Organometallics 1984, *3*, 1740–1743

Effect of Metal Complexation on the Gas-Phase Acidities of Alkylbenzenes

Scott D. Kahn and Warren J. Hehre*

Department of Chemistry, University of California, Irvine, California 92717

John E. Bartmess and Gary Caldwell

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Received January 13, 1984

Ion cyclotron resonance spectroscopy has been employed to measure the gas-phase acidities of three mixed chromium arenes $ArCr(C_6F_6)$, Ar = $C_6H_5CH_3$, 1,3-$C_6H_4(CH_3)_2$, and 1,4-$C_6H_4(CH_3)_2$. The data show that the π-complexed $Cr(C_6F_6)$ ligand increases the acidity of the free arenes by almost as much as does a para nitro substituent. Both the magnitudes and directions of methyl substituent effects on the acidity of $(C_6H_5CH_3)Cr(C_6F_6)$ are nearly identical with those for the free arene, suggesting that the deprotonated forms of the metal complexes incorporate true benzylic-like anions. Support for such a picture is provided by theoretical calculations.

Introduction

The study of substituent effects on the acid and base properties of molecules has commanded a central position in physical organic chemistry for several decades. In recent years, gas-phase techniques, especially ion cyclotron resonance spectroscopy[1] and high-pressure mass spectrometry,[2] have provided a wealth of quantitative thermochemical information about the strengths of free acids and bases. Combined with the results of solution-phase measurements, these data provide the means to assess the effects of real media.[3,4] By far the majority of work has centered on organic compounds. Far less attention has been given organometallic systems and, in particular, to the investigation of the role of a complexed metal as a substituent.

Nicholls and Whiting[5] were perhaps the first to quantify the effect of a complexed metal on the acid strength of an organic molecule. Their work showed that the acid-strengthening effect of a π-complexed chromium tricarbonyl ligand on both benzoic and phenyl acetic acids was roughly equivalent to that of a para nitro substituent. Later, by measuring the rates of reaction of fluoro- and chlorobenzene with methoxide anion, Brown and Raju[6] also equated the stabilization resulting from π-bound $Cr(CO)_3$ to that of a para nitro group. Most recently, Bland, Davis, and Durrant[7] furnished NMR evidence in support of the same conclusion that the electron-withdrawing ability of $Cr(CO)_3$ is "approximately equal" to that of a para nitro substituent when the former is π complexed to an arene.

Table I. Enthalpies of Deprotonation of Free and Complexed Arenes

arene	proton affinity[a]	
	arene	arene···$Cr(C_6F_6)$
$C_6H_5CH_3$	(0.0)	22.7 ± 0.4
m-$C_6H_4(CH_3)_2$	−0.6 ± 0.2	21.6 ± 0.7
p-$C_6H_4(CH_3)_2$	−1.4 ± 0.2	21.3 ± 0.4
p-$C_6H_4(CH_3)(NO_2)$	26.4[b]	
p-$C_6H_4(CH_3)(CHO)$	19.8 ± 0.2	
p-$C_6H_4(CH_3)(CN)$	16.7 ± 0.4	

[a] kcal mol^{-1}, relative to toluene. Quoted values correspond to averages from individual runs. See Table II. Experimental data from this work unless otherwise noted. [b] J. B. Cumming and P. Kebarle, *Can. J. Chem.*, 56, 1 (1978).

Our goals in the present research have been to determine the degree and more importantly the nature of the interaction of a metal-based ligand π complexed to an organic substrate. To this end, we report the gas-phase acidities of toluene and m- and p-xylene, both as free arenes and as π complexes of chromium. These have been determined by pulsed ion cyclotron resonance (ICR) spectroscopy using standard procedures described elsewhere.[8] The low volatility of (arene)chromium tricarbonyl complexes prompted the use of the analogous $Cr(C_6F_6)$ systems in their place.

Results and Discussion

The experimental data, in terms of the enthalpies of deprotonation relative to toluene, i.e.

$$AH + C_6H_5CH_2^- \rightleftharpoons A^- + C_6H_5CH_3 \tag{1}$$

are summarized in Table I. Included for comparison are the gas-phase acidities of several para-substituted toluenes.

