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AN MNDO STUDY OF STRUCTURES AND STABILITIES OF REPRESENTATIVE 1-CHLORO-1-ALKENES AND OF THEIR BERYLLIUM HYDRIDE DERIVATIVES.

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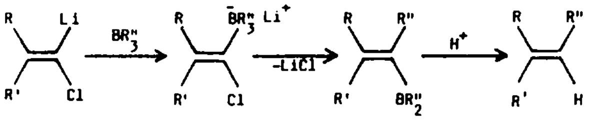
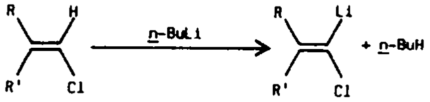
MNDO calculations were applied in order to investigate the inherent stabilities of 1-chloro-1-alkenes and their beryllium hydride derivatives. The calculated geometries and atomic charges are compared with applicable experimental findings. The calculations also explain the observed relative stabilities of metallated 1,2-dichloroalkenes. The two factors which increase the stabilization of compounds in this series are: the absence of a chlorine substituent trans to the metal and the degree of polarization of the C-Cl bond being broken.

Metallated 1-chloro-1-alkenes are potentially synthetically useful in reactions with organometals to generate trisubstituted alkenes, which are found in biologically active molecules such as prostaglandins and insect pheromones.



(1)

With proper choice of substituents (R,R'), metallated chloroalkenes have been formed by reacting n-butyllithium with chloroalkenes at low temperatures.[1-8]

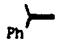
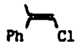
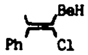
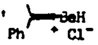
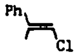
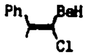
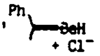
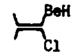
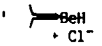
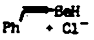
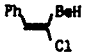
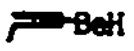
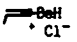


(2)

Usually, the substituents, R and R', were Ar or Cl.[1-5,7-11] In the absence of a stabilizing complexing agent such as TMEDA,[12] simple metallated compounds (R,R' = alkyl) are unstable even at low temperatures. However, biologically important trisubstituted alkenes do not necessarily possess the stabilizing substituents mentioned above, so the degree of generality of the reaction is of interest. An understanding of the factors influencing the stability of the system will enable the educated selection of substituents and increase the synthetic utility of the reaction. Consequently, it is desirable to investigate such factors of metallated chloroalkenyl compounds.

While the solvent probably plays an integral role in the stability of this system, it is also useful to examine the inherent stability of these molecules via molecular orbital calculations. MNDO has been shown to give reliable results for compounds containing chlorine.[13,14] Beryllium hydride has been used as a model for lithium in previous MNDO calculations,[15,16] and, therefore, it should be suitable for these studies as well. Accordingly, we have carried out MNDO calculations in order to investigate the structures and stabilities of a variety of 1-chloro-1-alkenes and of their beryllium hydride derivatives.

Table I. Optimized Bond Lengths or Distances Between Atoms of Various Chloroalkenes and Their Derivatives Calculated Using MNDO.

compd. no.	Bond Lengths or Distances Between Atoms (Å)				
	C(1)-C(2)	C(1)-4	C(1)-3	C(2)-H or Cl	C(2)-H or BeH
1 	1.354	1.514	1.489	1.087	1.090
2 	1.365	1.521	1.489	1.099	1.652
3 	1.359	1.526	1.487	1.747	1.092
4 	1.362	1.528	1.488	1.797	1.664
4' 	1.335	1.522	1.485	3.183	1.672
5 	1.364	1.495	1.513	1.104	1.656
6 	1.356	1.494	1.514	1.753	1.086
7 	1.364	1.498	1.513	1.788	1.666
7' 	1.335	1.483	1.525	3.173	1.675
8 	1.348	1.508	1.509	1.090	1.089
9 	1.357	1.513	1.511	1.106	1.647
10 	1.349	1.512	1.509	1.752	1.088
11 	1.355	1.514	1.510	1.810	1.659
11' 	1.325	1.516	1.517	3.182	1.673
12 	1.345	1.098	1.474	1.088	1.090
13 	1.354	1.101	1.477	1.104	1.643
14 	1.345	1.103	1.471	1.746	1.090
15 	1.351	1.105	1.473	1.799	1.656
15' 	1.325	1.105	1.469	3.109	1.675
16 	1.353	1.478	1.098	1.104	1.659
17 	1.346	1.473	1.097	1.753	1.086
18 	1.352	1.475	1.098	1.805	1.655
18' 	1.325	1.469	1.105	3.199	1.665
19 	1.340	1.096	1.496	1.089	1.090
20 	1.349	1.099	1.499	1.106	1.642
21 	1.341	1.098	1.495	1.750	1.088
22 	1.347	1.100	1.498	1.799	1.655
22' 	1.318	1.101	1.503	3.185	1.668

