Gas-phase generation of trifluoromethyl cyclopentadienides

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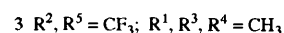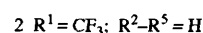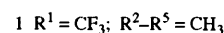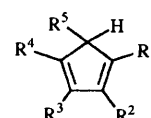
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Tetramethyltrifluoromethylcyclopentadienide 1a is unstable in solution but it can be readily generated in the gas phase. The proton affinities and fluoride binding energies of 1a and several other trifluoromethyl substituted cyclopentadienides are measured. The data is found to fit an additivity scheme, which suggests that pentakis(trifluoromethyl)cyclopentadiene is an exceptionally strong gas-phase acid, and indicates that substituted trifluoromethylcyclopentadienides may be accessible in solution under the appropriate reaction conditions.

Cyclopentadienes are synthetically useful and important ligands found in numerous organometallic compounds.[1] Their steric and electronic properties have a marked effect on the stoichiometric and catalytic activity of organo-transition metal complexes.[2] As a result, there is considerable interest in fluoro and trifluoromethyl substituted cyclopentadienes.[3,4] The synthetic potential of these compounds, however, is limited by the fact that some of the corresponding cyclopentadienides are unstable in solution. This has led to various indirect methods for preparing derivatives of these species. For example, transition metal complexes of the recently reported tetramethyltrifluoromethylcyclopentadienide [$C_5(CF_3)$-$(CH_3)_4^-$] are only accessible via the neutral 2,3,4,5- tetramethyl-1-trifluoromethylcyclopentadiene 1.[4] The preparation of metal complexes of pentafluorocyclopentadienide ($C_5F_5^-$) has been achieved by a circuitous route involving the thermolysis of the η^5-oxocyclohexadienyl complex, [$RuCp'(\eta^5-C_6F_5O)$] [$Cp' = C_5H_5$ or $C_5(CH_3)_5$].[3a,b] Trifluoromethylcyclopentadienide complexes, on the other hand, have been synthesized from thallium trifluoromethylcyclopentadienide.[5] Since cyclopentadienide anions are superior reagents for synthesis, we were interested in determining whether the instability of some trifluoromethyl substituted cyclopentadienides is an intrinsic limitation or related to solvent–counter-ion effects. In this paper we report a flowing afterglow study of 2,3,4,5-tetramethyl-1-trifluoromethylcyclopentadiene 1,[4a] 1-trifluoromethylcyclopentadiene 2[4b,5] and 1,3,4-trimethyl-2,5-bis(trifluoromethyl)-cyclopentadiene 3.[6] All three cyclopentadienes can be deprotonated to form stable anions in the gas phase. Their acidities ($\Delta H°_{acid}$) and the fluoride affinities ($\Delta H°_{F^-}$) of the corresponding difluorofulvenes were measured and compared with an additivity scheme. It was found that the propensity for these trifluoromethyl substituted cyclopentadienides to undergo fluoride loss is inversely related to the gas-phase acidity.

2,3,4,5-Tetramethyl-1-trifluoromethylcyclopentadiene 1 is readily deprotonated in the gas-phase in our variable temperature flowing afterglow device [reaction (1)].[7] By monitoring the appearance of the conjugate base 1a and using a number of reference bases [$B^- = NH_2^-$ (1689 kJ mol^{-1}), OH^- (1635), MeO^- (1596), Bu^tO^- (1567), F^-, (1554) $C_4H_4N^-$ (1501) and OAc^- (1459), all of which deprotonate 1], an upper limit for the acidity of 1 can be determined.[8] Likewise, 1a was allowed to react with a series of standard acids [BH = CH_3OH, CF_3CH_2OH (1514), C_4H_5N and HOAc, only the last of which is strong enough to protonate 1a], and in this way $\Delta H°_{acid}$ (1) = 1456 ± 13 kJ mol^{-1} was assigned. Combining

1 $R^1 = CF_3$; $R^2–R^5 = CH_3$

2 $R^1 = CF_3$; $R^2–R^5 = H$

3 $R^2, R^5 = CF_3$; $R^1, R^3, R^4 = CH_3$

$$+ B^- \xrightarrow{\quad} \quad + BH \quad (1)$$
$$\Delta H°_{rxn} = \Delta H°_{acid}(1) - \Delta H°_{acid}(BH)$$

