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## Investigations on the electronic influence of organyl ligands

### IX \*. *trans*-Influence in mercury organyl compounds. A pseudopotential *ab initio* study

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#### Abstract

Pseudopotential *ab initio*-calculations at the SCF level with partial geometry optimization have been performed on mercury organyl compounds L–Hg–CH<sub>3</sub> (L = C≡CH, CH=CH<sub>2</sub>, CH<sub>2</sub>–CH<sub>3</sub>, CH<sub>3</sub>). The *trans*-influence of L on the Hg–CH<sub>3</sub> bond increases, i.e. bond strength decreases, if the carbon atom bonded to Hg is itself only weakly bonded to its neighbouring carbon (CH<sub>2</sub>–CH<sub>3</sub> vs. CH=CH<sub>2</sub> vs. C≡CH) or if the chain length of L increases (CH<sub>2</sub>–CH<sub>3</sub> vs. CH<sub>3</sub>). This bond weakening leads to an elongation of the Hg–CH<sub>3</sub> bond distance as a result of geometry optimization. The results agree with coupling constants <sup>1</sup>J(<sup>199</sup>Hg–<sup>13</sup>C) known from experiment. The calculations show that a stronger *trans*-influence of L is connected with larger charge transfer to the Hg–CH<sub>3</sub> fragment, especially with an increasing s population on mercury, which for its part is responsible for lower values of the coupling constants. The amount of *trans*-influence can be traced back to the electronegativity of the *trans*-influencing group.

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#### Introduction

The *trans*-influence of a ligand L in a metal complex *trans*-ML<sub>n</sub>'LT is the extent to which that ligand weakens the bond M–T *trans* to itself in the ground state of the complex [1]. Innumerable papers refer directly or indirectly to *trans*-influence phenomena in metal complexes. Experimental studies have been made of bond strength M–T (bond lengths R(M–T), stretching frequencies ν(M–T), nuclear-magnetic coupling constants J(M–T)) and theoretical explanations have been proposed of the dependence of the M–T bond strength on the ligand L. There are some reviews of the development of the theoretical understanding of the *trans*-in-

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\* For Part VIII, see ref. 5c.

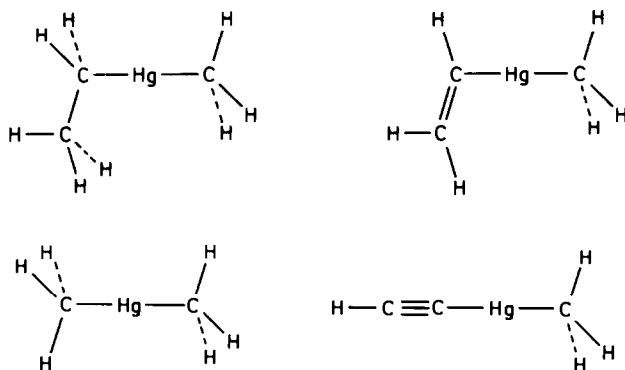
fluence [2]. Simple polarization theory [3] could explain why for  $\sigma$ -bonding ligands high polarizability leads to strong *trans*-influence. For  $\pi$ -bonding ligands it has been suggested [4] that high back-donating ability should stabilize the transition state of reactions exchanging the ligand T, thus causing a strong kinetic *trans*-effect [2a]. Most of the ideas are based on orbital interactions in the complex fragment L–M–T.