Two major points follow from analysis of the acidity data. The first and more apparent result is that the Cr-

---

(1) T. A. Lehman and M. M. Bursey, "Ion Cyclotron Resonance Spectroscopy", Wiley, New York, 1976.

(2) (a) J. P. Briggs, R. Yamdagni, and P. Kebarle, *J. Am. Chem. Soc.*, **94**, 5128 (1972); (b) R. Yamdagni and P. Kebarle, *ibid.*, **98**, 1320 (1976).

(3) Tabulations of gas-phase basicities include: (a) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977). (b) R. W. Taft in "Proton Transfer Equilibria", E. F. Caldin and V. Gold, Eds., Wiley-Halstead, New York, 1975. (c) D. H. Aue and M. T. Bowers in "Gas Phase Ion Chemistry", M. T. Bowers, Ed., Academic Press, New York, 1979, Vol. 2, p 1. (d) R. Walder and J. L. Franklin, *Int. J. Mass Spectrom. Ion Phys.*, **36**, 85 (1980). Tabulations of gas-phase acidities include: (e) J. E. Bartmess, J. A. Scott, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **101**, 6046, 6056 (1979). (f) J. E. Bartmess and R. T. McIver, Jr., in "Gas Phase Ion Chemistry", M. T. Bowers, Ed., Academic Press, New York, 1979, Vol. 2, p 87.

(4) For a recent review of solvent effects on gas-phase acidities and basicities, see: R. W. Taft, *Prog. Phys. Org. Chem.*, **14**, 247 (1983).

(5) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

(6) D. A. Brown and J. R. Raju, *J. Chem. Soc. A*, 40 (1966).

(7) W. J. Bland, R. Davis, and J. L. A. Durrant, *J. Organomet. Chem.*, **234**, C20 (1982).

(8) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 555 (1970); (b) J. D. Baldeschwieler and S. S. Woodgate, *Acc. Chem. Res.*, **4**, 114 (1971); (c) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Phys.*, **7**, 471 (1971); (d) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **49**, 111 (1978); (e) R. L. Hunter and R. T. McIver, Jr., *Chem. Phys. Lett.*, 577 (1977).

0276-7333/84/2303-1740$01.50/0

Table II. Changes in Free Energy[a]

compd	standard acid[b] pyrrole (19.3)	MeSH (19.6)	*m*-CF_3-aniline (20.5)	EtSH (21.2)	*n*-PrSH (22.2)	*i*-PrSH (23.0)
(toluene)$Cr(C_6F_6)$					0.3 ± 0.5 (3)	−0.1 ± 0.3 (5)
(*m*-xylene)$Cr(C_6F_6)$		2.0 (1)	0.5 ± 0.1 (6)	1.2 ± 0.3 (2)		
(*p*-xylene)$Cr(C_6F_6)$	2.3 (3)	1.9 ± 0.4 (7)	1.2 ± 0.5 (3)	1.0 (1)		

[a] Relative to standard acid; kcal mol^{-1}. [b] kcal mol^{-1}; standards are relative to toluene; the number of determinations is in parentheses.

Table III. Changes in Free Energy[a]

compd	standard acid[b] MeOH (−0.3)	CF_3CH_2OH (15.5)	*m*-F-aniline (16.5)	MeSH (19.6)	*p*-cresol (26.2)
p-xylene	−0.7 ± 0.2				
p -xylene	0.1 ± 0.5				
toluene	(0.3 ± 0.2)				
p-$C_6H_4(CH_3)CN$		0.8 ± 0.2	1.1 ± 0.2		
p-$C_6H_4(CH_3)CHO$			1.1 ± 0.	−1.8 ± 0.2	
p-$C_6H_4(CH_3)NO_2$					0.2[c]

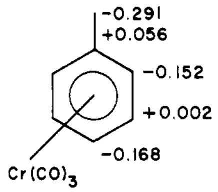
[a] Relative to standard acid; kcal mol^{-1}. [b] kcal mol^{-1}; standard acids are relative to toluene. [c] Reference given in footnote *b* in Table I.

