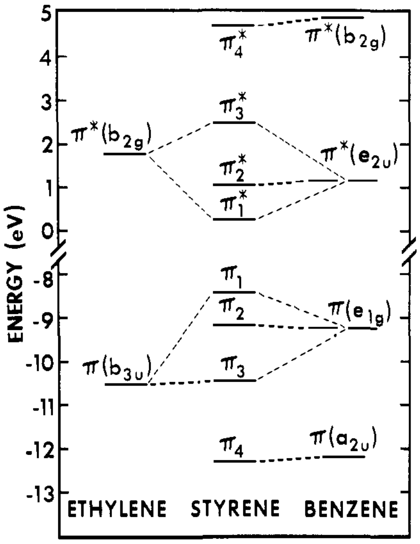


Figure 2. Correlation diagram showing experimental values for the anion and cation energies in ethylene, styrene, and benzene.

degenerate $e_{2u}(\pi^*)$ orbital, yielding the X^2E_{2u} ground state of the benzene anion. The lifetime of the anion is sufficiently long that a progression of vibrational levels of the symmetric breathing mode is observed. The feature near 4.85 eV is associated with the capture of an electron into the $b_{2g}(\pi^*)$ orbital.[9]

In styrene we expect four low-lying negative ion states. The bonding combination of the ethylene π^* orbital and the b_1 member[10] of the $e_{2u}(\pi^*)$ benzene orbital should lead to a negative ion ground state which is stabilized with respect to that of benzene. Similarly, the antibonding combination yields a state less stable than the X^2B_{2g} ethylene anion. We expect that the a_2 component[10] of the benzene $e_{2u}(\pi^*)$ orbital will be essentially unperturbed since, from symmetry considerations, it cannot mix directly with the ethylenic π^* orbital. Finally, the high-lying b_{2g} benzene orbital should be relatively unperturbed.

The four negative ion states of styrene are clearly distinguished in Figure 1 and are labeled as π_1^*–π_4^*. The lifetimes of the two lower states are sufficiently long to yield evidence of vibrational motion of the anion. The correlation diagram given in Figure 2 shows the experimentally determined anion and cation energies of styrene, benzene, and ethylene, and is in excellent agreement with the interaction picture described above. The EA's and IP's[11-13] for these three molecules are summarized in Table I.

In the right-hand column of the table, we list the values of (IP + EA) associated with each π, π^* pair. According to PPP theory, this quantity should be a constant for alternant hydrocarbons.[8] For comparison with the experimental data, the EA's and IP's generated by the semiempirical method of Younkin et al.[14] are also included. Although these calculations are based on the PPP method, certain modifications were introduced which cause the values of (IP + EA) to vary slightly. The spread is small, however, amounting to only 0.08 eV for the three molecules discussed here.

For styrene, the first three values of (IP + EA) determined from the experimental data are indeed consistent with a constant, 8.08 eV, to within ±0.11 eV, a spread which is commensurate with the experimental errors. Pairing of the lower-lying π and π^* levels in other alternant hydrocarbons we have studied also holds to good approximation and should allow the energies of stable anions to be predicted from those of the temporary anions. A detailed discussion of the negative ion states in the gas phase of several alternant hydrocarbons is in preparation.

The fourth anion state of styrene, as well as the third anion of benzene, lies considerably higher than the theoretical prediction. This displacement may result from the inadequacy of the theory in taking account of the increased diffuseness of the wave functions belonging to the high-lying states. Alternatively, the shift may be due to mixing with nearby doubly excited anion states.

Acknowledgments. We are grateful to R. N. Compton for providing us with a listing of the program described in ref 14. This work was supported in part by the National Science Foundation.

