

TABLE II
pH DEPENDENCE OF REACTIONS AT 25°
([COMPLEX] = 2.5 mM, [dien] = 50 mM, $\mu = 0.318$)

pH	10^3k_t , sec ⁻¹	% concn ^a	
		dien + dienH ⁺	dienH ₂ ²⁺
9.6	4.33	88	12
9.2	3.89	70	30
8.9	3.28	52	47
8.6	2.15	35	65
8.2	1.18	17	83
7.8	0.6 ^b	8	92
7.0	<0.1 ^b	1.2	99
6.0	No reaction in 1 week		

^a Calculated from data in ref 1. ^b Estimated from initial rates.

amine. This observation can be explained by assuming that only amine species containing at least two unpro-

tonated nitrogens are reactive. A possible mechanism consistent with these data could involve the initial formation of an axial bond from a nucleophilic nitrogen to platinum followed by attack by another unprotonated nitrogen site in the same amine molecule with resultant displacement of the first equatorial halide ligand. The geometrical situation would now be favorable for the rapid displacement of the second chloride ligand by a terminal nitrogen in the amine. Concurrent breakage of the initial weak axial bond would result in the product indicated in eq 1.

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Correspondence

Stereochemistry and the *cis* and *trans* Influences of Methido and Hydrido Ligands¹

Sir:

The experimental evidence for the *trans* effect, *i.e.*, the effect of a coordinated ligand L upon the rate of substitution reactions of the ligand Y *trans* to L,²⁻⁴ for platinum(II) complexes is overwhelming. There also is a good deal of extrakinetic structural evidence for bond-weakening effects in the ground state of complexes in which the ligands fall in essentially the same order of effectiveness as they do in their ability to labilize ligands in substitution reactions.

This communication is concerned primarily with observations on the ground states of complexes, and the assignment by Pidcock, *et al.*,^{5,6} of a *trans* "influence" to a ligand, *i.e.*, the ability to weaken a *trans* bond, will be adopted.

Briefly, the various explanations for the *trans* influence of ligands may be described as (a) σ -orbital rehybridization where the platinum-L bond has a greater share of the platinum 6s orbital than the platinum-Y bond *trans* to it,⁵ (b) σ -orbital rehybridization where the platinum-L bond has a greater share of a 6p orbital than the platinum-Y bond *trans* to it,^{7,8} (c) the classical polarization theory,⁹ and (d) the π -bonding theory.¹⁰

(1) Supported by the National Science Foundation, Grant GP-15083, and by the Petroleum Research Fund, Administered by the American Chemical Society.

(2) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

(3) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1968, p 351.

(4) A rather thorough review of the recent literature bearing on the *trans* effect in platinum(II) compounds is given by S. S. Zumdahl and R. S. Drago, *J. Am. Chem. Soc.*, **90**, 6660 (1968).

(5) A. Pidcock, R. E. Richards, and L. Venanzi, *J. Chem. Soc.*, **A**, 1707 (1966).

(6) L. Venanzi, *Chem. Brit.*, **3**, 162 (1967).

(7) Reference 3, p 372.

(8) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, p 25.

(9) Reference 3, p 370.

(10) Reference 3, p 371.

The cases to be considered here involve alkyl ligands they can be considered to be similar to the case where hydride is a ligand, and the π -acceptor model can be eliminated.

Effects analogous to those reported for the ground state of platinum(II) complexes recently have been observed with the complexes of the isoelectronic gold(III). Replacement of two halides of the square-planar anions AuX₄⁻ (X⁻ = Cl⁻, Br⁻) with two CH₃⁻ leads to complexes which have exclusively the *cis* structure and to a decrease in the Au-X stretching force constants by more than 30%.¹¹

The ligands, L, *trans* to the methyl groups decrease in their effectiveness in reducing the gold-carbon stretching frequencies in the sequence (CH₃)₂S > Br⁻ > Cl⁻ > en > OH⁻ > H₂O. Substitution of these ligands also proceeds very rapidly in the positions *trans* to the methyl groups. Oxygen-17 nmr spectra indicate that the average lifetime of a water molecule bound to (CH₃)₂Au⁺ in aqueous solution is only *ca.* 2 × 10⁻⁵ sec.¹²

Alkylation of these d⁸ transition metals is stereo-specific, for not only are the gold(III) dialkyls exclusively *cis* but also only *cis*-dialkylplatinum(II) complexes seem to have been isolated. Traces of the *trans* platinum compounds have been suggested only as impurities in the main (*cis*) product.¹³