RESULTS AND DISCUSSION

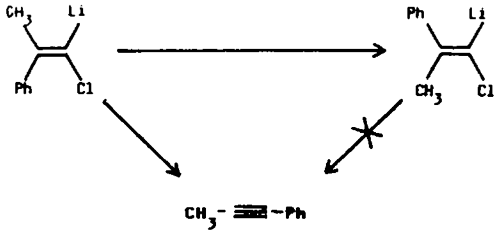
The effects of substituents upon the stabilities of metallated 1-chloro-1-alkenes are not understood.^{7} In order to analyze studies of such effects upon these compounds, it is helpful to classify them with respect to the type of substituent as well as to the substitution pattern on the double bond.

I. Alkyl Substituents

The two patterns of substitution we shall consider when C(2) has only alkyl substituents are 2,2-disubstituted compounds and 2-substituted compounds.

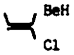
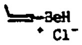
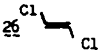
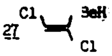
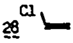
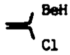
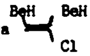
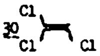
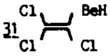
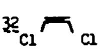
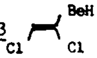
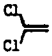
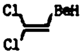
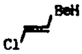
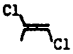
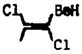
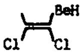
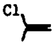
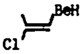
A. 2,2-Dialkyl Compounds (2-Alkyl-1-chloro-1-alkenes).

When R and/or R' is an aryl substituent, the metallated 2,2-disubstituted chloroalkenes can undergo two rearrangements which detract from their synthetic utility: the Fritsch-Buttenburg-Wiechell (FBW) rearrangement$^{17-19}$ and cis-trans isomerization. The FBW rearrangement is the migration of an aryl group occurring simultaneously with α-elimination of lithium chloride. The second rearrangement, cis-trans isomerization, has been studied in detail for metallated *Z*-2-chloro-1-methylstyrene (**4**).^{7} It has been found that the E isomer **7** does not undergo the cis-trans isomerization at temperatures at which the Z isomer will do so.^{7}

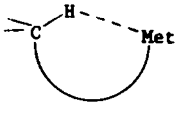


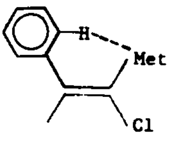
(3)

Table I. (Continued)

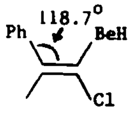
compd. no.	Bond Lengths or Distances Between Atoms (Å) C(1)-C(2)	C(1)-4	C(1)-3	C(2)-H or Cl	C(2)-H or BeH
23 	1.348	1.499	1.099	1.109	1.642
24 	1.342	1.499	1.095	1.751	1.087
25 	1.346	1.500	1.097	1.809	1.655
25' 	1.317	1.502	1.102	3.144	1.673
26 	1.339	1.748	1.087	1.747	1.087
27 	1.343	1.754	1.088	1.791	1.664
28 	1.336	1.751	1.087	1.090	1.088
29 	1.341	1.092	1.090	1.799	1.652
29a 	1.341	1.651	1.103	1.837	1.655
30 	1.343	1.743	1.734	1.740	1.089
31 	1.346	1.749	1.737	1.780	1.671
32 	1.339	1.089	1.742	1.742	1.089
33 	1.342	1.091	1.747	1.784	1.660
34 	1.339	1.742	1.742	1.089	1.089
35 	1.340	1.752	1.748	1.107	1.659
36 	1.339	1.089	1.761	1.106	1.647
37 	1.339	1.764	1.088	1.108	1.653
38 	1.346	1.763	1.499	1.747	1.088
39 	1.351	1.772	1.499	1.787	1.667
40 	1.346	1.503	1.754	1.742	1.089
41 	1.349	1.506	1.760	1.795	1.664
42 	1.343	1.764	1.499	1.090	1.089
43 	1.347	1.780	1.500	1.105	1.657
44 	1.346	1.502	1.775	1.111	1.651

