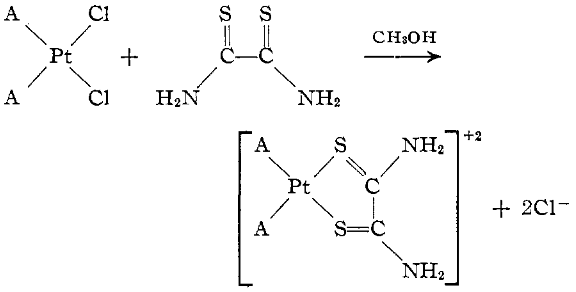
Correspondence

Aromaticity of Five-Membered Rings Containing Platinum(II)

Sir:

Displacement of platinum(II) has recently been discussed in a number of publications.[1] We wish to report some kinetic data which may be explained on the basis of aromaticity in platinum(II)–α-diimine chelate rings.

Because of the difficulties involved in treating consecutive first-order reactions,[2] the readily available *cis*-dichloride complexes of platinum(II) with neutral ligands have been used very little as substrates for kinetic investigations. We now find that when dithioöxamide is used as a nucleophile and methanol as solvent, pseudo-first-order kinetics are observed (eq. 1); presumably displacement of the first chloride



(1)

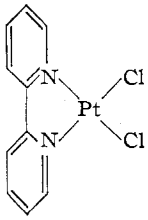
is the rate-determining step and the second chloride is displaced in a fast, intramolecular reaction. We therefore have studied conductometrically a variety of complexes using this technique. The results (Table I) show that the bipyridyl complex, **1**, reacts nearly 100 times faster than the *cis*-dipyridine complex, **2**, or the ethylenediamine complex, **3**. We have also studied a series of saturated diamine complexes and observe small but significant effects which will be reported and discussed in the full paper.

TABLE I

KINETICS OF DISPLACEMENT OF CHLORIDE BY DITHIOÖXAMIDE IN METHANOL AT 25.0°

Complex	[Complex], moles/l.	[Dithiooxamide], moles/l.	10^5k_{obsd},[d] sec.$^{-1}$
cis-Pt(py)$_2$Cl$_2$[a] (**2**)	0.0001	0.001	Slow
cis-Pt(py)$_2$Cl$_2$[a] (**2**)	.0001	.002	Slow
cis-Pt(py)$_2$Cl$_2$[a] (**2**)	.0001	.01	3.83
cis-Pt(py)$_2$Cl$_2$[a] (**2**)	.0001	.02	7.77
Pt(bipy)Cl$_2$[b] (**1**)	.00005	.001	38.8
Pt(bipy)Cl$_2$[b] (**1**)	.00005	.002	64.2
Pt(bipy)Cl$_2$[b] (**1**)	.00005	.01	342
Pt(en)Cl$_2$[c] (**3**)	.0001	.01	5.48
Pt(en)Cl$_2$[c] (**3**)	.0001	.02	9.14

[a] py = pyridine. [b] bipy = bipyridyl. [c] en = ethylenediamine. [d] Pseudo-first-order rate constants since nucleophile in excess.



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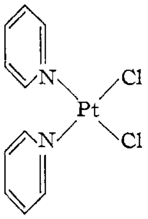

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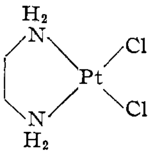

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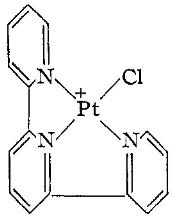

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These results can be rationalized on the basis of a strong *trans* effect[3] resulting from aromaticity in the platinum-α-diimine chelate ring in **1**.[4] The Pt–N π-bonding necessary for aromaticity is possible in at least two ways. (1) The 2p$_z$ orbitals on nitrogen could overlap with the 5d$_{xz}$ and 5d$_{yz}$ orbitals on the platinum (complex in *xy* plane) to produce an aromatic system with eight π-electrons in the five-membered ring.[5] A consequence would be low electron density on the chloride side of the complex and a large *trans* effect.[3] (2) Two pd^2 hybrid orbitals (from the filled 5d$_{xz}$ and 5d$_{yz}$ and the empty 6p$_z$ orbitals) at platinum could form a benzenoid system with the α-diimine chelate ring as suggested by Longuet-Higgins for thiophene.[7] The third pd^2 hybrid, containing an unshared pair, would then be located *between* the chloride ligands,

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[1] (a) F. Aprile and D. S. Martin, *Inorg. Chem.*, **1**, 551 (1962); (b) H. B Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962); (c) H. B. Gray and R. J. Olcott, *Inorg. Chem.*, **1**, 481 (1962); (d) F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 2207 (1961); (e) P. Haake, *Proc. Chem. Soc.*, 278 (1962).

[2] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, New York, N. Y., 1961, Chapter 8.

[3] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, Chapter 4.

[4] Although it seems intuitively unlikely, it is possible that not even one pyridine ring in **2** can be in the plane of the complex. If so, the increased rate in **1** could then be accounted for simply by overlap of filled d-orbitals with the aromatic rings which would be impossible in **2**.

[5] Calculation of a 5dπ–2pπ overlap integral using Slater orbitals[6] for Pt–N bonding gives $S = 0.16$.

