the metal ion. The order of donor strength which was proposed toward the organothallium and organolead compounds is observed in these studies of the similar acid trimethyltin chloride, *i.e.*, HMPA > DMA = DMSO > $(CH_3)_2CO$ > CH_3CN. It should be very interesting if it were shown that a quantitative relationship exists between the enthalpy of formation of these adducts and the spin–spin coupling constant. It is possible that coupling constant changes may be a very valuable tool for the evaluation of the enthalpy of adduct formation of a large number of heavy metal adducts.

$(CH_3)_3SnI \cdot DMA$. Trimethyltin iodide is a better acid toward DMA than is trimethyltin chloride. Since $J_{Sn^{119}-CH_3}$ is approximately the same for both of these adducts, it is reasonable that the rehybridization energy is similar in both cases. The larger observed enthalpy of formation of the iodide adduct may arise from differences in the magnitude of the ΔH_{Sn-X} term in eq 4. This may be due to a reduced sensitivity of the tin–halogen bond energy to changes in hybridization of the tin as the size of the halogen increases or to the fact that the Sn–I bond is originally much weaker than the Sn–Cl bond.

Acknowledgment. The authors acknowledge the generous support of the National Science Foundation through Grant GP −5498.

Nucleophilic Reactivity in Substitution Reactions of Square-Planar Metal Complexes. I. Effect of the Total Charge of the Substrate in Platinum(II) Complexes

L. Cattalini, A. Orio, and M. Nicolini

Contribution from Centro Chimica Composti di Coordinazione C.N.R., Istituto di Chimica Generale e Inorganica, Universitá di Padova, Padua, Italy.

Received August 1, 1966

Abstract: The behavior of a series of platinum(II) complexes in their displacement reactions with a range of nucleophiles is discussed. The relative index of nucleophilicity, n_{Pt}, defined for the standard substrate *trans*-[Pt(py)$_2$Cl$_2$], can also apply to the other compounds examined, except for the reactions with NO_2^-, $SeCN^-$, and thiourea. These reagents have decided biphilic behavior and their relative reactivity is markedly affected by the charge and nature of the substrate.

The rates of bimolecular nucleophilic substitution reactions are determined by several factors, relative to the nature of the substrate and reagent and to the conditions (solvent, temperature, etc.).[1] By measuring, under the same experimental conditions, the rate of displacement of the ligand X from a substrate M–X by various reagents Y, a quantitative sequence of relative reactivity can be obtained. In view of the number of variables that can affect the nucleophilicity it is desirable to limit the range of nucleophiles studied in order to eliminate certain structural factors such as steric hindrance and α effects. Following Pearson's classification of soft and hard acids and bases,[2] it appears that, in substitution reactions at soft reaction centers, the micropolarizability or "softness" of Y is the most important factor in determining nucleophilicity, whereas the basicity of Y plays only a minor role. Unfortunately, from a practical point of view, "softness" is not a property that can be quantitatively measured by a direct physical experiment. In fact, the polarizability of Y in a strong directional field (such as encountered in a transition state) is different, in principle, from its polarizability in a homogeneous weak field, which is the quantity that is usually determined experimentally. In kinetic studies, the word "softness" can be interpreted as the factor, or combination of factors, that is responsible for departures from a simple relationship between the nucleophilicity and the basicity of the entering reagent. In addition, when the substrate M–X is a transition metal complex, one must also consider the possible influence of π interactions between the substrate and the entering group in either the ground or transition states upon the nucleophilicity.

Platinum(II) square-planar complexes are typical soft reaction centers in which it is now generally accepted that nucleophilic displacement reactions occur with an associative mechanism.[3] An extensive study of the kinetic behavior of substrates of the type *trans*-[PtL$_2$Cl$_2$] have been recently made[4] and, by selecting as a standard the complex with L = pyridine, an index of nucleophilicity, "n_{Pt}," has been defined for each nucleophile Y. The reactions of these reagents toward the other platinum(II) complexes studied, followed the equation

$$\log k_Y = s(n_{Pt}) + \log k_S \qquad (1)$$

---

(1) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

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

(3) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 19–54.