1   1a

$$\Delta H°_{rxn} = \Delta H°_{F^-}(1F) \quad + F^- \quad (2)$$

1a   1F
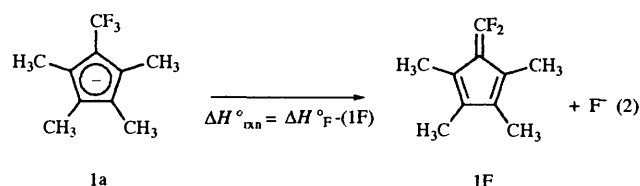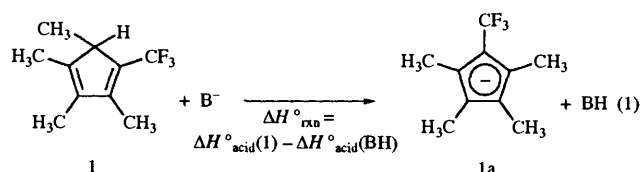
this value with the heats of formation of 1 (-657 kJ mol^{-1}) and its corresponding fulvene (1F, -304 kJ mol^{-1}), as determined using Benson's group equivalents,‡ a fluoride affinity ($\Delta H°_{F^-}$) for the fulvene of 179 kJ mol^{-1} is obtained [reaction (2)]. Experimentally, it was found that the conjugate base of 1 transfers fluoride to SO_2 ($\Delta H°_{F^-} = 227 ± 10$ kJ mol^{-1}) but not to COS or CS_2 ($\Delta H°_{F^-} = 133 ± 8$ and $131 ± 8$ kJ mol^{-1}, respectively) so $\Delta H°_{F^-}(1F) = 176 ± 46$ kJ mol^{-1}, which is in accord with the calculated value.[8]§

To gain insight and make predictions of the effect of additional trifluoromethyl groups on the cyclopentadiene ring an additivity scale was developed. The acidity difference between cyclopentadiene ($\Delta H°_{acid} = 1481$ kJ mol^{-1}) and pentamethylcyclopentadiene ($\Delta H°_{acid} = 1510$ kJ mol^{-1}) divided by five, for the number of methyl groups, gives a 5.8 kJ

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‡ In order to calculate the heat of formation of 1, we assumed C–($C_d)_2(C)(H) = -1.0$ kcal mol^{-1} since this value is not available. We also used C–(C_d)(F)$_3 = -160.0$ kcal mol^{-1} since this value leads to a calculated 1.6 kcal mol^{-1} difference between 1x and 1y, in accord with the observed 1 : 16 ratio. For further details, see: N. Cohen and S. W. Benson, Chem. Rev., 1993, 93, 2419.

§ The relatively strong fluoride binding energy of 1a seems to preclude the formation of a cluster product, i.e. $F^- \cdots 3$. This conclusion is reinforced by the success of our additivity scheme.

Table 1 Acidity and fluoride affinity data for a series of trifluoromethyl substituted cyclopentadienes and their corresponding fulvenes[a]

| Compound | Acidity | | Fluoride affinity | |
	Experimental	Calculated	Experimental	Calculated[b]
1	1456 ± 13	1459	176 ± 46	179
2	1418 ± 13[c]	1436	277 ± 54[e]	221
3	1397 ± 13[d]	1408	277 ± 54[e]	231
$C_5(CF_3)_3(CH_3)_2H$[f]	—	1358	—	329
$C_5(CF_3)_4(CH_3)H$[f]	—	1307	—	329
$C_5(CF_3)_5H$	—	1256	—	373

[a] All values are in kJ mol^{-1}. [b] The calculated fluoride affinities are based on the experimental acidities and therefore are no better than ± 20 kJ mol^{-1}. A ring correction of 25 kJ mol^{-1} was used for the fulvenes (see footnote‡ for more details). It is also worth noting that if the recommended group equivalents of Dolbier *et al.* (W. R. Dolbier, Jr., K. S. Medinger, A. Greenberg and J. F. Liebman, *Tetrahedron*, 1982, **38**, 2415) are used, the fluoride affinity decreases by 16 kJ mol^{-1} for **1F** and **2F**, 23 kJ mol^{-1} for **3F** and ≤8 kJ mol^{-1} for the other derivatives. [c] PhS$^-$ (1424), OAc$^-$ (1457) and F$^-$ (1554) abstract a proton from **2** whereas $CH_3CHBrCO_2^-$ (1410) does not. HCl (1396) and $CH_3CHBrCO_2H$ protonate **2a**, but PhSH, $(CF_3)_2CHOH$ (1443) and HOAc do not [parenthetical values are the acidities (in kJ mol^{-1}) of the reference acids]. [d] Cl$^-$ and OAc$^-$ undergo proton transfer with **3** but Br$^-$ (1354) does not. HCl and HBr protonate **3a** but HOAc does not. [e] Fluoride transfer occurs upon reaction with BF_3 ($\Delta H^\circ_{F^-}$ = 331 kJ mol^{-1}) but not with HCl, SO_2, CS_2 and COS ($\Delta H^\circ_{F^-}$ = 249, 222, 131 and 133 kJ mol^{-1}, respectively). Since HCl protonates **2a** and **3a**, 222 kJ mol^{-1} (SO_2) was used as the lower limit. [f] The most stable isomer was used but the choice has little impact (<7 kJ mol^{-1}) on the calculated fluoride affinities.