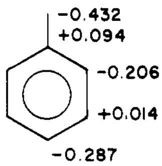
(C_6F_6) moiety, upon π complexation, greatly increases the enthalpy of deprotonation of the free arene (by 22.7 kcal mol^{-1} for toluene, and by 22.2 and 22.7 kcal mol^{-1} for *m*- and *p*-xylene, respectively). Thus, a π-complexed $Cr(C_6F_6)$ group is more effective than either the para cyano or para formyl groups (by 6.0 and 2.9 kcal mol^{-1}, respectively) in stabilizing a free benzyl anion (relative to the corresponding neutral arene) and only slightly less effective than a para nitro substituent (see Table I).

As earlier commented, previous work has generally involved use of $Cr(CO)_3$ as a complexing agent instead of $Cr(C_6F_6)$. NMR data suggest that the electron-withdrawing abilities of the two groups are comparable, although $Cr(CO)_3$ is probably slightly more effective. That is, both the methyl protons and ring carbons on arenes complexed to $Cr(CO)_3$ are slightly more deshielded than those in the analogous $Cr(C_6F_6)$ compounds.[9] Given the similarity of the two complexing groups, the gas-phase acidity data confirm previous (solution-phase) observations[5–7] that a π-complexed chromium tricarbonyl group exerts a comparable influence on arene stability and reactivity as a para nitro substituent.

The second and far more salient topic addressed here is the nature of the interaction of the benzyl ligand with the metal center. We are aware of only two papers[10,11] that have directly examined the nature of an aryl metallic anion; both concern anions π complexed to iron. As free arenes, the ordering of the gas-phase acidities: toluene > *m*-xylene > *p*-xylene, follows from standard arguments on the methyl group's intrinsic electron-releasing ability. This same ordering of acidities has been found in the π-complexed arenes, and we propose that the anion formed upon deprotonation closely resembles a free benzyl anion; i.e., the negative charge resides primarily on the organic ligand and not on the metal. Were the ligand to resemble more closely a benzyl free radical (or benzyl cation) the para methyl substituent would give rise to an increase in acidity and not the noted decrease.

Quantitative molecular orbital calculations provide additonal support for such an interpretation. At the STO-3G level,[12,13] ring π charges for benzyl anion complexed to chromium tricarbonyl are qualitatively similar to those in the free species.





In particular, the majority of the excess negative charge on the metal-complexed system resides on the formal carbanion center and on the ortho and para ring carbons. While complexation to $Cr(CO)_3$ has resulted in some reduction of the overall negative charge on benzyl anion (by approximately 0.3 electron), it has apparently done little to alter the distribution of charge. Further evidence follows from the similarity of the π-type molecular orbitals on the complexed system (Figure 1, left) to those on free benzyl anion (Figure 1, right).[14]

The STO-3G calculations indicate that the highest energy of the π functions on the chromium tricarbonyl complex of benzyl anion (labeled 37a′ in Figure 1) is not the system's highest occupied molecular orbital. The two

---

(9) For example, the ^{13}C chemical shifts in $(C_6H_6)Cr(C_6F_6)$ and $(C_6H_6)Cr(CO)_3$ are 85.8 and 93.5 ppm (relative to Me_4Si), respectively. The methyl protons in $(C_6H_5CH_3)Cr(C_6F_6)$ and $(C_6H_5CH_3)Cr(CO)_3$ resonate at 1.81 andf 2.13 ppm (relative to Me_4Si), respectively. Carbon data from: G. M. Boduer and L. J. Todd, *Inorg. Chem.*, 13, 360 (1974). Proton data on (toluene)chromium tricarbonyl from: C. Segard, B. Roques, C. Pommier, and G. Guiochon, *Anal. Chem.*, 43, 1146 (1971).

(10) J.-R. Hamon, D. Astruc, E. Ramân, P. Batail, and J. J. Mayerle, *J. Am. Chem. Soc.*, **103**, 2431 (1981).

(11) J. F. Helling and W. A. Hendrickson, *J. Organomet. Chem.*, 141, 99 (1977).