(4) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).

where k_Y is the second-order rate constant for the nucleophile Y and s and $\log k_S$ are two parameters of the substrate, called "nucleophilic discrimination factor" and "intrinsic reactivity," respectively. Any attempt to correlate the values of k_Y to thermodynamic properties of Y was without success.

In the course of studies of the reactivity of four-coordinate planar complexes with a central atom other than Pt(II), we have tried to examine the extent to which the nucleophilicity sequence expressed in terms of n_{Pt} can apply. However, this approach requires that we, first of all, examine how far it is possible to generalize the use of the n_{Pt} scale in the reactions of Pt(II), especially with reagents that can interact in a π fashion with the metal, since the ability to participate in π interactions will be very dependent on the oxidation state of the metal and its effective nuclear charge.

We report here the data for nucleophilic displacement reactions in the complex $[PtCl_4]^{2-}$ where the effect of basicity is thought to be even less than in the neutral complexes[1] (there are also some data in the literature for reactions with amines)[5] and where back-donation of negative charge by way of π interactions will probably be most important.[6]

Consequently, biphilic reagents might be expected to show deviations from the n_{Pt} scale through anomalous high reactivity (a similar explanation has been suggested by Gray for the behavior of NO_2^- in comparison with that of Cl^-).[7,8] On the other hand, cationic complexes might be expected to produce deviations in the opposite direction by reducing the extent of π interactions, and consequently we shall also discuss some data for such complexes, taken from the literature and augmented by new studies with a wider range of nucleophiles.

Experimental Section

Materials. The platinum(II) complexes used in this investigation are all known compounds and have been prepared by the methods reported in the literature. Each one was characterized by analysis and by comparison of the ultraviolet spectra with published values. References to the method of preparation are as follows: *trans*-$[Pt(PEt_3)_2Cl_2]$,[9] $[PtCl_4]^{2-}$,[10] $[Pt(dien)Br]^+$.[11] Anhydrous methanol obtained by distillation over $(CH_3O)_2Mg$ and doubly distilled water were used as solvents. Other materials were reagent grade.

Kinetics. The reactions were followed by measuring the changes in optical density in the ultraviolet region of the spectrum over a period of time. Freshly prepared solutions of $K_2[PtCl_4]$ were used for each kinetic run in order to avoid the solvolytic production of $[PtCl_3(H_2O)]^-$ in appreciable amount before the reagents were mixed. This solvolysis[12] has a half-life of 5 hr at 25°. All the reactions were carried out in the presence of a sufficient amount of the reagent Y to cause first-order kinetics, and the first-order rate constant, k_{obsd}, was calculated from the slope of the plot of log $(D_\infty - D_t)$ against time. The specific rate constants k_1 and k_2 are obtained from the intercept and the slope of the plot of k_{obsd} against the concentration of Y. In fact, all the reactions follow the two-term rate law that is now generally recognized[3] for substitutions on Pt(II) complexes

$$\text{rate} = (k_1 + k_2[Y])[\text{complex}]$$

and the observed rate constant, k_{obsd}, is related to k_1 and k_2 by the equation

$$k_{obsd} = k_1 + k_2[Y]$$

The values obtained are reported in Table I. The reactions of the ionic substrates, $[PtCl_4]^{2-}$ and $[Pt(dien)Br]^+$, in water at 25° were carried out at constant ionic strength in the presence of $LiClO_4$, and all the data reported in Table III are corrected to zero ionic strength, according to the equation

$$\log k^0 = \log k - (1.02 z_A z_B \sqrt{\mu})/(1 + \sqrt{\mu})$$

The validity of using this relationship was confirmed by making some preliminary experiments at other ionic strengths.

