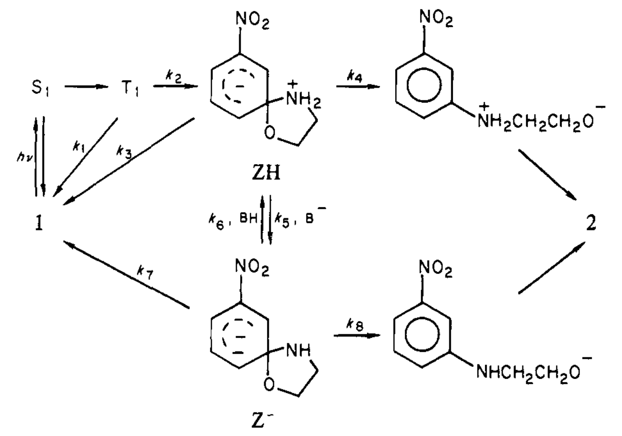
Scheme I



expressions below were derived by assuming a steady state for each intermediate. For the case of general base catalysis ($k_6 \ll k_7 + k_8$), eq 1 results, where $f = k_8/(k_7 + k_8)$ and $k_5[B]$ is the summation $\sum_i k_5^{B_i}[B_i]$. Inversion of this expression yields eq 2, for

$$\Phi = \Phi_{ISC}\left(\frac{k_2}{k_1 + k_2}\right)\left(\frac{k_4 + fk_5[B]}{k_3 + k_4 + fk_5[B]}\right) \tag{1}$$

$$\frac{1}{\Phi} = \frac{1}{\Phi_{ISC}}\left(1 + \frac{k_1}{k_2}\right)\left(1 + \frac{k_3}{k_4 + fk_5[B]}\right) \tag{2}$$

which two limiting conditions may be envisioned. At sufficiently low base concentration, $k_5[B]$ becomes small relative to k_4 in which case eq 2 is approximated by eq 3. At high base concentrations, $k_5[B]$ may become large relative to k_4 in which case eq 2 is approximated by eq 4. The behavior expected for eq 3 is shown in Figure 1 by the lack of dependence of quantum yield on hydroxide ion at low concentration. The behavior expected for eq 4 is shown by the linear region reached at high base concentration.

$$\frac{1}{\Phi} = \frac{1}{\Phi_{ISC}}\left(1 + \frac{k_1}{k_2}\right)\left(1 + \frac{k_3}{k_4}\right) \tag{3}$$

$$\frac{1}{\Phi} = \frac{1}{\Phi_{ISC}}\left(1 + \frac{k_1}{k_2}\right)\left(1 + \frac{k_3}{fk_5[B]}\right) \tag{4}$$

Were the reaction subject to specific base catalysis, the zwitterionic intermediate, ZH, would achieve prototropic equilibrium, and the general expression for the quantum yield in eq 5 would result, where f_{ZH} indicates the fraction of the intermediate in the protonated form. This fraction may also be represented by $K_b/(K_b + [OH^-])$ where K_b is the basicity constant of Z^-. Under the limiting condition of low hydroxide ion concentration, the relationship (inverted) is approximated by eq 3. At high hydroxide ion concentration, eq 6 becomes appropriate. These results show that kinetic expressions for general and specific base catalysis may both be derived for this photochemical system and that either description could satisfy the observed results for hydroxide ion catalysis. The observation of buffer enhancement of the quantum yield at constant pH forces the conclusion that the catalysis is general base catalysis.

$$\Phi = \Phi_{ISC}\left(\frac{k_2}{k_1 + k_2}\right)\left[f_{ZH}\left(\frac{k_4}{k_3 + k_4}\right) + (1 - f_{ZH})\left(\frac{k_8}{k_7 + k_8}\right)\right] \tag{5}$$

$$\frac{1}{\Phi} = \frac{1}{\Phi_{ISC}}\left(1 + \frac{k_1}{k_2}\right)\left(1 + \frac{K_b}{[OH^-]}\right)\left(1 + \frac{k_7}{k_8}\right) \tag{6}$$