References and Notes

(1) L. Sanche and G. J. Schulz, *Phys. Rev. A*, **5**, 1672 (1972).
(2) L. Sanche and G. J. Schulz, *J. Chem. Phys.*, **58**, 479 (1973).
(3) I. Nenner and G. J. Schulz, *J. Chem. Phys.*, **62**, 1747 (1975).
(4) K. D. Jordan, J. A. Michejda, and P. D. Burrow, *J. Am. Chem. Soc.*, **98**, 1295 (1976); *J. Am. Chem. Soc.*, in press.
(5) P. D. Burrow and K. D. Jordan, *Chem. Phys. Lett.*, **36**, 594 (1975).
(6) P. D. Burrow and J. A. Michejda, *Chem. Phys. Lett.*, in press.
(7) K. D. Jordan, J. A. Michejda, and P. D. Burrow, *Chem. Phys. Lett.*, in press.
(8) For a discussion of the pairing theorem and PPP theory, see, for example, L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, N.Y., 1966.
(9) See ref 3 for a discussion of the assignments.
(10) We label the e_{2u} orbitals of the interacting benzene according to the C_{2v} point group.
(11) P. Masclet, D. Grosjean, G. Mouvier, and J. Dubois, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 225 (1973).
(12) L. Asbrink, E. Lindholm, and O. Edqvist, *Chem. Phys. Lett.*, **5**, 609 (1970); B. O. Jonsson and E. Lindholm, *Ark. Fys.*, **39**, 65 (1969).
(13) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).
(14) J. M. Younkin, L. J. Smith, and R. N. Compton, *Theor. Chim. Acta*, **41**, 157 (1976).

P. D. Burrow,* J. A. Michejda, K. D. Jordan*
Department of Engineering and Applied Science
Mason Laboratory, Yale University
New Haven, Connecticut 06520

Received June 1, 1976

Concerning the Formation of Compounds Containing Metal-to-Metal Multiple Bonds. A Stereospecific Alkyl-for-Chlorine Exchange Reaction Involving Compounds with Tungsten-to-Tungsten Triple Bonds

Sir:

The ability of metals to form multiple bonds with themselves and each other is now well documented.[1] However, the mechanisms leading to compounds with M–M multiple bonds are generally not known and have received little attention.[2] For example, the first compounds which were shown to contain M–M triple bonds unsupported by bridging ligands, $M_2(CH_2SiMe_3)_6$, where M = Mo and W, were unexpected products obtained from metathetic reactions involving $MoCl_5$ and WCl_6, respectively.[3] Recently the compounds $M_2(NR_2)_6$, where M = Mo[4] and W[5] and NR_2 = NMe_2, NMeEt, and NEt_2, have been isolated from similar reactions (MCl_n + nLiNR$_2$; M = Mo, n = 5; W, n = 6 and 4). The reaction pathway leading to the dinuclear compounds M_2L_6 (L = CH_2SiMe_3 and NR_2) is clearly of interest. We now report that the reaction between *anti*-$W_2Cl_2(NEt_2)_4$ and $LiCH_2SiMe_3$ (2 equiv) proceeds to give *anti*-$W_2(CH_2SiMe_3)_2(NEt_2)_4$, which under thermodynamic control isomerizes according to eq 1. This observation is significant in both its synthetic and mechanistic implications.

$$\underset{\text{a-I}}{\textit{anti}\text{-}W_2(CH_2SiMe_3)_2(NEt_2)_4} \rightleftarrows \underset{\text{g-I}}{\textit{gauche}\text{-}W_2(CH_2SiMe_3)_2(NEt_2)_4} \quad (1)$$