An interesting aspect of this system is that the E isomer is unusually stable and does not undergo the elimination to form the alkyne, or revert to the Z isomer.[7] Thus, at low temperatures, having an aryl substituent cis to the metal substituent decreases the reactivity toward either the FBW rearrangement or the cis-trans isomerization. A possible explanation for the stability of the E isomer is the interaction of the ortho C-H of the phenyl group with the metal atom, similar to the agostic bond a carbon-hydrogen bond can form with a transition metal.[27]





Support for this possibility derives from Ph-C=C and C=C-B angles in **7** compared to those in **6** and **15**. (See Table II; a legend for atom numbering is provided in Chart 1.)



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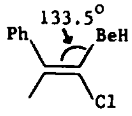

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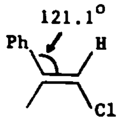

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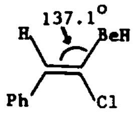
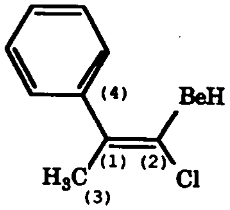


15

Table II. Optimized Bond Angles and Heats of Formation of Various Chloroalkenes and Their BeH Derivatives Calculated Using MNDO.

compd. no.	Bond Angles C(1)-C(2) -H or Be	3-C(1) -C(2)	4-C(1) -C(2)	C(1)-C(2) -H or Cl	ΔH$_f$ kcal/mol
1	122.9	123.2	117.9	125.5	36.7
2	121.6	125.2	116.2	121.0	24.1
3	122.1	128.5	111.5	131.3	33.8
4	135.7	130.6	112.1	127.9	17.0
4'	171.5	122.6	116.5	155.4	20.6
5	127.6	120.0	121.1	118.1	22.7
6	126.5	121.1	121.0	125.8	28.8
7	133.5	123.2	118.7	122.2	12.7
7'	177.4	114.9	124.2	149.1	20.8
8	123.7	121.1	121.8	123.6	-1.8
9	128.5	122.9	121.4	117.9	-14.8
10	125.4	123.7	119.7	124.9	-11.4
11	142.8	124.7	119.2	120.8	-26.6
11'	173.2	120.7	121.9	153.8	-16.7
12	121.6	128.9	116.9	125.5	39.0
13	127.0	129.7	117.3	119.5	24.9
14	122.0	134.1	113.0	128.8	31.6
15	137.0	135.4	112.5	125.0	15.5
15'	175.4	129.5	114.8	146.2	24.8
16	127.7	119.0	126.6	116.5	25.3
17	127.8	118.2	127.6	121.7	28.9
18	142.7	119.2	126.6	117.3	13.1
18'	174.1	113.7	130.5	153.7	24.6
19	122.4	127.0	119.3	124.5	4.9
20	128.0	127.1	119.8	118.0	-9.4
21	124.3	129.1	116.9	125.0	-4.8
22	138.3	130.0	116.8	120.9	-21.5
22'	172.8	127.0	118.4	154.3	-9.3