[6] (a) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 4493 (1950); (b) H. H. Jaffé, *J. Chem. Phys.*, **21**, 258 (1953).

[7] H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949). It seems likely that **1** is a more favorable case than thiophene for participation of pd^2 hybrids in an aromatic system because the 6p and 5d orbitals in platinum should be of more comparable energy than the 3p and 3d orbitals of sulfur.

resulting in low electron density along the platinum–chloride bonds.[3,8,9]

Besides the extensive evidence that six π-electrons are favored in aromatic systems, there are two experimental observations that indicate that the $6p_z$ orbital might be involved in pd^2 hybridization of platinum in **1**. (1) Whereas **2** and **3** are conveniently recrystallized from water, **1** is quite insoluble. Although dimethyl sulfoxide is a superior solvent for most of these neutral complexes, **1** is not even very soluble in that solvent. Since solvation probably involves bonding through the empty p_z orbital in square complexes, these observations suggest that in the bipyridyl complex, **1**, the p_z orbital is not available for bonding to solvent—a necessary consequence of the formation of hybrid pd^2 orbitals.[11] (2) An example of the solvolysis of **1** has been reported[12]; the rate constant for hydrolysis of **1** is *smaller* than that of **3** by a factor of four. Such a solvolysis result would be expected if the p_z orbital were not available for bonding with an incoming nucleophile[1e] as pd^2 hybridization would require. If this is correct it might mean that the initial interaction of dithioöxamide with platinum(II) complexes is electrophilic,[1b,1c] and, in fact, **1** may turn out to be diagnostically useful in distinguishing between electrophilic and nucleophilic reagents for displacement in square complexes.

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[8] A third possibility for π-bonding is that a single d orbital (d_{xz} or d_{yz}) on platinum might overlap with the p_z orbitals on both nitrogens.

[9] Displacement of chloride by pyridine in the tripyridyl complex, **4**, has been observed[10] to be 10^3 times faster than in the saturated diethylenetriamine complex. Although strain has been suggested as an explanation, aromaticity could also account for the large rate increase.

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

[11] An alternative explanation of the solubility relations would involve a high lattice energy due to close packing of the planar bipyridyl complex. This possibility was pointed out to us by Professor K. N. Trueblood.

[12] Reference 10; the result is in the text, top of p. 4203, second column.

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Crystal Field Theory of Halogen Cations

Sir:

Pasternack and Piper have discussed the way in which the energies of various states of the iodine cation would be modified by the approach of a single negatively charged "ligand."[1] They point out, in particular, that the $^1\Sigma$ level would fall below the $^3\Pi$ states when Δ reaches about 5000 cm.$^{-1}$. This is of interest since it shows how the energy levels would be modified during reaction with a nucleophile (N).

$$I^+_{\text{solv}} + N \rightleftharpoons IN^+$$

Thus the electrons are ultimately constrained to pair, leaving a vacant p-orbital which is then suitable for covalent bonding.

It has been suggested[2] that the iodine cation is unlikely to be symmetrically solvated, but rather that solvent molecules should interact strongly in the *xy*-plane, and weakly along the *z*-axis, for an ion having the configuration $4p_x$, $4p_y$, $4p_{z^2}$. If one ignores possible covalent interactions this is equivalent to a positive axial field and will lead to a $^3\Sigma$ ground state and three $^3\Pi$ excited states. Although crude, this model does seem to accommodate the spectral and magnetic results quite well[2] and there seems to be no compelling reason for abandoning it at present.

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[1] R. F. Pasternack and T. S. Piper, *Inorg. Chem.*, **2**, 429 (1963).

[2] J. Arotsky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, 11 (1961); J. Arotsky and M. C. R. Symons, *Quart. Rev.* (London), **16**, 282 (1962).

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Preparation of Silane from Silica

Sir:

The direct hydrogenation of silica to silane has been reported to require either high temperatures (1000–1200°) or high pressures (400–900 atmospheres)[1] and is therefore not easily adapted to laboratory preparations.

We have found that silane can be synthesized at 200°, either under vacuum or in an inert atmosphere, by simply heating a mixture of silica and lithium aluminum hydride. Yields averaging 10% silane, based upon hydride, have been obtained in this reaction. The only recognized impurity, detected by infrared spectra of product samples, was ether, which was an impurity in the lithium aluminum hydride. High purity material was obtained by vacuum fractionation of the mixture through a trap cooled by a Freon-12 slush at $-155°$, at which temperature the ether is effectively removed. In another preparation we removed nearly all the ether ahead of time by simply preheating the reactants at a lower temperature prior to collecting the products.

In a typical experiment 1 g. (16.6 mmoles) of silica gel, previously dried at 160° for 16 hr., and 0.15 g. (3.9 mmoles) of lithium aluminum hydride were placed in a Pyrex glass tube where they were mixed by shaking. The tube was evacuated, then heated to 170° with an oil bath. Vapors emanating from the reactor were collected in a trap cooled to $-196°$ with liquid nitrogen. The collected material, identified by infrared analysis to be ether containing a trace of silane, was discarded. The reactor tube was then heated slowly to 200°, and the condensable vapors were again collected. As the

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[1] H. L. Jackson, F. D. Marsh, and E. L. Muetterties., *Inorg. Chem.*, **2**, 43 (1963).