$$K \cong 4 \text{ at } 25\ ^\circ\text{C}$$

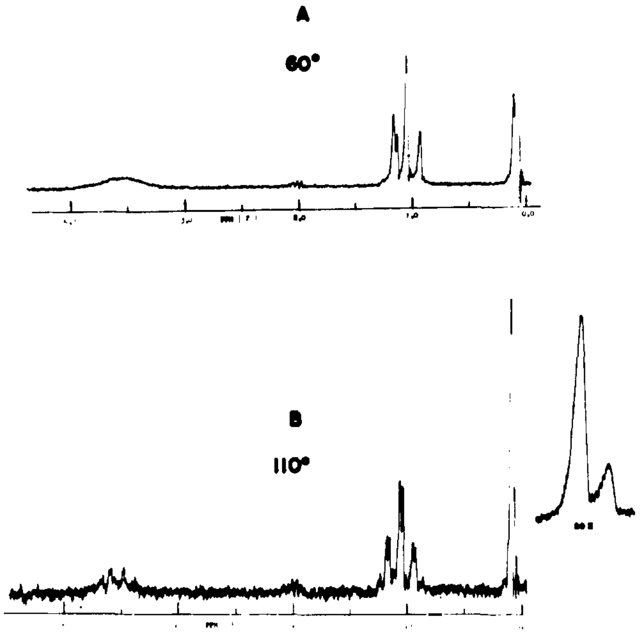


Figure 1. ^{1}H NMR spectra of $W_2(CH_2SiMe_3)_2(NEt_2)_4$ recorded in toluene-d_8 at 60 MHz: A, a-I rapidly heated to +60 °C; B, $t = \infty$ spectrum at +110 °C, [g-I]/[a-I] = ca. 5; the CH_2SiMe_3 resonances are shown at scale expansion ×50.

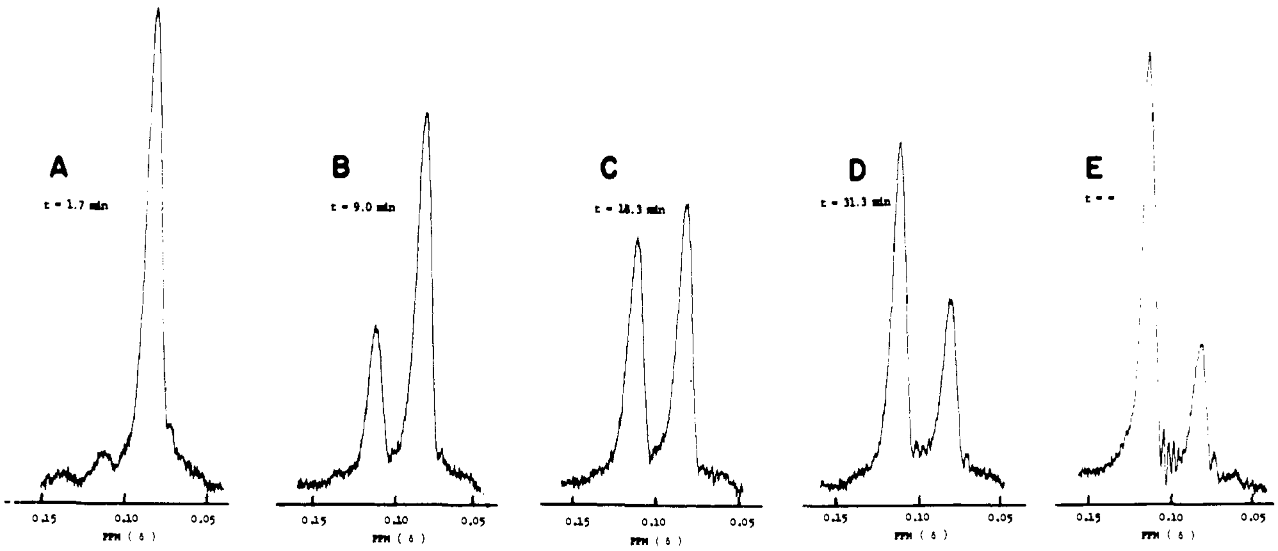


Figure 2. ^{1}H NMR spectra of the CH_2SiMe_3 resonances recorded at 54 °C during the anti to gauche isomerization reaction of $W_2(CH_2SiMe_3)_2(NEt_2)_4$: A, $t = 1.7$ min; B, $t = 9$ min; C, $t = 18.3$ min; D, $t = 31.3$ min, E, $t = \infty$.