compd. no.	Bond Angles C(1)-C(2) -H or Be	3-C(1) -C(2)	4-C(1) -C(2)	C(1)-C(2) -H or Cl	ΔH$_f$ kcal/mol
23	131.8	119.7	127.4	116.0	-8.6
24	126.5	120.5	124.8	122.4	-5.1
25	144.4	121.0	125.3	117.6	-21.5
25'	176.6	117.3	128.1	148.7	-9.1
26	126.6	126.8	121.2	121.5	-3.9
27	139.0	127.6	121.3	116.6	-21.1
28	124.5	125.8	122.9	121.5	4.8
29	139.3	125.0	121.7	118.2	-12.4
29a	147.8	120.6	121.6	119.9	-29.1
30	124.1	125.8	120.9	124.1	-6.6
31	136.4	127.1	120.6	120.0	-23.8
32	122.9	125.5	122.9	125.5	-2.6
33	135.6	126.5	123.0	121.6	-20.7
34	122.9	123.4	123.4	122.9	0.0
35	130.7	124.6	123.6	117.5	-15.8
36	128.5	123.7	126.6	118.8	-11.5
37	130.9	127.2	122.8	115.8	-10.6
38	125.5	128.9	116.2	123.5	-11.5
39	136.0	130.5	115.2	119.3	-28.0
40	123.6	121.1	124.1	125.5	-10.3
41	141.7	121.9	124.4	121.6	-26.4
42	123.9	126.8	118.3	122.5	-3.2
43	127.2	128.8	117.2	117.3	-17.9
44	131.8	119.4	128.2	117.8	-17.8



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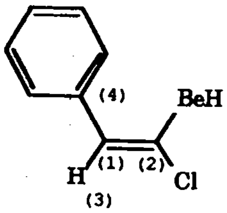

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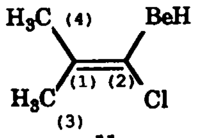

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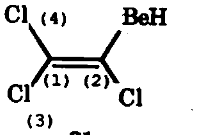

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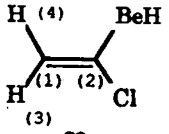

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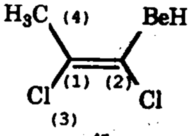


41

Chart 1

The bond angles in **7** are compressed relative to those in analogous structures without the metal or the phenyl group. In addition, bonding interactions of Be with the ortho C and H of phenyl are apparent in the bond order matrix.

Ionic intermediates in these stereospecific reactions and rearrangements of α-haloalkenylmetals were originally discounted due to reasoning that their linear geometry should prohibit stereospecificity.[7] However, Walborsky proposed tight ion pairs could retain the stereochemical identity of their precursor and allow stereospecific reactions.[20] Using MNDO, we have examined isomers of both covalent and ionic forms of α-chloromethylstyrylberyllium hydride in order to probe the existence of such intermediates. Energy minima were located corresponding to cis and trans isomers of both forms. It seems logical that the reactions of these compounds with nucleophiles would be more likely to go through the ionized form. Therefore, the relative resistance of the E isomer to reaction and cis-trans rearrangement is possibly founded not only upon its greater stability, but also upon its higher energy barriers to ionization and to isomerization.

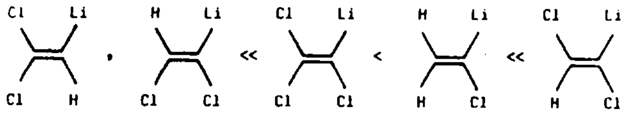
The metallated 1-chloro-2,2-dialkyl compounds do not undergo either of the rearrangements discussed above. Instead, they readily polymerize or undergo a rapid reaction with a second equivalent of n-butyllithium,[11] in the absence of a stabilizing compound such as TMEDA.[12] Our calculations reveal no basis for predicting an unusual nucleophilicity or electrophilicity of the covalent or ionic forms of these compounds. The difference in the reactivity of these compounds compared to those discussed above could be due to solvent effects which are not taken into consideration here.