Rather similar bond-weakening effects also are found with octahedral complexes of the heavy representative elements, *e.g.*, tin(IV), but they are directed differently. Stereochemically, a *cis* effect is observed. Replacement of two halide ions of SnX₆²⁻ (X⁻ = F⁻, Cl⁻, Br⁻) by methide ions gives complexes which have exclusively the *trans* structure and leads to a decrease in the Sn-X stretching force constants by up to 50%.¹⁴

(11) W. M. Scovell and R. S. Tobias, *Inorg. Chem.*, **9**, 945 (1970).

(12) G. E. Glass, W. B. Schwabacher, and R. S. Tobias, *ibid.*, **7**, 2471 (1968).

(13) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).

(14) C. W. Hobbs and R. S. Tobias, *Inorg. Chem.*, **9**, 1037 (1970).

It is likely that there is an analogous kinetic *cis* effect for these complexes, but currently there appear to be no data available bearing on this point. All of the tin(IV) complexes undergo substitution very rapidly and require relaxation methods for the study of these processes, so the replacement of, *e.g.*, a halide by CH_3^- does not give the striking and easily measured kinetic effect that it does with Pt(II). The upper limit to the average lifetime of a water molecule bound to $(\text{CH}_3)_2\text{Sn}^{2+}$ in aqueous solution is 10^{-5} sec, and it is probably much less.¹²

The force constant data for the Au(III) and Sn(IV) complexes are summarized in Table I. One interesting point is that the metal-carbon bonds are all of roughly the same strength, although the metal-halogen bonds are appreciably weaker in the tin than in the gold compounds. Au(III) and Sn(IV) are hard acids,¹⁵ but the dimethyl derivatives seem to form bonds with Cl^- and Br^- which are comparable in strength.

TABLE I
VALENCE FORCE CONSTANTS^a ILLUSTRATING THE
cis AND *trans* INFLUENCES OF CH_3^-

	AuCl_4^- ¹¹	<i>cis</i> -(CH_3) ₂ - AuCl_2^- ¹¹	AuBr_4^- ¹¹	<i>cis</i> -(CH_3) ₂ - AuBr_4^- ¹¹
$K(\text{M}-\text{C})$...	2.8 (0.1)	...	2.7 (0.1)
$K(\text{M}-\text{X})$	2.2 (0.3)	1.4 (0.1)	1.8 (0.1)	1.2 (0.2)
	SnCl_6^{2-} ¹⁴	<i>trans</i> -(CH_3) ₂ - SnCl_4^{2-} ¹⁴	SnBr_6^{2-} ¹⁴	<i>trans</i> -(CH_3) ₂ - SnBr_4^{2-} ¹⁴
$K(\text{M}-\text{C})$...	2.4 (0.1)	...	2.4 (0.1)
$K(\text{M}-\text{X})$	1.5 (0.2)	0.8 (0.1)	1.2 (0.1)	1.1 (0.1)

^a Force constants in $\text{mdyn}/\text{\AA}$; standard errors are given in parentheses.

One way in which these complexes differ from most inorganic coordination compounds is that the $(\text{CH}_3)_2\text{SnX}_4^{2-}$ ions cannot be treated even to a first approximation in terms of O_h symmetry nor can the $(\text{CH}_3)_2\text{AuX}_2^-$ ions be treated usefully in terms of D_{4h} symmetry. This is a consequence of the quite different nature of the bonds to carbon and to halide ions. It is true in spite of the fact that the bond angles to adjacent ligands are all still approximately 90° in the compounds for which structures have been determined. The bonds to the halides are very polar, while those to the carbanions are much less so.

It is useful to examine the metal AO's which can be used in bonding to the different sets of ligands in the isomeric forms of these complexes. Consider that $(\text{CH}_3)_2\text{SnCl}_4^{2-}$ is forced into a configuration where all six bonds from tin to the ligands are equivalent, O_h microsymmetry. If the octahedron is allowed to relax, it can do so by an e_g mode to give the *trans* structure or by a t_{1u} mode to give the *cis* structure, Figure 1. If the two configurations differ significantly in energy, one will predominate. If the energy difference is slight, it should be possible to adjust conditions to favor one structure or the other.

