

between C-5 and C-10 in a (hypothetical) type 8 intermediate. In view of the *exclusive* conversion $7 \rightarrow 9$ under identical irradiation conditions,^{11,13} the choice between the reaction paths $6 \rightarrow 2$ and $8a \rightarrow 9$ is evidently controlled by the size of ring B in the dienones 1 and 7, respectively.

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The Importance of Steric Factors in Substitution Reactions of Metal Complexes. A Pseudo-octahedral Complex

Sir:

With the rebirth of the crystal field theory¹ and its application to metal complexes, the importance of the electronic structures in these systems in explaining their properties is well documented. We wish to report here an example where steric factors, not electronic structure, are responsible for the substitution reaction of a metal complex.

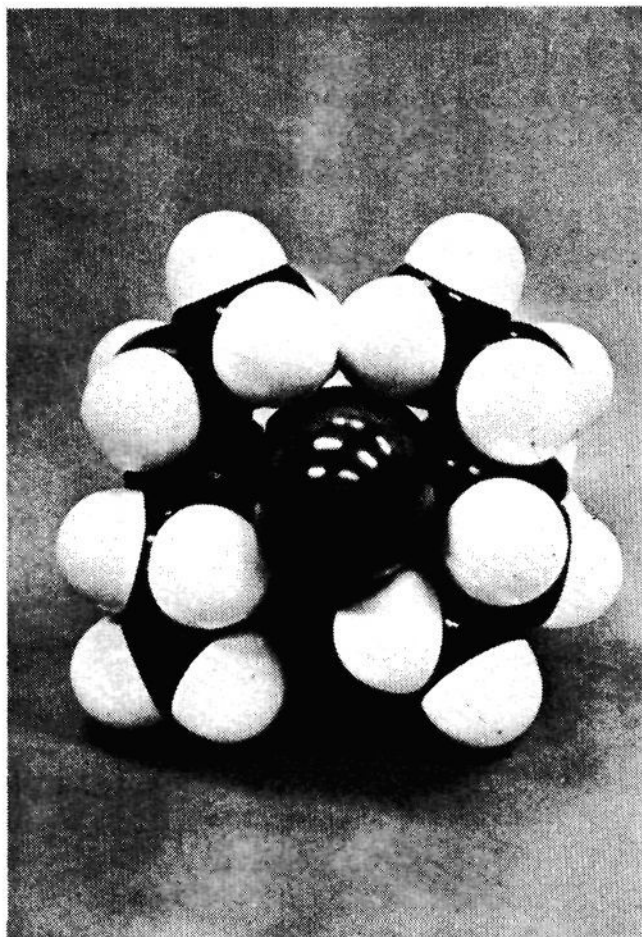


Fig. 1.—Molecular model of the pseudo-octahedral complex $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]^+$.

The rates of substitution reactions of octahedral metal complexes do not generally depend on the reagent.² For square-planar complexes, the rates of reaction do depend on the reagent.³ The question arises as

(1) H. Bethe, *Ann. Physik*, [5] **3**, 133 (1929).

(2) (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, Chapter 3; (b) M. Eigen, *Pure Appl. Chem.*, **6**, No. 1, 97 (1962).

(3) F. Basolo and R. G. Pearson, "Progress in Inorganic Chemistry," Vol. 4, F. A. Cotton, Ed., Interscience Publishers, Inc., New York, N. Y., 1962.

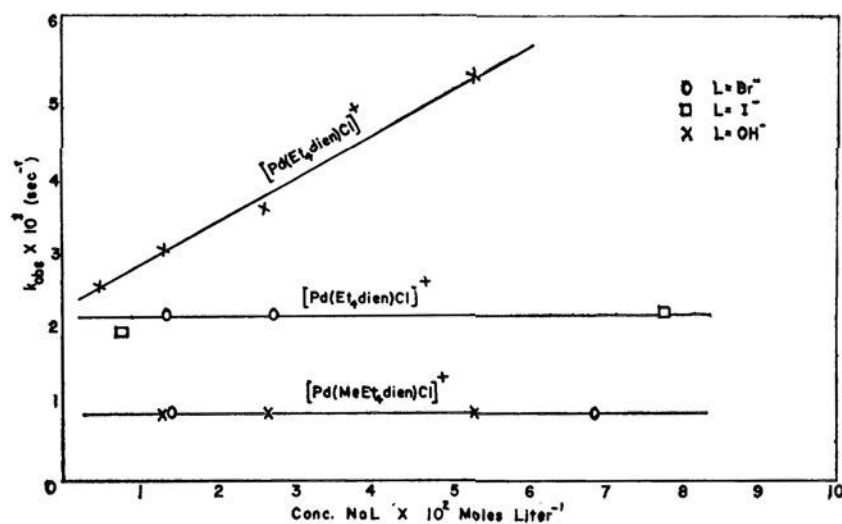


Fig. 2.—Rates of reaction of pseudo-octahedral Pd(II) substrates with various reagents at 25° in water.

to whether this difference in behavior between octahedral and square-planar substrates is due to a difference in electronic structure or in molecular (steric) structure. It would appear that the reactions differ in type because of steric factors. For example the low-spin d^8 complex⁴ $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]^+$ looks like and reacts like an octahedral complex (Fig. 1). Because of this we call it a *pseudo-octahedral* complex.