B. 2-alkyl Compounds (1-Chloro-1-alkenes).

Metallated 2-substituted chloroalkenes are not stable regardless of the character of the substituents, R.[7] These compounds decompose by eliminating hydrogen halides probably through an E2 mechanism.[2,5,7] A base such as n-butyllithium or a second molecule of the metallated chloroalkene probably abstracts the olefinic proton, resulting in the formation of the lithium acetylide.[2,5,7] Data from our calculations predict no unusual nucleophilicity or electrophilicity of the covalent or ionic form of this system. Therefore, the reason for the apparent instability is probably the propensity of this system toward the E2 mechanism, as proposed earlier.[2,5,7] This is in agreement with the observation that the metallated cis compounds are less stable than the trans isomers even in the presence of the stabilizing complexing agent TMEDA.[12]

II. Chloro Substituents.

The observed order of increasing stability of metallated chloroalkenes[2,7] is:



This ordering probably arises at least partially from the lowered stability of compounds, such as **35**, **33**, and **31**, having a chlorine substituent trans to the metal.[7] A trans alignment of these leaving groups greatly facilitates elimination, and affects the stabilities of the compounds. Therefore, these compounds are grouped according to the relationship of the metal to the chlorine atom(s).

Table III. Atomic Charges ~~of~~ Various Chloroalkenes and Their BeH Derivatives

compd.	Atomic Charges					
	C(1)	C(2)	H or Cl	3	4	H or Be
1	-0.101	-0.033	0.040	-0.026	0.076	0.038
2	-0.040	-0.281	0.039	-0.036	0.074	0.464
3	-0.056	0.007	-0.123	-0.038	0.066	0.073
4	-0.015	-0.174	-0.173	-0.050	0.069	0.489
4'	-0.147	0.316	-0.374	-0.065	0.078	0.183
5	-0.052	-0.267	0.038	0.071	-0.020	0.438
6	-0.062	0.014	-0.131	0.067	-0.041	0.080
7	-0.036	-0.167	-0.167	0.064	-0.033	0.477
7'	-0.148	0.318	-0.375	0.077	-0.065	0.183
8	-0.172	-0.033	0.038	0.080	0.081	0.038
9	-0.095	-0.284	0.034	0.068	0.071	0.475
10	-0.139	0.020	-0.133	0.075	0.076	0.081
11	-0.089	-0.157	-0.187	0.067	0.072	0.496
11'	-0.247	0.342	-0.369	0.089	0.089	0.183
12	-0.062	-0.053	0.042	-0.043	0.045	0.039
13	0.027	-0.311	0.039	-0.061	0.026	0.478
14	-0.025	-0.003	-0.125	-0.057	0.054	0.077
15	0.031	-0.188	-0.177	-0.070	0.046	0.497
15'	-0.126	-0.318	-0.384	-0.074	0.129	0.186
16	0.000	-0.294	0.039	0.037	-0.049	0.458
17	-0.029	-0.001	-0.134	0.066	-0.057	0.085
18	0.020	-0.181	-0.185	0.061	-0.064	0.498
18'	-0.124	0.305	-0.369	0.129	-0.072	0.183
19	-0.129	-0.053	0.040	0.068	0.049	0.037
20	-0.039	-0.310	0.038	0.053	0.030	0.478
21	-0.099	0.005	-0.131	0.065	0.063	0.081
22	-0.044	-0.181	-0.181	0.055	0.054	0.504
22'	-0.220	0.334	-0.369	0.087	0.137	0.183
23	-0.042	-0.309	0.035	0.035	0.055	0.478
24	-0.101	0.004	-0.133	0.072	0.064	0.084
25	-0.048	-0.173	-0.189	0.065	0.059	0.501
25'	-0.223	0.339	-0.372	0.142	0.086	0.183
26	0.003	0.002	-0.105	0.103	-0.106	0.103
27	0.054	-0.184	-0.152	0.098	-0.121	0.530
28	-0.015	-0.055	0.057	0.084	-0.134	0.063
29	0.003	-0.204	-0.182	0.055	0.049	0.510
29a	-0.266	-0.097	-0.227	0.066	0.503	0.481
30	0.030	0.024	-0.073	-0.035	-0.055	0.110
31	0.083	-0.168	-0.114	-0.045	-0.070	0.537
32	-0.004	-0.004	-0.091	-0.091	0.094	0.094
33	0.058	-0.201	-0.131	-0.108	0.086	0.522
34	0.018	-0.022	0.073	-0.071	-0.071	0.073
35	0.105	0.281	0.076	-0.091	-0.097	0.518
36	0.080	-0.320	0.068	-0.162	0.070	0.501
37	0.071	-0.308	0.059	0.075	-0.165	0.504
38	-0.028	0.019	-0.106	-0.070	-0.112	0.101
39	0.021	-0.166	-0.151	0.064	-0.130	0.528
40	-0.037	0.013	-0.091	-0.092	0.070	0.093
41	0.021	-0.176	-0.135	-0.107	0.065	0.510
42	-0.051	-0.033	0.055	0.073	-0.135	0.062
43	0.027	-0.280	0.056	0.065	-0.166	0.500
44	0.037	-0.296	0.062	-0.162	0.064	0.500