Results and Discussion

The replacement of chloride in $[PtCl_4]^{2-}$ is never a simple process since a number of stages of reaction are involved. The *trans* effects of the nucleophiles Y used are always greater than the *trans* effects of chloride, and therefore the slow replacement of the first chloride is followed by a rapid second step

$$\underset{A}{PtCl_4} + Y \xrightarrow{k_a} \underset{B}{PtCl_3Y} + Cl^-$$

$$\underset{B}{PtCl_3Y} + Y \xrightarrow{\text{fast}} \underset{C}{trans\text{-}PtCl_2Y_2}$$

(The charges of the complexes are omitted because Y can be uncharged, uninegative, or dinegative). The change from $[PtCl_4]^{2-}$ to *trans*-$[PtCl_2Y_2]$ corresponds to a single detectable step in the change of the spectrum. The intermediate species *trans*-$[PtCl_2Y_2]$ can also react with Y

$$\underset{C}{trans\text{-}[PtCl_2Y_2]} + Y \xrightarrow{k_c} \underset{D}{PtClY_3} + Cl^-$$

$$\underset{D}{[PtClY_3]} + Y \xrightarrow{\text{fast}} \underset{E}{PtY_4} + Cl^-$$

The differences between k_c and k_a are determined by the *cis* effect of Y and by the total charge of the intermediate complex. If the two constants differ considerably from each other (*i.e.*, $k_a \ll k_c$ or $k_a \gg k_c$), only one reaction step will be observed in the spectrophotometric measurements. However, we usually find two identifiable steps, suggesting that k_a and k_c are not greatly different, and the second is fortunately slower than the first. The rate constants reported and discussed here are always those corresponding to the replacement of the first chloride, and they were obtained either by doing calculations at wavelengths where an isosbestic point appears at the end of the first stage or by applying the treatment for consecutive reactions. The over-all process can be written as

$$A \xrightarrow{k_a} B \xrightarrow{\text{fast}} C \xrightarrow{k_c} D \xrightarrow{\text{fast}} E$$

---

(5) A. A. Grinberg and D. B. Smolenskaya, *Russ. J. Inorg. Chem.*, **6**, 46 (1961).

(6) F. Basolo, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 88.

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

(8) H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962).

(9) K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **229**, 225 (1936).

(10) R. N. Keller, *Inorg. Syn.*, **2**, 247 (1946).

(11) F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960).

(12) L. F. Grantham, T. S. Elleman, and D. S. Martin, Jr., *ibid.*, **77**, 2965 (1955).

Table I. First-Order Rate Constants for Some Pt(II) Complexes (25°)

Complex concn, *M*	Solvent	Reagent concn, *M*	Added substance concn, *M*	k_{obsd}, sec^{-1}
$[Pt(dien)Br]^+$				
0.003	H_2O	SO_3^{2-} 0.1	...	4.35×10^{-2}
		0.05	$LiClO_4$ 0.05	2.3×10^{-2}
		0.025	0.075	1.13×10^{-2}
		0.01	0.09	3.9×10^{-3}
		NO_2^- 0.1	NaOH 0.01	2.76×10^{-4}
		0.05	0.005, $LiClO_4$ 0.05	2.06×10^{-4}
		0.025	0.0025 0.075	1.70×10^{-4}
0.0005		$SeCN^-$ 0.01	$LiClO_4$ 0.09	2.4×10^{-2}
		0.005	0.095	1.3×10^{-2}
		$S_2O_3^{2-}$ 0.005	...	Fast
trans-$[Pt(PEt_3)_2Cl_2]$ (30°)				
0.00005	MeOH	Thiourea 0.0015	...	6.70×10^{-2}
		0.0010	...	4.15×10^{-2}
		0.0005	...	2.30×10^{-2}
$[PtCl_4]^{2-}$				
0.002	H_2O	NO_2^- 0.356	NaOH 0.036	1.34×10^{-3}
		0.1	0.01	1.26×10^{-4}
		0.05	0.005, $LiClO_4$ 0.05	8.3×10^{-5}
0.001		Br^- 0.1	...	1.8×10^{-4}
		0.05	$LiClO_4$ 0.05	1.38×10^{-4}
		0.025	0.075	8.4×10^{-5}
0.00025		I^- 0.1	...	7.3×10^{-4}
		0.075	$LiClO_4$ 0.025	5.0×10^{-4}
		0.025	0.075	2.3×10^{-4}
		0.0185	0.0815	1.5×10^{-4}
0.001		SCN^- 0.1	...	2.4×10^{-4}
		0.05	$LiClO_4$ 0.05	1.33×10^{-4}
		0.025	0.075	8.26×10^{-5}
0.0002		Thiourea 0.1	...	2.95×10^{-2}
		0.05	...	1.54×10^{-2}
		0.025	...	6.9×10^{-3}
		0.01	...	2.8×10^{-3}
0.0001		$SeCN^-$ 0.1	...	5.7×10^{-2}
		0.05	$LiClO_4$ 0.05	2.54×10^{-2}
		0.025	0.075	1.12×10^{-2}
0.0005		$S_2O_3^{2-}$ 0.1	...	2.2×10^{-3}
		0.075	$LiClO_4$ 0.025	1.64×10^{-3}
		0.05	0.05	1.08×10^{-3}