The reaction of $[\text{Pd}(\text{dien})\text{Cl}]^+$ with OH^- and Br^- at 10^{-3} M concentration of reactants is too fast to study at room temperature by the stopped flow method which means it has a $t_{1/2} < 10^{-3}$ sec. However $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]^+$ reacts with various reagents at 25° with $t_{1/2} = 6$ min. Except for OH^- , the rate of reaction 1 does



not depend on L^- (Fig. 2.). This most striking result is reminiscent of reactions of chloroamminecobalt(III) complexes.^{2a} The unique behavior of OH^- is due to a rapid acid-base pre-equilibrium forming the more reactive amido species $[\text{Pd}(\text{Et}_4\text{dien-H})\text{Cl}]$, an $\text{S}_{\text{N}}1\text{CB}$ mechanism. That this is correct is supported by the fact that OH^- has no effect on the rate of reaction of $[\text{Pd}(\text{MeEt}_4\text{dien})\text{Cl}]^+$ which contains no N-H hydrogen.

Therefore, these pseudo-octahedral substrates behave unlike their low-spin d^8 relatives, but like octahedral complexes. This provides striking evidence of the importance of steric factors in these systems.

The complexes $[\text{Pd}(\text{Et}_4\text{dien})\text{X}]$, where $\text{X} = \text{Cl}^-$, Br^- , were prepared quite simply by mixing H_2PdCl_4 with an excess of the amine and warming the solution for a few minutes on a steam bath. Addition of excess LiX to the resulting clear orange solution caused the complex to separate as yellow crystals. The solid was separated by filtration and recrystallized from aqueous ethanol. *Anal.* Calcd. for $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]\text{Cl}$: Pd, 27.1. Found: Pd, 27.4. Conductivity measurements show the complex to be a 1:1 electrolyte in water. *Anal.* Calcd. for $[\text{Pd}(\text{Et}_4\text{dien})\text{Br}]\text{Br}$: Pd, 22.1; C, 29.9; H, 6.1. Found; Pd, 22.4; C, 30.1; H, 6.4. The cation $[\text{Pd}(\text{MeEt}_4\text{dien})\text{Cl}]^+$ could not be isolated as the chloride, since a sticky, oily material always resulted. It was therefore isolated as the hexafluorophosphate. *Anal.* Calcd. for $[\text{Pd}(\text{MeEt}_4\text{dien})\text{Cl}]\text{PF}_6$: C, 30.2; H, 6.0. Found: C, 30.6; H, 6.0. Conductivity measurements show this complex to be a 1:1 electrolyte in both water and nitrobenzene.

(4) dien = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$, $\text{Et}_4\text{dien} = (\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$, $\text{MeEt}_4\text{dien} = (\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$.

Acknowledgment.—We wish to thank Professor R. G. Pearson for his interest and helpful advice. We wish to thank Mr. G. Haller for the isolation and purification of the compound $[\text{Pd}(\text{MeEt}_4\text{dien})\text{Cl}]\text{PF}_6$. This research is supported in part by the U.S. Atomic Energy Commission under Grant At(11-1)-1087 and in part by National Institutes of Health Grant RG-7488.

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High Frequency Titrimetric Determination of the Electron Deficiency in Lithium Alkyls¹

Sir:

Organometallic reagents, including lithium alkyls, are generally referred to as strong bases because of their "carbanion character" and gross reactions, *i.e.*, proton abstraction or attachment to Lewis acids.² Various authors have, however, conceived of the structure of certain organometallics in terms of a bonding electron deficiency.³ This deficiency could result in character-

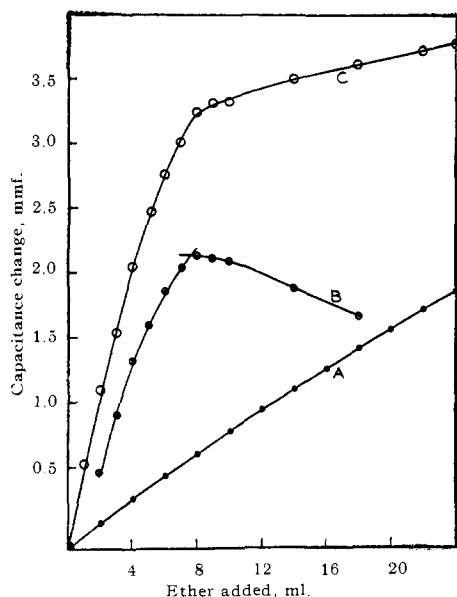


Fig. 1.—Curve A shows the change in capacitance of a cell containing 90 ml. of a hexane solution to which was added increments of ether. Curve C shows same except 0.144 equiv. of butyllithium was present. Curve B is the difference between C and A. Titrations were carried out at 25° (ether = 9.5 M).