A. Metallated Compounds without Trans Chlorine.

The stability of these compounds is most likely due to absence of a trans elimination pathway for decomposition. Compounds **27** and **29** belong to this category. The reason for the greater reactivity of compound **29**[2,5,7] is probably that it can undergo a second deprotonation in a manner similar to the compounds discussed in Section I.B. above.

B. Metallated Compounds with Trans Chlorine.

These compounds, such as **35**, **33**, and **31** lack stability because a trans elimination of LiCl is possible. Our calculations show that electronic features may account for the order of stability among these compounds. It has been observed that the metallated 1,1-dichloroethylene **35** and metallated *cis*-dichloroethylene **33** are less stable than the metallated trichloro compound **31**.[2,7] The polarization (Table III) of the C-Cl bond trans to the metal correlated with the relative reactivities of the compounds. Our MNDO calculations indicate that the C-Cl bond is more polarized in **35** (0.105-(-0.091) = 0.195) and **33** (0.050-(-0.108) = 0.166) than in **31** (0.083-(-0.045) = 0.128) and that chlorine in each of **35** and **33** has more negative charge and therefore should be a better leaving group. (However, it should be noted that when there is a chlorine substituent cis to the metal, the C-Cl bond is more polarized and the corresponding chlorine atom bears more negative charge than in the trans isomer. Thus, the trans orientation of leaving groups must be the major influence upon the reactivity of these systems).

Metallated vinyl chloride **29** is a unique case. Upon exposure to *n*-butyllithium, initially the proton α to chlorine is replaced by the metal because it is the most acidic one.[2,7] However, **29** does not have a chlorine substituent trans to the metal and the C-Cl bond is not greatly polarized. The subsequent formation of the lithium acetylide from the analog of **29a**[2,5,7] is probably via an E2 elimination, similar to the compounds in Section I.B. above.

C. Metallated 2-Chloropropenes.

Metallated 2-chloropropenes such as **39**, **41**, **43**, and **44** should behave in a manner similar to compounds in Sections II.A. and II.B. above. While the effect is diminished, our calculations again show a greater increase in C-Cl bond polarization when the metal is trans to chlorine. The increase in polarization of the electron density in the C-Cl bond in **41** compared to that in the parent compound **40** is 0.73 (=0.128 - 0.055). The corresponding C-Cl bond polarization increase in **39** compared to **38** is less (0.067 = 0.151 - 0.084). The C-Cl bond in **44** is slightly more polarized than that in **43**. Thus, **39** and **43** are predicted to be more stable than **41** and **44**, respectively.

CONCLUSION.

The resistance of metallated E-2-chloro-1-methylstyrene towards reaction and cis-trans rearrangement is probably due not only to its greater stability, but also to higher energy barriers to ionization and isomerization. Our calculations reveal no inherent reason for the highly reactive and unstable nature of the 2-alkyl-1-chloroalkenes. Similarly, we also found no inherent lack of stability of the metallated 1-chloroalkenes; the apparent instability is probably due to the propensity of this system for an E2 elimination. 1,2-Dichloroalkenes metallated trans to chlorine have lengthened C-Cl bonds as well as increased electron densities on chlorine, and therefore, the trans relationship should increase the likelihood of an elimination. As a secondary consideration, the degree of polarization of the C-Cl bond which is being broken correlates with the stability of the compound.