with k_a greater than k_c. The concentration of A at longer time is negligible and k_c can be calculated. Extrapolation to time 0 gives a value of optical density approximating that of the complex C, provided k_a is at least 10 times greater than k_c. By applying this value to measurements done at shorter time, when the concentrations of D and E are negligible, k_a can be obtained. In our cases k_a differs considerably from k_c so that the values calculated for k_a in different kinetic runs usually agree to better than ±5%. Deviations of such an order of magnitude cannot significantly affect the following arguments where the data are discussed in terms of log *k*.

In the reactions of $[PtCl_4]^{2-}$ with bromide, the two observable stages had fairly similar rates and it was not possible, either by inspection or extrapolation, to determine the appropriate value for *D* for the first stage. The problem was resolved by preparing the intermediate *trans*-$[PtCl_2Br_2]^{2-}$ in solution by adding 1 equiv of silver nitrate to $[PtCl_4]^{2-}$ and then, after the reaction was completed, adding 2 equiv of bromide

$$PtCl_4^{2-} + Ag^+ + H_2O \longrightarrow PtCl_3(H_2O)^- + AgCl$$

$$PtCl_3(H_2O)^- + 2Br^- \longrightarrow trans\text{-}PtCl_2Br_2^{2-} + Cl^- + H_2O$$

The absorption spectrum of the filtered solution was measured, and the appropriate extinction coefficients were used in the calculation of the rate constant. The second observable step led to departure from linearity in the plot of log ($D_\infty - D_t$) against time but did not interfere significantly during the first 40% of reaction, and the slope of this linear portion was used to determine the rate constant of the first stage.

The reaction of *trans*-$[Pt(PEt_3)_2Cl_2]$ with thiourea does not present any difficulty since the replacement of the second chloride is fast, because of the high *trans* effect of thiourea, and only one reaction step is detectable. The calculations of the rate constant for the reactions of $[Pt(dien)Br]^+$ are simple because only the bromine atom is replaceable.

Reactions with the basic entering group NO_2^- were studied in basic solutions (Table I) in order to prevent the formation of the conjugate acid HNO_2 that might be responsible for electrophilic catalysis.[13] Hydroxide has been shown[7] to divert the k_1 (solvolytic) path to form the stable hydroxo product but to have no effect upon the values of k_1 and k_2. Provided the solvolytic path made only a small contribution to the over-all change or experimental values of D_∞ which were used on every occasion, the presence of hydroxide should have no effect on the determination of k_2.