Mercury organyl compounds of the type L–Hg–T are an especially suitable system for discussing *trans*-influence phenomena. There are a number of reasons for this. First, there are no *cis*-groups, i.e. the changes of the Hg–T bond properties are exclusively caused by the *trans*-influence of L if the latter group is varied. Second, at least formally, there are no  $\pi$  interactions between mercury and the two organyl groups. All the effects can be considered as being of  $\sigma$  *trans*-influence type. Third, for more sophisticated quantum chemical investigations it is desirable to consider the whole molecule instead of picking out only a fragment. For metal complexes *trans*-ML<sub>n</sub>LT of square-planar, trigonal-bipyramidal or octahedral structure the calculation of the whole system requires much computation. For L–Hg–T, however, the compound itself consists of the linear *trans*-bonding fragment, thus making these compounds suitable for quantum chemical investigations. Finally, for the mercury organyl complexes L–Hg–T (T = <sup>i</sup>Bu) the coupling constants <sup>1</sup>J(<sup>199</sup>Hg–<sup>13</sup>C<sub>iBu</sub>) have been measured for a large number of organyl ligands L [5]. These coupling constants are a sensitive experimental measure for the *trans*-influence of the ligands L and can be compared with calculated *trans*-influence parameters.

In the present paper we report nonempirical molecular orbital calculations on complexes L–Hg–CH<sub>3</sub>. The methyl group simulates the isobutyl group, for which experimental data are available. Typical organyl ligands L have been chosen for the calculations: L = C≡CH, CH=CH<sub>2</sub>, CH<sub>2</sub>–CH<sub>3</sub>, CH<sub>3</sub>. These ligands can be grouped together in two different ways which is important for the discussion: In the row C≡CH, CH=CH<sub>2</sub>, CH<sub>2</sub>–CH<sub>3</sub> the carbon atom that will be bonded to mercury is itself a triple-, double- or single-bonded atom, respectively. Effects of chain elongation can most easily be studied by comparing CH<sub>2</sub>–CH<sub>3</sub> with CH<sub>3</sub>. The properties of the central atom Hg and the *trans*-influenced CH<sub>3</sub> group as well as the Hg–CH<sub>3</sub> bond itself are calculated and discussed in relation to the nature of L and are compared with the experimental coupling constants J(Hg–C<sub>iBu</sub>) of the complexes L–Hg–T (T = <sup>i</sup>Bu) [5]. Moreover, to extend the discussion parameters for further free organyl ligands L have been calculated: L = C≡CH, CH=CH<sub>2</sub>, CH<sub>2</sub>–CH<sub>3</sub>, CH<sub>3</sub>, <sup>n</sup>C<sub>3</sub>H<sub>7</sub>, <sup>i</sup>C<sub>3</sub>H<sub>7</sub>, CH<sub>2</sub>–CH=CH<sub>2</sub>, CH<sub>2</sub>–S–CH<sub>3</sub>. It is shown which of the free-ligand properties determine the *trans*-influence in the mercury complexes.

## Computational details

*Ab initio* calculations have been performed at the SCF level. For the atoms of the organyl ligands the conventional 3–21 G basis set [6] has been used throughout the calculations. This is the simplest basis set from which realistic optimized molecular geometries can be expected. The core electrons of Hg (Xe core) were replaced by a pseudopotential of Durand–Barthelat type [7]. Flexible valence functions were used, (5s, 5p, 3d) [8] contracted to (311, 221, 21).



Scheme 1.

Partial geometry optimizations of the mercury organyl compounds were performed [9] assuming  $C_s$  symmetry with a linear  $C_L$ -Hg- $C_T$  unit (see Scheme 1). The internal geometry of the organyl groups was kept fixed at the bond lengths and bond angles optimized for the molecules  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $CH_4$  with the 3-21G basis set [6]. Consequently we consider only the two *trans*-standing Hg-C bond lengths that we have optimized by means of a step-by-step process.

The free organyl anions were optimized completely or partially (keeping some functional groups fixed) [10]. For analysis of the cations we used experimental geometries [11] of the corresponding molecules.

### Mercury organyl compounds

The optimized geometrical parameters and the calculated charge-transfer data are given in Table 1. There exists an X-ray diffraction study for the symmetric compound  $H_3C$ -Hg- $CH_3$  showing a Hg-C distance of  $(2.083 \pm 0.005)$  Å [12].