With a tin(IV) complex, it is unlikely that the ultimate d orbitals contribute to the bonding in a

major way. In the *trans* isomer, the lowest energy valence orbital, the 5s together with one 5p orbital, can be used in bonding to the carbanion ligands. Symmetry alone offers few restrictions on the orbitals which can be used in the *cis* complex, but in order to form two equivalent bonds directed at 90° to one another, these would have to involve two 5p orbitals. Of these two alternatives, which are admittedly extremes, the former clearly should lead to a lower energy state for the complex. If the 5d orbitals do not contribute appreciably, the bonds to the four halide ligands in the equatorial plane are essentially three-center two-electron bonds using σ orbitals on

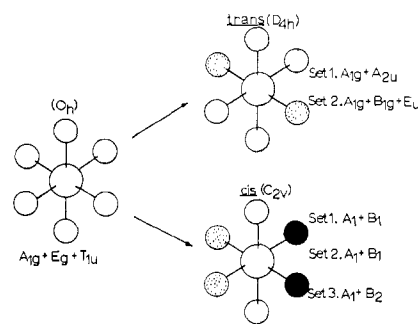


Figure 1.—Distortions from O_h microsymmetry to *cis*- and *trans* MX_2Y_4 isomers.

the four ligands and the remaining two 5p tin orbitals. The observed stereochemistry, pmr, and vibrational spectra of all of these $(\text{CH}_3)_2\text{SnX}_4^{2-}$ anions are consistent with the use of the lowest energy tin orbitals in the bonds to the carbanion ligands. The idea of maximization of the s character in the bonds to alkyl groups in tin compounds was first advanced on the basis of spin-spin coupling constant data by Holmes and Kaesz.¹⁶

The similarity of the "*cis*" effect with dialkyltin(IV) compounds and the *trans* effect with d^6 and d^8 transition metal complexes suggests that the origin is analogous. It is difficult to account for the differences in the stereochemistry in terms of the contribution of the spherically symmetric s orbitals alone. Since only the p orbital is directed exclusively to the *trans* positions, it is reasonable to ask if the σ *trans* effect arises from a maximization of the p orbital to only one of a pair of *trans* ligands.^{7,8} It has been suggested for platinum(II) that a large overlap with the platinum 6p orbital will reduce the ability of that orbital to participate in bonding to a *trans* ligand. This effect alone does not seem to be the answer, for in the tin complexes a single 5p orbital is used in forming two strong, inert *trans* bonds. Consequently, the effect does not appear to lie strictly with the p orbitals either.

If the relaxation from a D_{4h} structure by b_{1g} or e_u vibrations to the isomeric $(\text{CH}_3)_2\text{AuX}_2^-$ ions is considered, Figure 2, the two sets of bond vectors for the *cis* complex both transform as $A_1 + B_1$. For the *trans* isomer with D_{2h} microsymmetry the two

(15) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(16) J. R. Holmes and H. D. Kaesz, *ibid.*, **83**, 3903 (1961).