---

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

Table II. Specific Rate Constants[a] for Some Platinum(II) Complexes

	Y											
	H_2O[c]	Cl^-	py	NO_2^-	N_3^-	Br^-	I^-	SCN^-	SO_3^{2-}	$SeCN^-$	Thiourea	$S_2O_3^{2-}$
	n_{Pt}[b]											
Complex	0	1.65	1.74	1.81	2.19	2.79	4.03	4.26	4.40	5.71	5.78	5.95
$[Pt(dien)Cl]^+$[d] H_2O, 30°	1.11×10^{-4}	...	...	...	5.2	7	170	270	...	2500	580	...
$[Pt(dien)Br]^+$ H_2O, 25°	1.32×10^{-4}[e]	0.88[e]	3.3[e]	1.45	7.7[e]	...	230[e]	430[e]	430	2500	830[e]	Fast
trans-$[Pt(PEt_3)_2Cl_2]$ MeOH, 30°	...	0.029[b]	...	0.027[b]	0.2[b]	0.93[b]	236[b]	371[b]	...	6950[b]	47,100	...
trans-$[Pt(PEt_3)(C_5H_{11}N)Cl_2]$[f] MeOH, 30°	...	0.07	...	...	...	2.15	208	319	...	2200	12,600	...
$[PtCl_4]^{2-}$ H_2O, 25°	4×10^{-5}[g]	...	...	0.9	...	1.78	6.5	2.1	...	530	290	22

[a] Values of $10^3 \times k_Y$ in M^{-1} sec^{-1}. [b] Data from ref 4. [c] Values of k_1 in sec^{-1}. [d] Data from ref 15. [e] Data from ref 8. [f] Data from ref 16. [g] Data from ref 12.

Table III. Observed and Calculated Values of Log k_Y and Deviations, Δ[a]

Complex	H_2O	Cl^-	py	NO_2^-	N_3^-	Br^-	I^-	SCN^-	SO_3^{2-}	$SeCN^-$	Th	$S_2O_3^{2-}$
$[Pt(dien)Cl]^+$	−3.955				−2.039	−1.91	−0.525	−0.324		+0.643	−0.237	
$s = 0.86$	(−4.035)				(−2.147)	(−1.63)	(−0.561)	(−0.363)		(+0.887)	(+0.947)	
$\log k_S = -4.05$	*+0.08*				*+0.108*	*−0.28*	*+0.036*	*+0.039*		*−0.244*	*−1.184*	
$[Pt(dien)Br]^+$	−3.88	−2.616	−2.482	−2.694	−2.100		−0.624	−0.352	+0.138	+0.643	−0.081	
$s = 0.87$	(−3.97)	(−2.535)	(−2.456)	(−2.395)	(−2.065)		(−0.464)	(−0.264)	(−0.142)	(+0.997)	(+1.058)	
$\log k_S = -3.97$	*+0.09*	*−0.081*	*−0.026*	*−0.299*	*−0.035*		*−0.16*	*−0.088*	*+0.28*	*−0.354*	*−1.139*	
trans-$[Pt(PEt_3)_2Cl_2]$		−4.538		−4.569	−3.699	−3.032	−0.627	−0.431		+0.842	+1.673	
$s = 1.62$		(−4.626)		(−4.367)	(−3.751)	(−2.779)	(−0.770)	(−0.398)		(+1.951)	(+2.065)	
$\log k_S = -7.3$-		*+0.088*		*−0.202*	*+0.052*	*−0.253*	*+0.143*	*−0.033*		*−1.109*	*−0.392*	
trans-$[Pt(PEt_3)$-$(C_5H_{11}N)Cl_2]$		−4.155				−2.668	−0.682	−0.483		+0.342	+1.100	
$s = 1.44$		(−4.207)				(−2.563)	(−0.775)	(−0.443)		(+1.648)	(+1.749)	
$\log k_S = -6.59$		*+0.052*				*−0.105*	*+0.093*	*−0.04*		*−1.306*	*−0.649*	
$[PtCl_4]^{2-}$	−4.398			−3.536		−3.440	−2.671	−3.068		−0.766	−0.538	−2.638
$s = 0.312$	(−4.305)			(−3.740)		(−3.435)	(−3.048)	(−2.976)		(−2.523)	(−2.814)	(−2.449)
$\log k_S = -4.3$	*−0.093*			*+0.204*		*−0.005*	*+0.377*	*−0.092*		*+1.757*	*+2.276*	*−0.189*

[a] Calculated values are shown in parentheses and deviations, Δ, are italicized.