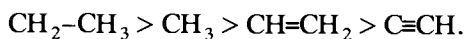
Table 1

Optimized Hg-C bond lengths (in pm), fragment charges and selected populations for L-Hg-T (T =  $CH_3$ )

L	$CH_2-CH_3$	$CH_3$	$CH=CH_2$	$C\equiv CH$
$R(Hg-C_L)^a$	214	212	210	203
$R(Hg-C_T)^a$	212.5	212.3	211.8	209.9
$q(L)$	-0.241	-0.254	-0.283	-0.392
$q(Hg)$	0.505	0.508	0.529	0.618
$q(T)$	-0.264	-0.254	-0.246	-0.226
$s(Hg)$	1.022	1.003	0.987	0.926
$p\sigma(Hg)$	0.390	0.390	0.361	0.304
$p\pi(Hg)$	0.061	0.066	0.090	0.106
$d(Hg)$	0.022	0.033	0.033	0.046
$s(C_T)$	3.484	3.483	3.484	3.485
$p\sigma(C_T)$	1.247	1.242	1.233	1.212
$p\pi(C_T)$	2.120	2.120	2.128	2.150
$s(Hg) \times s(C_T)$	3.561	3.493	3.439	3.227

<sup>a</sup> The *trans*-influenced Hg- $C_T$  bond lengths have been determined more accurately than the Hg- $C_L$  bond lengths.

Comparison of this value with the calculated bond length leads in to conclude that the latter are systematically too large. As expected, the calculated bond lengths  $R(\text{Hg}-\text{C}_L)$  between mercury and the neighbouring atom  $\text{C}_L$  of the *trans*-influencing organyl ligands L clearly differ from each other. However, the influenced bond lengths  $R(\text{Hg}-\text{C}_T)$  between mercury and the carbon atom  $\text{C}_T$  of the methyl group also show a small but significant variation. The result is that the *trans*-influence of organyl ligands increases if the carbon atom bound to mercury is itself more weakly bound to the next carbon atom (single vs. double vs. triple bond) or, in other words, if the carbon atom bound to mercury is *sp*-hybridized instead of *sp*<sup>2</sup> or even *sp*<sup>3</sup>. Furthermore, it is indicated that the *trans*-influence of an alkyl group increases if the chain length increases. To summarize we find the *trans*-influence series



This *trans*-influence series corresponds to the charge distribution parameters determined by Mulliken population analysis. Generally, the mercury-carbon bond is considered to be rather covalent in character. Nevertheless, a certain polarity results for the bonds. The ethyl group has the smallest negative charge and the ethynyl group has the largest. This is consistent with the polarity of the C-H bond in  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$  or with the group electronegativity of the ethyl, vinyl and ethynyl groups. In this sense the mercury compounds under study can be considered as molecules  $\text{C}_2\text{H}_5\text{R}$ ,  $\text{C}_2\text{H}_3\text{R}$ ,  $\text{C}_2\text{HR}$  with the substituent  $\text{R} = \text{HgCH}_3$ . The relation between the methyl and the ethyl groups is considered to be caused by the larger (+I)-effect of the latter. However the differences between various alkyl groups are much smaller than those between groups with different carbon hybridization.

In terms of the usual *trans*-influence theories the organyl anions  $\text{L}^-$  donate electronic density to the  $(\text{HgCH}_3)^+$  fragment. Formally, this donation goes into a mercury *sp*<sub>σ</sub> hybrid orbital that shares its overlap between the two σ donor orbitals of  $\text{L}^-$  and  $\text{T}^-$ . From the population analysis (see Tab. 1) it follows that for the stronger *trans*-influencing organyl ligands the donation into the mercury *s* and *p*<sub>σ</sub> orbitals increases, whereas the influence on the corresponding  $\text{C}_T$  orbitals and the π system is rather low.