(12) First row: (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 51, 2657 (1969). First- and second-row transiton metals: (b) W. J. Pietro and W. J. Hehre, *J. Comput. Chem.*, 4, 241 (1983).

(13) Calculations were preformed on the chromium tricarbonyl systems rather than the analogous perfluorobenzene complexes both because of size constraints and due to the lack of crystal structure data on the latter. Benzyl anion was fully optimized by assuming C_{2v} symmetry. The metal-complexed anion was constructed from the optimized benzyl anion structure and a standard $Cr(CO)_3$ unit from the literature (M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 4, 1314 (1965)): C–O = 1.150 Å, Cr–(CO) = 1.842 Å, ring–Cr = 1.724 Å, ring–Cr–(CO) = 125.8°.

(14) (a) R. F. Hout, Jr., W. J. Pietro, and W. J. Hehre, *J. Comput. Chem.*, 4, 276 (1983). (b) R. F. Hout, Jr., W. J. Pietro, and W. J. Hehre, "A Pictorial Approach to Molecular Structures and Reactivity", Wiley-Interscience, New York, 1984.

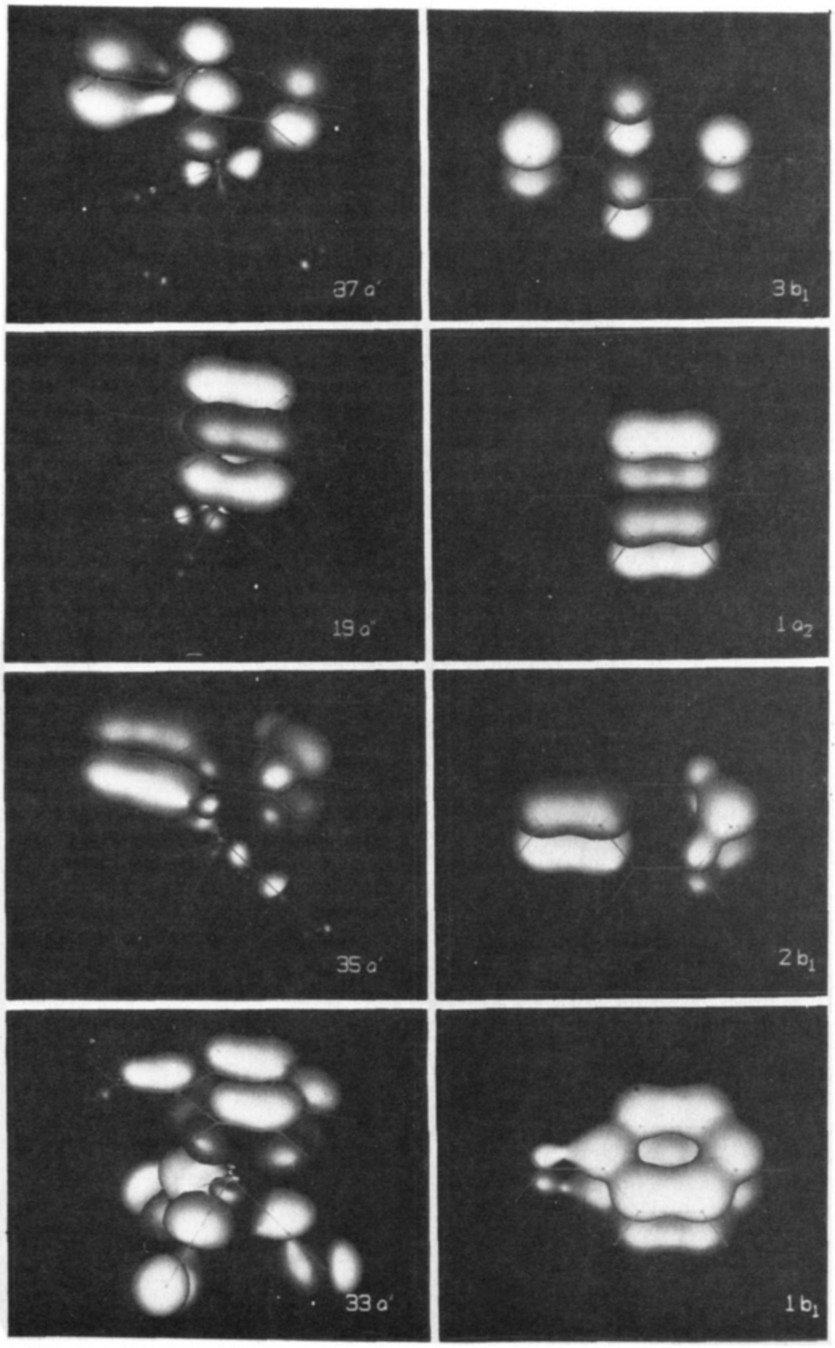


Figure 1. Filled π-type molecular orbitals for benzyl anion chromium tricarbonyl (left) and benzyl anion (right), from lowest energy (bottom) to highest energy (top) (STO-3G//STO-3G).

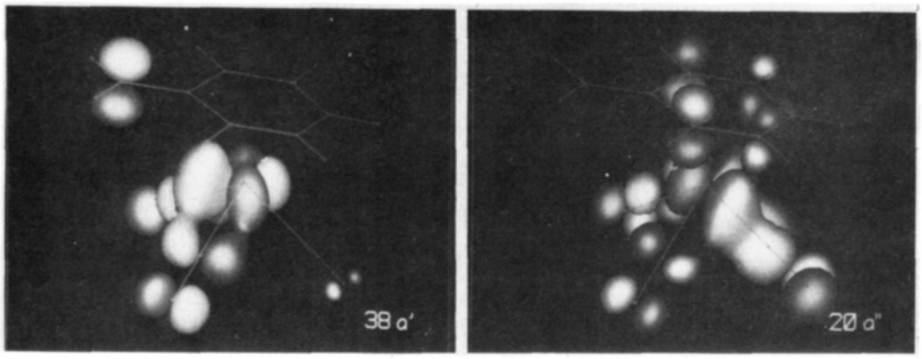


Figure 2. Two highest-occupied molecular orbitals of benzyl anion chromium tricarbonyl (STO-3G//STO-3G).

functions shown in Figure 2, which may be best described as metal lone pairs, are both predicted to be higher in energy. While this is in accord with the observation that, in the gas phase, simple transition-metal carbonyl compounds and metal arenes protonate on the metal and not on the ligands,[15] it needs to be reconciled with the fact that the proton-transfer reactions studied here have been established by all standard criteria[16] to be