$LiCH_2SiMe_3$ (333 mg, 2.54 mmol) in hexane (35 ml) was added dropwise to a magnetically stirred solution of $W_2Cl_2(NEt_2)_4$[6,7] (1.27 g, 1.77 mmol) in hexane (40 ml).[8] The solution was warmed to ca. 50 °C and a fine white precipitate (LiCl) formed. After 30 min the solvent was stripped, and the solids were extracted with hexane (50 ml). The LiCl was removed by centrifugation. The red hexane solution was concentrated to ca. 10 ml and cooled to −15 °C. Large red crystals of I were collected by filtration and dried in vacuo (25 °C, 10^{-4} cmHg, 1 h). Anal. Calcd for $W_2(CH_2SiMe_3)_2(NEt_2)_4$: C, 34.70; H, 7.52; N, 6.75. Found: C, 34.81; H, 7.35; N, 6.72.

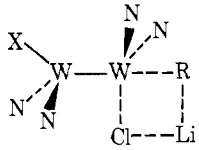
I is moisture sensitive but thermally quite stable and gives a strong parent ion, $W_2(CH_2SiMe_3)_2(NEt_2)_4^+$, in the mass spectrometer. I dissolved in toluene-d_8 showed a single resonance at δ 0.08 ppm (rel Me_4Si) assignable to the CH_2SiMe_3 protons. With time a new resonance at δ 0.12 ppm (rel Me_4Si) grew at the expense of the former. This we attribute to eq 1.

The assignment of anti and gauche rotamers of I is made on the basis of NMR studies. For example, crystals of I (prepared above) when dissolved in toluene-d_8 and rapidly heated to +60 °C in the probe of an A60 ^{1}H NMR spectrometer gave the spectrum shown in Figure 1A. At this temperature the rate of proximal–distal ethyl exchange[4] was sufficiently fast on the NMR time scale to give a 1:2:1 triplet for the $N(CH_2CH_3)_2$ protons, $J_{HH} = 7$ Hz. In the anti rotamer all eight diethylamido ethyl groups are equivalenced by the combined operations of the symmetry group C_{2h}, to which the $W_2Cl_2N_4$ moiety belongs, and W–N bond rotations. Under the above conditions, *rapid* heating of freshly dissolved I to 60 °C, the concentration of the gauche rotamer, [g-I], was small relative to that of the anti rotamer, [a-I]. With time the spectrum became more complex and then relatively simple when [g-I] > [a-I]. The $t = \infty$ spectrum, recorded at 110 °C, is shown in Figure 1B. The $N(CH_2CH_3)_2$ resonances appeared as two sets of overlapping 1:2:1 triplets. This was expected for the gauche rotamer since there are two independent pairs of NEt_2 ligands: the $W_2Cl_2N_4$ moiety belongs to the symmetry group C_2.

We have monitored the anti to gauche isomerization reaction by ^{1}H NMR spectroscopy at 20, 54, 61, and 76 °C (see Figure 2) making the assumption that [a-I] and [g-I] can be determined by the measurement of the peak heights of the CH_2SiMe_3 proton resonances. For the reaction a-I to g-I we calculate $\Delta G^\ddagger = 24.2 \pm 1.0$ kcal mol^{-1} and $\Delta S^\ddagger = 2.4 \pm 3.4$ eu.

The stereochemistry of the substitution reaction leading to I has been investigated as follows. $W_2Cl_2(NEt_2)_4$ (0.026 mmol) and $LiCH_2SiMe_3$ (0.07 mmol) were dissolved in toluene-d_8 (0.6 ml) in an NMR tube. The reaction was then followed by ^{1}H NMR spectroscopy at 40 °C. The CH_2SiMe_3 resonances of $LiCH_2SiMe_3$, a-I, and g-I were monitored. Within ca. 22 min the formation of I was complete and the [a-I] to [g-I] ratio was ca. 4 to 1. The equilibrium concentration of rotamers, [a-I]/[g-I] = ca. 1/4, was attained within ca. 48 h at 40 °C.