By making use of eq 3 and 4, the intercept of Figure 1 ($1/\Phi = 2.36$), the slope to intercept ratio at high hydroxide ion concentration (0.00445), and the value of the asymptote ($1/\Phi = 11.37$),[8] several rate constants and rate constant ratios may be evaluated. We assume that k_5 for hydroxide ion is diffusion controlled ($k_5^{OH} = 2.0 \times 10^{10}$ M^{-1} s^{-1}),[9] and that the partitioning factor, f, in eq 2 and 4 is unity.[10,11] We calculate that $k_4 = 2.3 \times 10^7$ s^{-1} and $k_3 = 8.9 \times 10^7$ s^{-1}. The rate constants in step k_5 for HPO_4^{2-} and acetate ion, calculated according to eq 2, are 5.9×10^8 and 3.2×10^7 M^{-1} s^{-1}, respectively.[12]

These experiments establish the first case known to us of a photoreaction subject to general base catalysis. In addition, they provide compelling evidence that nucleophilic aromatic photosubstitution reactions on nitrophenyl ethers proceed through intermediate σ complexes.[13] The photo-Smiles rearrangement of 2-(4′-nitrophenoxy)-1-anilinoethane studied by Mutai et al.[2i] involves electron transfer prior to σ-complex formation, and their reaction also shows catalysis by a base. The strikingly different regiospecificities of their systems[14] and ours[3] may be attributed to the absence of electron transfer preceding the σ complex in our reactions. Electron transfer is favored in their system by the lower ionization potential of the RNHPh moiety compared with that of a primary amine.

Acknowledgment. We thank the National Science Foundation for an Undergraduate Research Participation grant and a grant to purchase a UV-VIS spectrophotometer used in this research. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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(8) This is the value of the asymptote corrected for the small portion of **1** (7.9%) which is protonated at pH 10.35. The pK_a of **1** is 9.25 ± 0.20.

(9) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1-19.

(10) We cannot evaluate f directly, but since the leaving group abilities of RNH$^-$ and RO$^-$ differ greatly in a system sensitive to such differences,[11] we expect that f would be close to unity.

(11) Bernasconi, C. F. *Acc. Chem. Res.* **1978**, *10*, 147-153.

(12) An alternative treatment of the kinetics is possible if k_4 were negligible and the "uncatalyzed" reaction were actually due to base catalysis by water in k_5. This seems unlikely for two reasons: **1** appears to photorearrange in acetonitrile with modest efficiency, and the rapid falloff of k_5 with decreasing base strength suggests that 55 M water acting as a base could not account for the residual quantum yield.

(13) Cornelisse, J.; Havinga, E. *Chem. Rev.* **1975**, *75*, 353-388. Cornelisse, J.; Lodder, G.; Havinga, E. *Rev. Chem. Intermed.* **1979**, *2*, 231-265.

(14) Mutai, K.; Kanno, S; Kobayashi, K. *Tetrahedron Lett.* **1978**, 1273-1276.

Identification and Structure of the Benzene-Hydrogen Chloride Complex from Microwave Spectroscopy

W. G. Read, E. J. Campbell,* Giles Henderson, and
W. H. Flygare†

Noyes Chemical Laboratory
University of Illinois, Urbana, Illinois 61801

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We wish to report the identification and structural characterization of a 1:1 gas phase complex formed between benzene and hydrogen chloride. The experimental technique used here is pulsed Fourier-transform microwave spectroscopy carried out in a Fabry-Perot cavity with a pulsed supersonic expansion of gas used to generate the molecular complexes.[1,2] A gas mixture of 2% benzene and 3% hydrogen chloride in argon at 2 atm of pressure was pulsed into the evacuated region between the Fabry-Perot mirrors. A $\pi/2$ microwave pulse is used to polarize the gas. After the polarizing radiation has dissipated the coherent emission from all the polarized rotational transitions within the bandwidth of the cavity is observed as a beat with the local

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† Deceased.