The calculated *trans*-influence data can be compared with the coupling constants  $^1J(^{199}\text{Hg}-^{13}\text{C}_{\text{Bu}})$  that have been measured for the mercury organyl complexes  $\text{L}-\text{Hg}-\text{T}$  ( $\text{T} = {}^i\text{Bu}$ ) [5]. The coupling constants are the only experimentally determined quantity for these compounds that is directly related to the Hg-T bond strength. From the values in Table 2 it can be seen that the same *trans*-influence order  $\text{CH}_2-\text{CH}_3 > \text{CH}_3 > \text{CH}=\text{CH}_2 > \text{C}\equiv\text{CH}$  follows as we obtained for

Table 2

Coupling constants  $^1J(^{199}\text{Hg}-^{13}\text{C}_{\text{Bu}})$  (in Hz) for the systems  $\text{L}-\text{Hg}-\text{T}$  ( $\text{T} = {}^i\text{Bu}$ ) [5].

L	J	L	J
$\text{CH}_2-\text{CH}_3$	660	${}^i\text{C}_3\text{H}_7$	582
$\text{CH}_3$	760	${}^n\text{C}_3\text{H}_7$	666
$\text{CH}=\text{CH}_2$	819	$\text{CH}_2-\text{CH}=\text{CH}_2$	743
$\text{C}\equiv\text{CH}$	1211	$\text{CH}_2-\text{S}-\text{CH}_3$	849

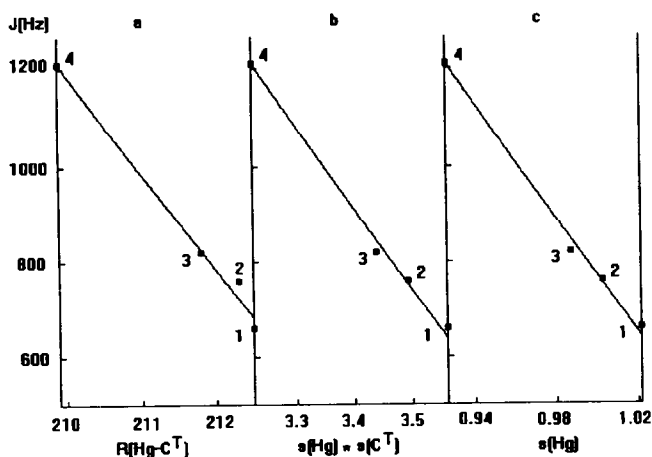


Fig. 1. Experimental coupling constants  $^1J(^{199}\text{Hg}-^{13}\text{C}_{\text{Bu}})$  for L-Hg-T ( $T = \text{}^i\text{Bu}$ ) [5] vs. calculated quantities for the model compounds L-Hg-T ( $T = \text{CH}_3$ ): (a) optimized bond lengths  $R(\text{Hg}-\text{C}_T)$  (in pm), (b) product of the  $s$  populations of Hg and  $\text{C}_T$ , (c)  $s$  population of Hg. 1:  $\text{CH}_2-\text{CH}_3$ , 2:  $\text{CH}_3$ , 3:  $\text{CH}=\text{CH}_2$ , 4:  $\text{C}=\text{CH}$ .

the calculated Hg- $\text{C}_T$  bond lengths in the model compounds L-Hg-T ( $T = \text{CH}_3$ ). Figure 1a shows that the relation between the two quantities is almost linear. We conclude from this relationship that the experimental coupling constant as well as the calculated bond distances are suitable measures to describe the bond strength between mercury and the *trans*-influenced organyl ligand.

From the theory of coupling constants it is known that their value should depend on the product of the  $s$  electron densities of the coupled atoms [13]. We check this assumption for the present coupling. Figure 1b indeed shows a clear linear relationship between the coupling constants and the product of the  $s$  populations of Hg and  $\text{C}_T$  (see the values in Tab. 1), thus confirming the usual assumptions. We split up the influences of the two coupled atoms. It emerges that the  $s$  population of the carbon atom of the *trans*-influenced group is almost unaffected. The  $s$  population of mercury is alone responsible for the changing of the coupling constants depending on the *trans*-influencing ligand (Fig. 1c).