TABLE II^a

Complex	Symmetry	Representation for bonds	"Best" orbitals for R	Orbitals for X	Examples
d ⁶ Configuration					
MRX ₅	C _{4v}	R A ₁ X _{trans} A ₁ X ₄ A ₁ + B ₁ + E	d or s	p (d or s)dp ²	(C ₂ H ₅)Rh(NH ₃) ₅ ²⁺ ^b
<i>cis</i> -MR ₂ X ₄ ^a	C _{2v}	R ₂ A ₁ + B ₁ X _{2,trans} A ₁ + B ₁ X ₂ A ₁ + B ₂	(d or s)d	p ² (d or s)p	<i>cis</i> -(CH ₃) ₂ PtI ₂ (PR ₃) ₂ ^c
<i>trans</i> -MR ₂ X ₄	D _{4h}	R ₂ A _{1g} + A _{2u} X ₄ A _{1g} + B _{1g} + E _u	(d or s)p	(d or s)dp ²	...
<i>cis</i> -MR ₃ X ₃ ^a	C _{3v}	R ₃ A ₁ + E X _{3,trans} A ₁ + E	d ² s	p ³	<i>cis</i> -(CH ₃) ₃ Pt(NH ₃) ₃ ⁺ ^d
<i>trans</i> -MR ₃ X ₃	C _{2v}	R A ₁ X _{trans} A ₁ R ₂ A ₁ + B ₁ X ₂ A ₁ + B ₂	d or s (d or s)p	p (d or s)p	...
d ⁸ Configuration					
MRX ₃	C _{2v}	R A ₁ X _{trans} A ₁ X ₂ A ₁ + B ₁	d or s	p (d or s)p	<i>trans</i> -(CH ₃)IPt(PR ₃) ₂ ^e
<i>cis</i> -MR ₂ X ₂ ^a	C _{2v}	R ₂ A ₁ + B ₁ X _{2,trans} A ₁ + B ₁	ds	p ²	{ <i>cis</i> -(CH ₃) ₂ AuCl ₂ ⁻ <i>cis</i> -(CH ₃) ₂ Pt(PR ₃) ₂ }
<i>trans</i> -MR ₂ X ₂	D _{2h}	R ₂ A _g + B _{2u} X ₂ A _g + B _{3u}	(d or s)p	(d or s)p	...
d ¹⁰ Configuration					
<i>cis</i> -MR ₂ X ₄	C _{2v}	R ₂ A ₁ + B ₁ X _{2,trans} A ₁ + B ₁ X ₂ A ₁ + B ₂	p ²	s p	...
<i>trans</i> -MR ₂ X ₄ ^a	D _{4h}	R ₂ A _{1g} + A _{2u} X ₄ A _{1g} + B _{1g} + E _u	sp	p ²	{ <i>trans</i> -(CH ₃) ₂ SnCl ₄ ²⁻ (CH ₃) ₂ TiI ₄ (C ₆ H ₅) ₂ PbCl ₄ ^g }

^a Favored structure. ^b A. C. Skapski and P. G. H. Troughton, *Chem. Commun.*, 666 (1969). ^c G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 2, Methuen and Co. Ltd., London, 1968, p 229. ^d D. E. Clegg and J. R. Hall, *Australian J. Chem.*, **20**, 2025 (1967). ^e J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959). ^f H. M. Powell and D. Crowfoot, *Z. Krist.*, **87**, 370 (1934). ^g M. Mammì, V. Buseti, and A. Del Pra, *Inorg. Chim. Acta*, **1**, 419 (1967). ^h NOTE ADDED IN PROOF.—The results of a detailed investigation [J. D. Ruddick and B. L. Shaw, *J. Chem. Soc., A*, 2801 (1969)] of the stereochemistry of methyl derivatives of platinum(II) and -(IV) are in accord with the predictions outlined in this table.

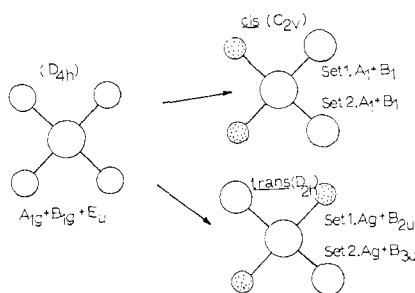


Figure 2.—Distortions from D_{4h} microsymmetry to *cis*- and *trans*-MX₂Y₂ isomers.

sets transform as A_g + B_{2u} and A_g + B_{3u}. Clearly the two lowest energy valence orbitals of gold, one 5d and one 6s, can be involved in bonding to the carbanion ligands only in the *cis* isomer, and this would be expected to be the lowest energy structure. As noted above, only the *cis* isomer is stable with platinum(II) and gold(III) dialkyls. Nmr studies of platinum(II) complexes indicate that the 6s orbital of the platinum atom also is concentrated in the bonds to an alkyl group.¹⁷

In Table II, representations for the transformations of the σ bonds in a series of complexes are considered. Assuming that the bonds to the alkyl groups will involve maximization of the $(n-1)d$ and ns contributions, the orbitals for the "best bonds" are given for the extreme case. The orbitals available for bonding to the other ligands also are given for this limiting case. The bonds to the more electronegative, hard-base ligands *trans* to the alkyl groups are found to involve predominantly metal p AO's in the more stable structures. These conclusions are a consequence of the symmetry of the complexes, and in some cases the limitation to *ca.* 90° for the bond angles to adjacent ligands provides an additional constraint. The hydrogen-like orbitals tend to separate into two groups, the d and s on the one hand and the p's on the other, mainly because the former are centrosymmetric. Examples of typical compounds having essentially the type of stereochemistry described also are tabulated.

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(17) F. H. Allen and A. Pidcock, *J. Chem. Soc., A*, 2700 (1968).