, 0, ^1/_2) + (x, y, z;\ \bar{x}, ^1/_2 + y, \bar{z})$. In space group B2$_1$/m: (a) the Pt, 2P, 2Cl, and one of the three carbon atoms on each phosphorus could lie in the mirror plane at $y = ^1/_4$: $(0, 0, 0;\ ^1/_2, 0, ^1/_2) + (x, ^1/_4, z;\ \bar{x}, ^3/_4, \bar{z})$ and the remaining carbon atoms in the general positions $(0, 0, 0;\ ^1/_2, 0, ^1/_2) + (x, y, z;\ \bar{x}, \bar{y}, \bar{z};\ x, ^1/_2 - y, z;\ \bar{x}, ^1/_2 + y, \bar{z})$; (b) the Pt could lie in the mirror

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