(1) T. J. Balle, E. J. Campbell, M. R. Keenan, and W. H. Flygare, *J. Chem. Phys.*, **71**, 2723 (1979); **72**, 922 (1980).

(2) T. J. Balle and W. H. Flygare, *Rev. Sci. Instrum.*, **52**, 33 (1981).

(3) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy", McGraw-Hill, New York, 1955.

0002-7863/81/1503-7670$01.25/0

Table I. Spectroscopic Constants for the Benzene-Hydrogen Chloride Complex

isotope	B_0, MHz	D_J, kHz	D_{JK}, kHz	$\chi_{aa}{}^{Cl}$, MHz
benzene-$H^{35}Cl$	1237.68362 (52)	1.223 (13)	13.35 (2)	−52.189 (18)
benzene-$H^{37}Cl$	1201.92498 (170)	1.155 (39)	13.41 (81)	−41.248 (275)
benzene-$D^{35}Cl$	1228.24396 (58)	1.186 (15)	14.57 (3)	−54.705 (22)

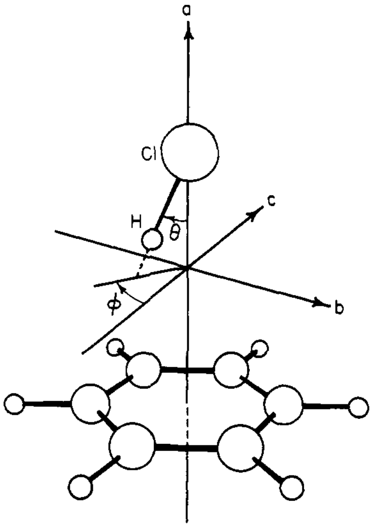

Figure 1. Intermolecular coordinate system and identification of the inertia axes (*abc*) in benzene–hydrogen chloride. The distance R_0 used in the text separates the centers of mass of the two subunits. The average displacement of the H and Cl atoms from the benzene C_6 axis is zero.

oscillator field. This signal is digitized, averaged, and Fourier transformed to give the frequency spectrum. Our resolution in the frequency domain is approximately 20–30 kHz.

The observed vibrational ground-state rotational spectrum is characteristic of a symmetric top molecule with a fully resolved nuclear quadrupole hyperfine structure resulting from a spin $^3/_2$ nucleus. A total of 56 hyperfine components have been measured and assigned for the $J = 3 \rightarrow 4$ and $J = 4 \rightarrow 5$ transitions in benzene-$H^{35}Cl$, -$H^{37}Cl$, and -$D^{35}Cl$. The spectroscopic constants B_0, D_J, D_{JK} and the chlorine nuclear quadrupole coupling constant, χ_{aa}, for each of these species was obtained from a least-squares fit to a distorted symmetric top Hamiltonian, with the results shown in Table I. No deuterium hyperfine structure was resolved in the benzene $D^{35}Cl$ spectrum, indicating that these splittings are probably no more than 10–20 kHz for the transitions observed here.

The exact symmetric top spectrum seen here indicates that the time-averaged displacement of the H and Cl atoms from the benzene C_6 axis is zero. Within the limits of uncertainty of this experiment (approximately 30 kHz for the $J = 4 \rightarrow 5$ transition) those pairs of transitions characterized by the prolate symmetric top quantum numbers $K = +1$ and $K = -1$ occurred at exactly the same frequency. Since these lines would be separated by $(J + 1)(B - C)$ for the $J \rightarrow J + 1$ transition in a slightly asymmetric top, we have established an upper bound on $B-C$ of approximately 3 kHz. In contrast, a structure with the HCl axis perpendicular to the benzene plane but positioned over the center of a carbon-to-carbon bond would yield a $B - C$ of 23 MHz, and a planar structure, analagous to that observed for cyclopropane–HCl,[4] would give $B - C$ of 270 MHz.