THEORETICAL PROCEDURE.

The calculations were carried out using the MNDO molecular orbital approximation[22] obtained through QCPE.[23] The computations were executed following the recommended procedure.[24] Minimum energy geometries were found by using the standard Davidon-Fletcher-Powell[25,26] optimization procedure.

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REFERENCES

1. Köbrich, G.; et al. *Chem. Ber.* **1966**, *99*, 670, 680, 1782, 1793.
2. Köbrich, G.; Flory, K. *Chem. Ber.* **1966**, *99*, 1773-1781.
3. Köbrich, G.; et al. *Chem. Ber.* **1967**, *100*, 961, 2011.
4. Köbrich, G.; Trapp, H.; Hornke, I. *Tetrahedron Lett.* **1964**, 1131-1136.
5. Köbrich, G.; Flory, K. *Tetrahedron Lett.* **1964**, 1137-1142.
6. Cohen, B.J.; Kraus, M.A.; Patchornik, A. *J. Am. Chem. Soc.* **1981**, *103*, 7620-7629.
7. Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 41-52.
8. Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 473-485.
9. Köbrich, G.; Merkel, D.; Thiem, K.W. *Chem. Ber.* **1972**, *105*, 1683-1693.
10. Köbrich, G.; Merkel, D. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 243-244.
11. Köbrich, G. *Angew Chem., Int. Ed. Engl.* **1965**, *4*, 49-68.
12. (a) Nelson, D.J. Unpublished results.
    (b) Cunico, R.F.; Han, Y.-K. *J. Organomet. Chem.* **1978**, *162*, 1-16.
13. Dewar, M.J.S.; McKee, M.L.; Rzepa, H.S. *J. Am. Chem. Soc.* **1978**, *100*, 3607.
14. Nelson, D.J.; Dewar, M.J.S.; Buschek, J.M.; McCarthy, E.J. *J. Org. Chem.* **1979**, *44*, 4109-4113.
15. Dewar, M.J.S.; Rzepa, H.S. *J. Am. Chem. Soc.* **1978**, *100*, 777-790.
16. (a) Dewar, M.J.S.; Fox, M.A.; Nelson, D.J. *J. Organometal. Chem.* **1980**, *185*, 157-181.
    (b) Dewar, M.J.S.; Nelson, D.J. *J. Org. Chem.* **1982**, *47*, 2614-2618.
    (c) Nelson, D.J. *J. Org. Chem.* **1986**, *51*, 3185.
17. Fritsch, P. *Liebigs Ann. Chem.* **1894**, *279*, 319-323.
18. Buttenburg, W.P. *Liebigs Ann. Chem.* **1894**, *279*, 324-337.
19. Wiechell, H. *Liebigs Anan. Chem.* **1894**, *279*, 337-344.
20. (a) Walborsky, H.M.; Duraisamy, M. *Tetrahedron Lett.* **1985**, 2743-6.
    (b) Duraisamy, M.; Walborsky, H.M. *J. Am. Chem. Soc.* **1984**, *106*, 5035-7.
21. Tobey, S.W. *J. Org. Chem.* **1969**, *34*, 1281-98. NMR data indicate that the phenyl group is coplanar with the double bond in chlorostyrene. Therefore, this geometrical constraint was imposed in all our calculations.
22. (a) Dewar, M.J.S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899-4907.
    (b) Dewar, M.J.S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907-4917.
23. *Quantum Chemistry Program Exchange*, Indiana University, Bloomington, IN. Program 353.
24. Dewar, M.J.S. *Faraday Discuss. Chem. Soc.* **1977**, *62*, 197.
25. Fletcher, R.; Powell, M.J.D. *Comput. J.* **1963**, *6*, 163-168.
26. Davidon, W.C. *Comput. J.* **1968**, *10*, 406-410.
27. Brookhart, M.; Green, M.L.H. *J. Organomet. Chem.* **1983**, *250*, 395-408.