true equilibria. In particular, the present experimental data suggest either that the benzyl anion is (kinetically) the favored reprotonation site or, alternatively that rearrangement from an initially metal reprotonated species to the thermodynamically more stable ligand reprotonated form, i.e., (toluene)chromium tricarbonyl, is rapid on the ICR time scale.

Experimental Section

Perfluorobenzene was purchased from Alfa Ventron and used without further purification. Toluene and *m*- and *p*-xylene were vacuum distilled prior to use. Chromium arenes were prepared by using a metal atom reactor.[17] Typical experimental conditions: 3.1 g of toluene and 6.1 g of perfluorobenzene were degassed and cocondensed with chromium vapor (produced by resistive heating of 0.32 g of chromium powder (from MCB) in a molybdenum boat) onto the 77 K walls of the reactor over a period of approximately 30 min. Upon warming to room temperature, the initial reddish brown matrix yielded a brownish yellow solution. This was filtered (under argon), the solvent removed in vacuo, and the resulting fine yellow powder exposed to air to oxidize any bis(toluene)chromium.[18] Yellow crystals resulted from sublimation at 60 °C and recrystallization from benzene–diethylether.

Gas-phase acidities were established relative to several "standard" acids. While, due to experimental constraints,[19] it was not always possible to bracket the acidities of the chromium arene complexes, the acidity of each compound was established with respect to at least two standards. The experimental free energies and error limits are provided in Tables II and III. The corresponding enthalpies, presented in Table I, have been obtained from the free energy data by assuming entropy changes due to symmetry-number effects alone,[20] and a temperature of 300 K.