The simplest and most logical interpretation of this finding is that substitution of CH_2SiMe_3 for Cl occurs with retention of configuration at tungsten and proceeds via a bimolecular four-center mechanism. Schematically this exchange is depicted by II below. If the chlorine atom, the methylene carbon, and the two tungsten atoms are contained in the same plane, then the exchange of CH_2SiMe_3 for Cl will clearly proceed with retention of configuration at tungsten.



II

N = NEt$_2$
X = Cl or R
R = CH$_2$SiMe$_3$

The relative concentration of g-I at t = 22 min, [g-I]/[a-I] $\simeq$ 0.25, is ca. 10% larger than that expected from isomerization of the initially formed a-I. The presence of significant[9] concentrations of *gauche*-$W_2Cl_2(NEt_2)_4$ in equilibrium with *anti*-$W_2Cl_2(NEt_2)_4$, or anti to gauche isomerization of an intermediate such as $W_2Cl(CH_2SiMe_3)(NEt_2)_4$, could contribute to the formation of g-I.

The above, together with previous findings,[7] indicate that compounds containing metal-to-metal triple bonds may be systematically synthesized by metathetic reactions involving compounds already containing metal-to-metal triple bonds. Moreover, in the present study the stereochemical course of the substitution reaction leading to I implies that cleavage of the tungsten-to-tungsten bond does *not* occur during the alkyl-for-chlorine exchange process. It seems likely that reactions analogous to that reported here are responsible for the ultimate formation of the dinuclear compounds M_2L_6 (M = Mo or W, L = CH_2SiMe_3 or NR_2) from metathetic reactions involving molybdenum and tungsten halides.

The mechanism of isomerization reactions of type 1 is currently under investigation.[10]

References and Notes

(1) F. A. Cotton, Chemical Society Centenary Lecture 1974; *Chem. Soc. Rev.*, **4**, 27 (1975).

(2) Rather interestingly the reverse reaction, cleavage of M–M multiple bonds by either chemical or photochemical means, has received more attention. For example, the $Re_2Cl_8^{2-}$ anion, which provided the first example of a quadruple bond (ref 1), has recently been shown to undergo a photocleavage reaction:

$$Re_2Cl_8^{2-} \xrightarrow[CH_3CN]{h\nu} 2ReCl_4(CH_3CN)_2^-$$

G. L. Geoffroy, H. B. Gray, and G. S. Hammond, *J. Am. Chem. Soc.*, **96**, 5565 (1974); **98**, 48 (1976).

(3) (a) F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1709 (1971); (b) W. Mowat, A. J. Shortland, G. Yagupski, M. Yagupski, N. J. Hill, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 533 (1972).

(4) (a) M. H. Chisholm and W. W. Reichert, *J. Am. Chem. Soc.*, **96**, 1249 (1974); (b) M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, and L. Shive *J. Chem. Soc., Chem. Commun.*, 480 (1974); (c) M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, L. W. Shive, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4469 (1976).

(5) (a) M. H. Chisholm, F. A. Cotton, M. Extine, B. R. Stults, and J. M. Troup, *J. Am. Chem. Soc.*, **97**, 1242 (1975); (b) M. H. Chisholm, F. A. Cotton, M. Extine, and B. R. Stults, *ibid.*, **98**, 4477 (1976).

(6) M. H. Chisholm and M. Extine, *J. Am. Chem. Soc.*, **97**, 5625 (1975).