The isotopic substitution data allow us to show that the acid proton lies between the benzene and the Cl atom. We consider the coordinate system in Figure 1. The distance R_0 separates the center of mass of the two subunits, with the HCl center of mass positioned on the benzene C_6 axis. The zero-point motion of the HCl includes contributions from two nearly degenerate large amplitude bending modes. The instantaneous orientation of the HCl axis with respect to the benzene C_6 axis is described by the angles ϕ and θ. Because of the delocalized nature of the benzene π-electron density, we expect that for $R \simeq R_0$, the intermolecular potential is nearly isotropic in ϕ. Accordingly, for arbitrary θ, we treat the H and Cl masses as uniform rings about the benzene C_6 axis with radii $r_H \sin\theta$ and $r_{Cl} \sin\theta$, where r_H and r_{Cl} are the respective HCl center-of-mass-to-nuclear distances. We obtain for the moment of inertia of the entire complex about the *b*-inertial axis.

Table II. Comparison of Benzene Center-of-Mass-to-Chlorine Distance R for Several Fixed Values of the HCl Bending Angle θ

	R,[a] Å		
θ, deg	$BzH^{35}Cl$	$BzD^{35}Cl$	difference, Å
0	3.6286	3.6379	0.0093
20	3.6270	3.6347	0.0077
90	3.5972	3.5769	0.0203
160	3.5594	3.5036	0.0558
180	3.5567	3.4984	0.0583

[a] Cl position is taken to be the projection of the HCl center-of-mass-to-Cl distance onto the benzene C_6 axis.

$$I_{bb} = I_{bb}(\text{benzene}) + I_{HCl}(\tfrac{1}{2}\sin^2\theta + \cos^2\theta) + \mu R_0{}^2 \quad (1)$$

where I_{bb}(benzene) and I_{HCl} are the appropriate moments of inertia of free benzene and free HCl, and μ is given by

$$\mu = m_{Bz}m_{HCl}/(m_{Bz} + m_{HCl})$$

where m denotes mass. The values of the benzene-to-chlorine distance that reproduce B_0 for various values of θ are shown in Table II. A comparison of the change in the benzene center-of-mass-to-chlorine distance in going from $H^{35}Cl$ to $D^{35}Cl$ for $\theta = 0°$ and $\theta = 180°$ shows that the H atom lies toward the benzene. The benzene $H^{37}Cl$ data are consistent with this result.

Further information on the HCl zero-point bending motion can be obtained from the chlorine nuclear quadrupole coupling constant χ_{aa}. χ_{aa} depends on the product of the chlorine nuclear quadrupole moment and the projection onto the *a*-inertial axis of the electric field gradient at the chlorine nuclear site averaged over the zero-point motion of the HCl, as

$$\chi_{aa} = \tfrac{1}{2}\chi^0\langle 3\cos^2\theta - 1\rangle \quad (2)$$

where χ^0 is the chlorine quadrupole coupling constant in free HCl. There will be small modifications to this equation resulting from the polarization of the HCl by the nonzero electric multipole moments of the benzene, which will not be considered here. Since the moments of inertia of $H^{35}Cl$ and $H^{37}Cl$ differ by only 0.1%, the zero-point averaging of these two isotopes can be expected to be nearly identical, and thus the measured ratio $\chi_{aa}{}^{35}/\chi_{aa}{}^{37}$ of 1.2652 is nearly equal to the ratio $Q^{35}/Q^{37} = 1.2688$ of the chlorine nuclear quadrupole moments. Using eq 2 we obtain the operationally defined angles $\theta^* = \arccos(\langle\cos^2\theta\rangle)^{1/2}$ of 23° and 20.7° for benzene–$H^{35}Cl$ and -$D^{35}Cl$, respectively.

The above discussion does not rely on any assumed value for the equilibrium value of the angle θ. Studies of complexes between HCl and acetylene,[5] ethylene,[6] and cyclopropane[4] indicate that in those systems the acid hydrogen seeks out the high electron density at the centers of the carbon–carbon bonds. Thus an equilibrium value of θ of approximately 20° with the HCl axis pointed at the π electron density should be considered as an alternative to an equilibrium C_{6v} structure. As long as the barrier

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[4] A. C. Legon, P. D. Aldrich, and W. H. Flygare, *J. Am. Chem. Soc.*, **102**, 7584 (1980).