Acknowledgment. We wish to thank Dr. W. J. Pietro for discussions in the early stages of this work. This research was supported in part by a grant from the National Science Foundation.

Note Added in Proof. A recent negative ion mass spectral study of (arene)$Cr(CO)_3$ compounds[21] has reached the conclusion that $Cr(CO)_3$ is a strong electron-withdrawing group in the gas phase. In this case stabilization is with respect to the radical anion ($M^{-}\cdot$) and not, as discussed here, to the deprotonated form $(M-H)^-$.

Registry No. $(C_6H_5CH_3)Cr(C_6F_6)$, 91711-70-5; $(1,3\text{-}C_6H_4(CH_3)_2)Cr(C_6F_6)$, 91711-71-6; $(1,4\text{-}C_6H_4(CH_3)_2)Cr(C_6F_6)$, 91711-72-7; $C_6H_5CH_3$, 108-88-3; *m*-$C_6H_4(CH_3)_2$, 108-38-3; *p*-$C_6H_4(CH_3)_2$, 106-42-3; *p*-$C_6H_4(CH_3)(CHO)$, 104-87-0; *p*-$C_6H_4(CH_3)(CN)$, 104-85-8.

---

[15] A. E. Stevens and J. L. Beauchamp, *J. Am. Chem. Soc.*, **103**, 190 (1981).

[16] For a discussion, see: J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977).

[17] (a) P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, 14, 121 (1972); (b) R. Middleton, J. R. Hull, S. R. Simpson, C. H. Tomlinson, and P. L. Timms, *J. Chem. Soc., Dalton Trans.*, 120 (1973); (c) P. S. Skell, L. D. Wescott, J. P. Goldstein, and R. R. Engel, *J. Am. Chem. Soc.*, **87** 2829 (1965).

[18] M. J. McGlinchey and T.-S. Tan, *J. Am. Chem. Soc.*, **98** 2271 (1976).

[19] The low volatility of the chromium complexes reduced the working partial pressures into the range of (1–5) × 10^{-7} torr. Under these conditions the introduction of standards that were even slightly more acidic led to unacceptable reductions in signal strength.

[20] S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.

[21] P. M. Lansarot, L. Operti, G. A. Vaglio, and M. Valle, *Inorg. Chim. Acta*, **60**, 185 (1982), and references therein.

Purification of Air-Sensitive Organometallic Compounds by a Modified Flash Chromatography Procedure

Kenneth A. M. Kremer* and Paul Helquist

Department of Chemistry, State University of New York, Stony Brook, New York 11794-3400

Received April 23, 1984

Still's "flash chromatography" procedure has been modified to permit the routine purification of organometallic compounds that would rapidly decompose under normal aerobic chromatographic conditions. In order to maintain an inert atmosphere during sample purification, appropriate changes have been made in the design of the glass apparatus and in the techniques for packing and elution of the column. A key component of the modified chromatographic apparatus is a specially designed flow controller. Two specific examples of the procedure are given.

A very commonly encountered problem in organometallic chemistry is the purification of air-sensitive compounds.[1] For this purpose, we have developed a modified form of the flash chromatography technique reported by Still[2] that permits the entire procedure to be performed under an inert atmosphere. We have found this technique to be a fast and convenient method for the purification of a number of organometallic compounds, including the iron complexes involved in our earlier work.[3] The total time required for packing, preparation, and elution of the column is only 1–2 h. We recommend, though, that before attempting the use of the techniques described below, the user should first become familiar with Still's original procedure.

In comparison with the apparatus described by Still,[2] we have designed a special solvent reservoir and we have redesigned the flow controller and chromatography columns (Figure 1).[4] The solvent with which the column is eluted is stored under nitrogen in solvent reservoirs of 2-L capacity.[5] These reservoirs are easily constructed from

---

[1] Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.

[2] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

[3] (a) Kremer, K. A. M.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 1862. (b) Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *Ibid.* **1982**, *104*, 6119.

[4] As used in our laboratory, all of the glassware depicted in this paper is fitted with 24/40 ground glass joints and nos. 2 and 4 Teflon stopcocks.