istic acidic properties. Specifically, it recently has been suggested that the basic structural unit of a lithium alkyl is a dimer R_2Li_2 ,^{1,4} which associates with itself $(\text{R}_2\text{Li}_2)_n$ as a solid and in nonpolar solvents. If this specific suggestion is correct, by application of the $2(n-1)$ rule of Longuet-Higgins,^{3a} it may be predicted that just two electrons are needed to satisfy the deficiency of each dimer structure. To investigate this

(1) Paper IV in the series "Solvent Effects in Organometallic Reactions." Paper III: Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *J. Am. Chem. Soc.*, **85**, 3517 (1963).

(2) Cf. R. Waack and M. A. Doran, *ibid.*, **85**, 4042 (1963); G. Wittig, *Bull. soc. chim. France*, [5] 1352 (1963).

(3) Cf. (a) H. C. Longuet-Higgins, *Quart. Rev.* (London), **11**, 121 (1957); (b) G. E. Coates, "Organometallic Compounds," 2nd Ed., Methuen, London, 1960, pp. 44, 57, 131, 152 ff.; (c) M. Weiner and R. West, *J. Am. Chem. Soc.*, **85**, 485 (1963).

(4) V. H. Dietrich, *Acta Cryst.*, **16**, 681 (1963).

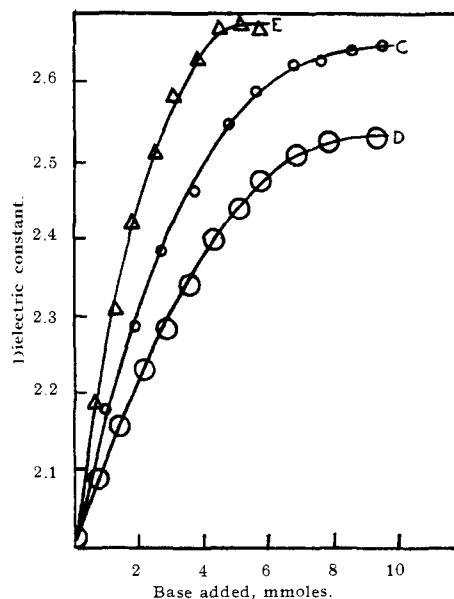
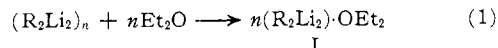


Fig. 2.—Apparent dielectric constants of three hexane solutions, each of 7 ml. volume and containing 11.2 mequiv. of butyllithium, to which Lewis bases were added: D, triethylamine; C, diethyl ether; E, tetrahydrofuran.

prediction experimentally, we have measured the change in dielectric properties of several lithium alkyls consequent to their titration with Lewis bases.

Figure 1 shows the changes in dielectric properties of 90 ml. of hexane solution in a high frequency capacitance cell⁵ to which increments of diethyl ether (Et_2O) were added: curve A for hexane originally alone and curve C for hexane containing 0.144 equiv. of RLi , *n*-butyllithium. Although an RLi solution in hexane is hardly more polar than hexane alone, it is seen that addition of ether causes a relatively steep rise in the dielectric character of the solution (more change in the dielectric than ether alone causes) and that this rise is complete when the ratio of RLi to Et_2O is 2:1. This latter fact is more apparent from a plot B of the difference between curves A and C. In effect, C is a titration curve for a reaction (eq. 1) in which the lithium alkyl is an "acid." There would seem to be some practical potential in titrations of this type, particularly with a differential curve like B, for nondestructive analysis of alkyllithium solutions.



It was conceivable that the Et_2O titration curve did not corroborate the prediction of each R_2Li_2 unit accepting just one pair of electrons to satisfy the organometallic's bonding electron deficiency; Et_2O does have two pairs of nonbonding electrons which it could be contributing in structure I. To check this consideration, high frequency titrations of butyllithium in hexane were carried out with triethylamine (Et_3N) instead of Et_2O as the base. As Fig. 2, curve D, shows, Et_3N also causes a rise in dielectric character, and the steep rise is complete with the addition of one pair of nonbonding electrons from the base for every R_2Li_2 unit in solution. Hydrocarbon solutions of several lithium alkyls (ethyl, *sec*-butyl, *t*-butyl, *n*-butyl), each with several different

(5) A 5-Mc. signal was applied concentrically to the all-glass cell and measured with the circuit of a Sargent Model V oscilloscope modified so that capacitance change was linear with dielectric constant change within the cell and so that the cell could be operated in a controlled atmosphere.