[5] A. C. Legon, P. D. Aldrich, and W. H. Flygare, *J. Chem. Phys.*, **75**, 625 (1981).

[6] P. D. Aldrich, A. C. Legon, and W. H. Flygare, *J. Chem. Phys.*, **75**, 2126 (1981).

J. Am. Chem. Soc. 1981, 103, 7672–7674

to the C_{6v} form is sufficiently low, the molecular spectrum will show all the characteristics of a symmetric top. The only direct evidence from experimental data bearing on this question is the observed decrease in θ^* upon deuteration of the HCl. Similar decreases have been observed in the intensively studied linear inert gas–hydrogen halide systems.[1,7] As in those more carefully studied systems, the observed decrease in θ^* determined from the chlorine quadrupole coupling constants above tends to suggest a C_{6v} equilibrium structure with $\theta = 0$ in which all of the delocalized π electrons contribute equally to the bonding interaction.

We are presently undertaking further investigations of the benzene–HCl complex.

Acknowledgment. We would like to thank Dr. Paul Soper for his participation in the early phases of this project. The support of the National Science Foundation is gratefully acknowledged.

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(7) M. R. Keenan, E. J. Campbell, T. J. Balle, L. W. Buxton, T. K. Minton, P. D. Soper, and W. H. Flygare, *J. Chem. Phys.*, **72**, 3070 (1980).

Chemistry of Higher Order, Mixed Organocuprates. 1. Substitution Reactions at Unactivated Secondary Centers[†]

Bruce H. Lipshutz*[1] and Robert S. Wilhelm

Department of Chemistry, University of California
Santa Barbara, California 93106

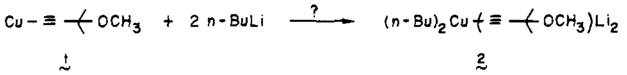
David M. Floyd

Agricultural Chemical Group, FMC Corporation
Princeton, New Jersey 08540

Received July 30, 1981

The variety of reactions which organocopper reagents are known to undergo has proven to be an invaluable tool for the construction of carbon–carbon bonds.[2] In general, relatively mild conditions prevail and efficient coupling processes are observed. One of the key transformations associated with Gilman-type reagents, R_2CuLi, is the facility with which they undergo substitution reactions at primary positions.[2a] While primary halides are excellent substrates in this regard, the literature consistently alludes to the inability of these reagents to transfer ligands to an *unactivated secondary* center in an efficacious manner. As examples, 2-bromopentane reacts with *n*-Bu_2CuLi to afford 4-methyloctane in 12% yield,[3] cyclohexyl bromide gives *n*-butylcyclohexane in 25% yield,[3] and iodocyclohexane upon treatment with Me_2CuLi leads to methylcyclohexane in 21% yield.[4] The main reaction pathways appear to follow a reduction and/or elimination mode. Surprisingly, this fundamental problem has received very little attention,[4] and yet a solution would be a valuable addition to the arsenal of synthetic methodology. We now report our preliminary studies in this area which have led to the development of a new procedure for effecting the desired coupling with minimal side reactions.

Initially we investigated the reaction between the cuprous acetylide **1**[5] and 2 equiv of *n*-BuLi. Literature precedent had shown that higher order organocopper species could be formed, although these were always derived from CuI and 3 equiv of RLi.[6] Adding *n*-BuLi (2 equiv) to **1** at −78 °C, which presumably formed the mixed cuprate **2**, followed by 0.5 equiv of iodocyclohexane and warming the mixture to −20 °C overnight gave *n*-butylcyclohexane in ca. 60% yield. This result, which is considerably better than that which had been achieved earlier on secondary halides with Gilman reagents,[3,7] suggested that further experimentation was warranted.