(7) *anti*-$W_2Cl_2(NEt_2)_4$ has been characterized by x-ray studies. The anti rotamer is the only NMR detectable species present in benzene, toluene, and mesitylene solutions. M. H. Chisholm, F. A. Cotton, M. Extine, M. Millar, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4486 (1976). $W_2Cl_2(NEt_2)_4$ has been shown to react with MeLi to give $W_2Me_2(NEt_2)_4$, which exists in solution as a mixture of anti and gauche rotamers. M. H. Chisholm, F. A. Cotton, M. Extine, and B. R. Stults, *Inorg. Chem.*

(8) Standard techniques for the manipulation of air-sensitive compounds were used at all times. D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.

(9) If a $\rightleftarrows$ g isomerization were facile for $W_2Cl_2(NEt_2)_4$ and the gauche rotamer were kinetically more labile to substitution than the anti rotamer, then significant concentrations of g-I would be formed initially.

(10) We thank Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant No. MPS 73-05016) for their support of this work.

Malcolm H. Chisholm,* Michael W. Extine
Department of Chemistry, Princeton University
Princeton, New Jersey 08540
Received June 10, 1976

Reaction Ergodography. Methane–Tritium Reaction

Sir:

Detailed description of chemical reactions has long been one of the goals of theoretical chemistry. Since chemical reactions are usually attended with much complexity in the modes of nuclear rearrangements corresponding to the change of the reacting system from initial to final, the concept of the reaction coordinate has been conveniently utilized to abstract the essential feature for the rationalization of chemical reactions. Many theoretical attempts have been made to determine the reaction coordinate or the minimum energy path of various types of chemical reactions with the aid of semiempirical and ab initio molecular orbital procedures.[1] The only difficulty in this direction of research is the multidimensionality of the potential-energy surfaces. In this connection, a proposal was made previously about the theoretical formulation of the reaction coordinate and it is named the intrinsic reaction coordinate.[2] Such a theoretical formulation of the reaction coordinate enables a theoretical tracing of the change of geometry of the reacting system along the reaction path, which was called reaction ergodography.[3] Also an analysis was made on the potential-energy gradient on the reaction coordinate to discuss the favorableness or the unfavorableness of a given reaction path in relation to the mode of interaction between two reacting species.[4]

Another utility of the reaction coordinate is demonstrated in the description of the reactive collision process. Marcus[5] defined the natural collision coordinate in the three-body reactive scattering. In order to treat the dynamics of a polyatomic system, a more generalized definition of the reaction coordinate is required. The intrinsic reaction coordinate is suitable for such a purpose.

In this communication, we illustrate the intrinsic reaction coordinate of the methane–tritium reaction system and its isotopic analogy.[6] Both the abstraction,

$$CH_4 + T \rightarrow CH_3 + HT \qquad (I)$$

$$CD_4 + T \rightarrow CD_3 + DT \qquad (II)$$

and the substitution,

$$CH_4 + T \rightarrow CH_3T + H \qquad (III)$$

$$CD_4 + T \rightarrow CD_3T + D \qquad (IV)$$

were examined.

Since the formulation of the intrinsic reaction coordinate was given previously,[2-4] we give a brief description here. Consider a reacting system composed of N atoms, the reaction coordinate is defined in terms of the gradient of the potential-energy function, $W(\xi_1, \xi_2, \ldots, \xi_f)$, in which ξ_i is the independent internal coordinate such as the bond length or the bond angle, and f is the number of the internal degrees of freedom. At a nonequilibrium point on the reaction coordinate, the direction of the displacement vector along the reaction coordinate is defined as

$$\frac{\sum_{j=1}^{f} g_{ij}(\xi)\mathrm{d}\xi_j}{\partial W/\partial \xi_i} = \text{constant} \quad (i = 1, 2, \ldots, f) \qquad (1)$$

and

$$g_{ij}(\xi) = \sum_{k=1}^{3N} \frac{\partial x_k}{\partial \xi_i}\frac{\partial x_k}{\partial \xi_j}$$

where x_k is the mass-weighted Cartesian coordinate which represents the position of an atom in the configuration space. Equation 1 can be rewritten with the mass-weighted Cartesian coordinates as follows,