The data that are to be considered in the discussion are collected in Table II. Apart from certain notable exceptions[14] the solvent seems to play a minor role in determining the sequence of nucleophilic reactivity of reagents toward Pt(II) complexes[17] so that we can compare kinetic data obtained in such similar solvents as methanol and water. The n_{Pt} scale has been obtained in methanol, but in the same work[4] it was pointed out that the relationship shown in eq 1 can also apply to reactions in water. In addition, the change in temperature from 25 to 30° does not significantly alter the sequence of reactivity, as can be seen from the data obtained with the complex $[Pt(dien)Br]^+$ at 25 and 30°.[8,15] Moreover it has been observed[15] that changing the leaving group from Cl to Br has practically no influence upon the intrinsic reactivity and nucleophilic discrimination factor (in fact log k_S and s are equal) for the complexes $[Pt(dien)Br]^+$ and $[Pt(dien)Cl]^+$.

When log k_Y is plotted against n_{Pt} for each complex, a large number of points lie on a straight line, and from these points the parameters s and log k_S were calculated for each complex using the method of least squares.[18] In Table III the observed and calculated values of log k_Y have been reported, together with the deviations

$$\Delta = \log k_Y(\text{obsd}) - \log k_Y(\text{calcd})$$

Small values of Δ can easily be due to experimental error or to unknown factors exercising a small influence on nucleophilicity. Therefore the following discussion is limited to the cases where significant values of Δ are observed for various substrates.

The nucleophiles H_2O, py, Cl^-, Br^-, N_3^-, I^-, SCN^-, SO_3^{2-}, $S_2O_3^{2-}$ follow the n_{Pt} scale, irrespective of the charge and nature of the complex, and therefore π interactions, if present, do not have a significant influence on the reactivity. The second-order rate constants observed for the complex $[Pt(dien)(H_2O)]^{2+}$ when the coordinated water is replaced by halides[7] also agree closely with the n_{Pt} scale. The value of Δ for pyridine in the complex $[Pt(dien)Br]^+$ is negligible, and it might be an indication that even in this cationic complex the basicity of the entering group is not strongly related to the reactivity. Back-donation of charge to azide has been observed in neutral Au(III) complexes[19] but it does not seems to be operating to any considerable extent in the Pt(II) substrates.

---

(14) U. Belluco, private communication.

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

(16) M. Martelli and A. Orio, *Ric. Sci.*, **35**, 1089 (1965).

(17) U. Belluco, M. Martelli, and A. Orio, *Inorg. Chem.*, **5**, 582 (1966).

(18) More recently eq 1 has been modified in order to have the values of n_{Pt} dimensionless. However, it corresponds to adding a constant and does not affect the arguments reported here (U. Belluco, private communication).

(19) L. Cattalini and M. L. Tobe, *Inorg. Chem.*, **5**, 1145 (1966).

On the other hand, thiourea and $SeCN^-$, and NO_2^- to a lesser extent, show significant values of Δ. The quantity which, by definition, is zero for the standard complex *trans*-$[Pt(py)_2Cl_2]$ becomes negative when cationic complexes are used as substrates and also in the reactions of the neutral complexes containing phosphine ligands, in which π interactions can delocalize charge from the reaction center. In the reactions on $[PtCl_4]^{2-}$ the deviations are positive so that the over-all behavior strongly suggests that back-donation of charge from the metal to those entering groups can decrease the activation free energy.

It should be pointed out that, whereas the presence of a significant value of Δ and its dependence upon the electronic density at the reaction center is good evidence for biphilic behavior, one cannot compare the values of Δ for different reagents arguing, for example, that, because of the greater value of Δ, thiourea has a greater biphilic ability than NO_2^-. In fact, the actual deviations must also be related to the degree of formation of the new bond in the transition state which may be different for the various entering reagents even though all the reactions are bimolecular second-order processes.