We take the opportunity to mention that it is not possible to consider the  $s$  character of the two coupled atoms in only one special molecular orbital describing the Hg- $\text{C}_T$  bond as is sometimes done for proton coupling. In the present cases it is not possible to identify one single molecular orbital as being exclusively Hg- $\text{C}_T$  bonding. There are other orbitals of the same symmetry which mainly describe other bonds but which really have some Hg- $\text{C}_T$  bonding character as well. Therefore, the total  $s$  population of the coupled atoms has to be considered.

### trans-Influencing groups

As has been shown in the last section, experimental and calculated quantities describing the bond strength between mercury and the *trans*-influenced organyl group correspond to each other and can be understood in terms of the properties of the *trans*-influencing groups. Due to the computational effort of nonempirical geometry optimizations the investigation had to be restricted to some representa-

Table 3

Energy (in a.u.) and  $s$  character (see text) of the valence hybrid orbital for the anions  $L^-$  and the electronegativity-type energy quantity  $E_N$  (in a.u., see text) for the free organyl ligands  $L$

L	HOMO ( $L^-$ )	$s$ char. ( $L^-$ )	$E_N$ (L)
${}^iC_3H_7$	0.016	0.12	1.07
$CH_2-CH_3$	0.014	0.18	1.22
${}^nC_3H_7$	0.006	0.15	1.32
$CH_2-CH=CH_2$	-0.005	0.13	1.32
$CH_3$	0.020	0.22	1.40
$CH=CH_2$	-0.030	0.28	1.56
$CH_2-S-CH_3$	-0.064	0.15	1.72
$C\equiv CH$	-0.112	0.48	2.80

tive compounds. The question arises whether it is possible to correlate coupling constants  $J(Hg-C_T)$  measured for the complexes  $L-Hg-T$  with properties of the free organyl ligands  $L$ . We carried out calculations for a number of such ligands  $L$ . Table 2 contains the corresponding experimental coupling constants, which show the following *trans*-influence series:

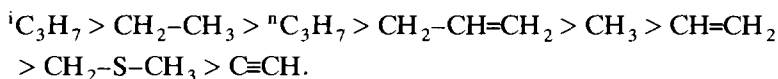


Table 3 shows calculated values for these organyl ligands which are in principle related to their donor ability. First, one would look at the energetic position of the HOMO of the organyl anions  $L^-$  which is considered as the valence hybrid donor orbital effecting the  $\sigma$  bond between  $L^-$  and the acceptor  $(Hg-T)^+$ . It turns out that the position of the HOMO does not correlate with the coupling constants. The same is true for the  $s$  character of the valence hybrid orbital.

We calculated a Mulliken-type electronegativity  $E_N = (I + A)/2$  for the organyl groups  $L$ . With ionization potential  $I = E(L^+) - E(L)$  and electron affinity  $A = E(L) - E(L^-)$  we have

$$E_N = (E(L^+) - E(L^-))/2,$$

with  $E(L^+)$  and  $E(L^-)$  denoting the total energies of the cation and the anion, respectively. We did not scale the calculated  $E_N$  values (see Tab. 3) in order to make them comparable with the Pauling values. The numerical values themselves are not important for the discussion of *trans*-influence series, but only their relative order and the differences between them. In Fig. 2 we show the relationship between these  $E_N$  values of the free organyl ligands  $L$  and the experimental coupling constants  $J(Hg-C_T)$  for the mercury complexes  $L-Hg-T$  ( $T = {}^iBu$ ). It emerges that there is a clear relationship between both quantities. In particular, the methylmercaptomethyl ligand  $CH_2-S-CH_3$  with a  $sp^3$ -hybridized carbon atom is correctly placed between  $CH=CH_2$  and  $C\equiv CH$  in agreement with the position of the coupling constants of the corresponding compounds. This agrees, moreover, with the order of the inductive substituent constants of Charton [14] and shows the remarkable influence of heteroatoms on the electronic properties of organyl ligands.