In order to minimize manipulation of the copper-containing precursor prior to addition of RLi, we sought a readily available source of Cu(I) which already possessed a nontransferable "dummy" ligand attached to copper. Cuprous cyanide (CuCN) seemed to be ideal for the following reasons: (1) it is far less expensive than CuI;[8] (2) it is not hygroscopic; (3) it is quite stable as, and in fact prefers, the Cu(I) oxidation state;[9] (4) it is not light sensitive. Hence, treatment of CuCN in THF with 2 equiv of *n*-BuLi gave, by analogy with the formation of **2**, complex **3**, as a clear, tan solution.[10] Introducing cyclohexyl iodide (0.5 equiv)

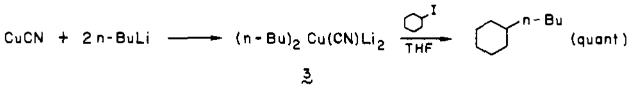
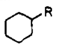
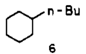
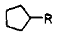
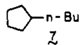
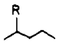
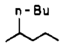


Table I. Reactions of Secondary Halides/Sulfonates with $(n\text{-Bu})_2Cu(CN)Li_2$

Substrate	Conditions[a]	Product[b]	Yield[c] (%)
		 **6**	
R = I	−50°, 1 h	**6**	100
Br	rt, 2 h	**6**	22[d]
OMs	0°, 2 h	e	—
OTs	rt, 3h	**6**	5[f]
		 **7**	
R = I	−78°, 2h	**7**	82
Br	0°, 6 h	**7**	86
OTs	0°, 5 h	**7**	35[f]
		 **8**	
R = I	−50°, 2h	**8**	99
Br	0°, 2 h → rt, 1 h	**8**	94
Cl	rt, 11 h	**8**	28
OMs	0°, 2h → rt, 1 h	e	—
OTs	−25°, 24 h[g]	**8**	40
OTs	rt, 7 h	**8**	58
	rt, 3h	e	—

[a] All reactions were conducted in THF unless specified otherwise. [b] Products were identified by comparison with authentic samples. [c] By quantitative GC using *tert*-butylcyclohexane as an internal standard. [d] 52% starting material remained. [e] None of the desired product was observed. [f] Starting material still observed. [g] Reaction was run in Et_2O; see ref 15.

[†] Dedicated to Professor H. H. Wasserman on the occasion of his sixtieth birthday.

(1) Recipient of an American Cancer Society Junior Faculty Research Award, 1981–1983.

(2) (a) Posner, G. H. *Org. React.* **1975**, *22*, 253. (b) Jukes, A. E. *Adv. Organomet. Chem.* **1974**, *12*, 215. (c) Normant, J. F. *Pure Appl. Chem.* **1978**, *50*, 709. (d) Smith, R. A. J.; Hannah, D. J. *Tetrahedron* **1979**, *35*, 1183.

(3) Whitesides, G. M.; Fischer, W. F.; San Filippo, J.; Bashe, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871.

(4) (a) Ashby, E. C.; Lin, J. J. *J. Org. Chem.* **1977**, *42*, 2805. (b) Ashby, E. C.; Lin, J. J.; Watkins, J. J. *Ibid.* **1977**, *42*, 1099. (c) Corey, E. J.; Posner, G. *J. Am. Chem. Soc.* **1967**, *89*, 3911. Interestingly in this work, reaction of iodocyclohexane with Me_2CuLi (5 equiv., 0 °C, 10 h) gives methylcyclohexane in 75% yield.

(5) Corey, E. J.; Floyd, D. M.; Lipshutz, B. H. *J. Org. Chem.* **1978**, *43*, 3418.

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(7) Corey, E. J.; Posner, G. H. *J. Am. Chem. Soc.* **1968**, *90*, 5615.

(8) For example, Ventron sells CuCN for $30/kg, and CuI, usually purchased "ultrapure" (unless it is to be recrystallized), is listed at $83/100 g.

(9) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1972.

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