From the above argument one can conclude that, as far as reactions of Pt(II) substrates are concerned, the potential entering ligands can be divided into four groups according to their behavior. In the first, the nucleophiles exibit a sequence of relative reactivity that is practically independent of the nature of the Pt(II) substrate. The basicity plays a minor role, negligible in most cases, so that in this group the values of n_{Pt} can be mainly regarded as an index of softness which is probably related to high micropolarizability, which "...results from the existence of low-lying excited states, which, when mixed with the ground state, produce polarity."[1]

In the second group one can consider reagents in which the empty, low-lying orbitals not only contribute to the softness but also have the right symmetry and energy to contribute to the stabilization of the transition state by a direct overlap with the filled d orbitals of the metal. The position of such reagents (NO_2^-, thiourea, $SeCN^-$) in the sequence of relative reactivity appears to be influenced by the charge and nature of the Pt(II) substrate. The requirement that the empty orbitals used for back-donation must have the right energy to give a good overlap may explain why $SeCN^-$ has biphilic properties whereas N_3^- and SCN^-, with similar outer electronic configurations, do not. Although adequate kinetic data are not yet available, it seems reasonable to predict that reagents such as PR_3, olefins, allyl alcohol, and carbon monoxide would fit into this group.[20]

The third group contains those nucleophiles that are hard and, even when strongly basic, do not react with Pt(II) complexes, *e.g.*, F^-, OH^-, CH_3O^-.

Finally, there are some species, such as HNO_2 and H_3BO_3, for which back-donation of charge *via* π bonding is the most important factor. These can act as catalysts[13] in substitution reactions in a way that can best be regarded as an electrophilic attack on the metal, which, in such cases, functions as a Lewis base.

Acknowledgments. We thank Dr. M. L. Tobe for helpful stimulating discussions.

---

[20] NOTE ADDED IN PROOF. Recent results on the reactions of allyl derivatives seem to agree with the idea pointed out here (L. Venanzi, private communication).

Structure of Dimethylgold(III) Compounds. Spectroscopic Studies on the Aquo Ion and Several Coordination Compounds[1]

Malcolm G. Miles,[2a] Gary E. Glass,[2b] and R. Stuart Tobias

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received July 5, 1966*

Abstract: Dimethylgold(III) hydroxide has been synthesized and used to prepare aqueous solutions of $(CH_3)_2AuNO_3$, $(CH_3)_2AuClO_4$, and $Na[(CH_3)_2Au(OH)_2]$. Raman and pmr spectra indicate that the aquo ion and the hydroxo complex exist in solution exclusively as the *cis* isomer. For comparison, 2,4-pentanedionatodimethylgold(III), dimethyl(ethylenediamine)gold(III) iodide, and di-μ-iodo-tetramethyldigold have been synthesized and their Raman, infrared, and pmr spectra determined. The vibrational frequencies of dimethylgold(III) are compared with those of the isoelectronic dimethylplatinum(II) and also with the dimethylthallium(III) moieties.

Only a relatively small number of organogold(III) compounds have been synthesized, and most of our knowledge of these stems from the research of Gibson and co-workers. Among the compounds prepared are the dialkylgold(III) halides $(C_2H_5)_2AuBr$,[3,4] $(CH_3)_2AuBr$,[5] and $(CH_3)_2AuI$,[5] together with the ethylenediamine chelates of dimethylgold(III),[5]

---

[1] Supported, in part, by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research Grant No. AF-AFOSR-691-65.

[2] (a) Research Fellow in Chemistry; (b) NASA Predoctoral Fellow.

[3] C. S. Gibson and W. M. Colles, *J. Chem. Soc.*, 2407 (1931).

[4] A. Burawoy and C. S. Gibson, *ibid.*, 860 (1934).

[5] F. H. Brain and C. S. Gibson, *ibid.*, 762 (1939).