We would mention that the general results described in the present section do not depend significantly on the molecular geometry of the organyl groups. We

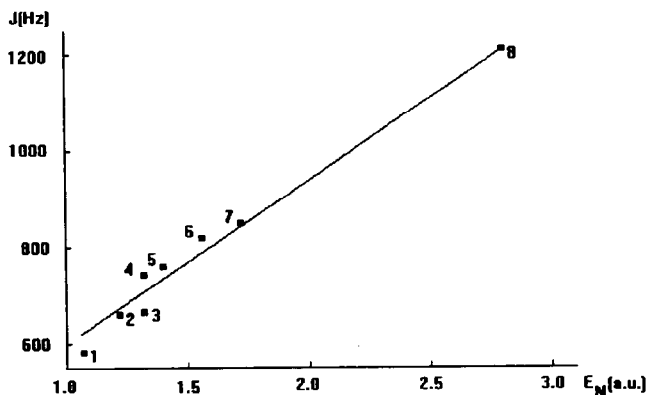


Fig. 2. Experimental coupling constants  ${}^1J({}^{199}\text{Hg}-{}^{13}\text{C}_{\text{Bu}}^i)$  for L-Hg-T (T =  ${}^i\text{Bu}$ ) [5] vs. the calculated electronegativity-type energy quantity  $E_N$  for the free organyl ligands L. 1:  ${}^1\text{C}_3\text{H}_7$ , 2:  $\text{CH}_2\text{-CH}_3$ , 3:  ${}^n\text{C}_3\text{H}_7$ , 4:  $\text{CH}_2\text{-CH=CH}_2$ , 5:  $\text{CH}_3$ , 6:  $\text{CH=CH}_2$ , 7:  $\text{CH}_2\text{-S-CH}_3$ , 8:  $\text{C}\equiv\text{CH}$ .

checked the effect of using only partially optimized geometries for the anions and of adopting model geometries for the cations fitted to experimental values of the corresponding molecules. We repeated the calculations using the same geometries for the anions as we had chosen for the cations. Again, neither the energetic position nor the *s* character of the anion donor valence hybrid orbital are suitable to describe the *trans*-influence on the coupling constants. Only the electronegativity-like energy quantity is able to describe the influence on the mercury *s* population in the complexes, which is consequently related to the coupling constants.

## Conclusions

In mercury organyl compounds L-Hg-T organyl groups L that are bound to Hg via a  $sp^3$ -hybridized carbon atom show the largest *trans*-influence, i.e. have the greatest weakening effect on Hg-T bond, whereas organyl groups that are bound to Hg via a  $sp$ -hybridized carbon atom show the smallest *trans*-influence, i.e. tend to strengthen this bond. In the case of  $sp^2$  hybridization an intermediate situation results. Increasing chain length of alkyl groups increases the *trans*-influence. This follows from the calculated bond lengths Hg-C<sub>T</sub> that we obtained from the geometry optimization of the model compounds L-Hg-CH<sub>3</sub>. It completely agrees with the order of the experimental coupling constants  $J(\text{Hg-C}_T)$  in L-Hg-T (T =  ${}^i\text{Bu}$ ). Larger *trans*-influence of L is connected with a more marked transfer of electronic density of L to Hg-T, i.e. with a lower electronegativity of L. From the analysis of the charge transfer values it follows that it is essentially the size of the total *s* electron population of mercury that influences the coupling constants. It seems to be possible to deduce from the properties of the free organyl ligands their *trans*-influence in mercury organyl complexes. However, only an electronegativity-like quantity allows such conclusions.

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