mol^{-1} value for the *deacidifying* effect per methyl group. This compares favourably with a 0.08 eV (7.7 kJ mol^{-1}) lowering of the binding energy of the inner shell electrons of a variety of complexed transition metals.[4] For the trifluoromethyl group, we took the difference in acidity between phenol (ΔH°_{acid} = 1461 kJ mol^{-1}) and the average of the *meta* (ΔH°_{acid} = 1421 kJ mol^{-1}) and *para* (ΔH°_{acid} = 1410 kJ mol^{-1}) trifluoromethyl phenol derivatives to obtain a 45 kJ mol^{-1} value for the *acidifying* effect per trifluoromethyl group. This result is also in qualitative accord with an approximate 0.35 eV (34 kJ mol^{-1}) raising of the electron binding energy of transition metal complexes.[4] Using this additivity scheme the acidity of **1a** is calculated to be 1459 kJ mol^{-1}, which is the same as our experimental result. To test further the validity of this additivity scheme we measured the acidities and fluoride affinities of **2** and **3** and **2F** and **3F**, respectively (Table 1). The data reveals that there is good agreement between the experimental and calculated acidities and fluoride affinities.

Our results indicate that the replacement of a methyl group by a trifluoromethyl substituent increases the acidity of the cyclopentadiene system as one would expect. However, if the trend holds throughout the series and levelling effects do not come into play then pentakis(trifluoromethyl)cyclopentadiene is predicted to have an acidity of approximately 1256 kJ mol^{-1}. This would make it one of the most acidic compounds in the gas-phase, even stronger than CF_3SO_3H.[9] Our data also indicates that as the acidity of the neutral cyclopentadiene increases the stability of the anion increases and its propensity to eliminate fluoride decreases, which is consistent with the fact that pentakis(trifluoromethyl)cyclopentadienide is stable in aqueous solution at room temperature.[10] Although presently only **2a** (as the thallium salt),[5] $C_5(CF_3)_5^-$ and $C_5F_5^{-3b}$ have been prepared in solution, it appears that under the appropriate conditions (*e.g.* aprotic solvents) it may be possible to form deprotonated anions from **1** and **3** since their anions can be formed in the gas-phase and are intrinsically stable.

Experimental

Nuclear magnetic resonance spectra were obtained in $CDCl_3$ on a Varian VXR-300S spectrometer and are reported in parts per million (δ) relative to tetramethylsilane at 0.0 δ. Mass spectral data were obtained on a Finnigan 4000 gas chromatograph–mass spectrometer (GC–MS).

The gas-phase experiments were carried out with a variable temperature flowing afterglow device, which is a mass spectrometer specifically designed for studying ion–molecule reactions. This instrument consists of three regions: an ion source, a reaction region and a detector.[11] In our apparatus[7]

ions are generated by electron ionization of an appropriate precursor (*e.g.* electron impact on NF_3, a 1:1 mixture of N_2O and CH_4, and NH_3 lead to F$^-$, OH$^-$ and NH_2^-, respectively), and then swept down a meter long flow tube ($P \approx 0.4$ Torr) with a constant stream of helium ($v_{He} \approx 8000$ cm s^{-1}). Neutral reagents can be added at various points along the flow tube and in this way *in situ* multistep transformations can be carried out. The ionic products are mass filtered and continuously detected with an Extrel quadrupole and its associated electronics. In this way, titrations can be carried out either by adding a series of standard acids to an anion of interest and observing the occurrence or non-occurrence of proton transfer (bracketing) or by reversing the process and examining the reactions of an unknown acid with a variety of bases of known strength. By probing the acidity of a compound in both directions the reliability of this method is improved since misleading conclusions based upon slow proton transfer reactions resulting from kinetic barriers can be avoided. Consequently, in this work acidities were measured by examining both neutral acids (**1–3**) and their conjugate bases (**1a–3a**). In a similar manner fluoride transfer reactions were also explored, but only one direction was investigated since the fulvenes **4–6** were not available to us. The fact that the fluorinated cyclopentadienes exist as isomeric mixtures is of little consequence since the energy differences, as determined by the isomeric ratios, are negligible (<7 kJ mol^{-1} in all three cases).

Trifluoromethylcyclopentadiene 2

An isomeric mixture of trifluoromethylcyclopentadienes was prepared by a modification of the procedure reported by Olsson and Wennerström, which made no use of a solvent.[4b] Thus, a mixture of sublimed dicyclopentadienylnickel (3.5 g, 18 mmol, Strem) and triphenylphosphine (9.7 g, 37 mmol) was finely ground in a mortar and pestle. The solid mixture was added to a 40 cm^3 Carius tube with a Teflon plug and CF_3I (12 g, 61 mmol, PCR) was condensed in at − 78 °C. The tube was sealed with the Teflon plug and warmed to room temperature. A slightly exothermic reaction occurred as the colour of the contents turned from green to deep red. After allowing the reaction to stand overnight the volatile components were condensed into a liquid nitrogen cooled flask to afford 1.9 g (78%) of a colourless liquid after warming to room temperature. The product was dissolved in decalin (10 cm^3), washed with 5% aqueous sodium thiosulfate and saturated brine, and dried over anhydrous magnesium sulfate. The formation of **2** along with a small amount (*ca.* 4%) of dimeric product was confirmed by GC–MS (m/z = 134 and 238, respectively). To prevent further dimerization, the decalin solution was stored at − 78 °C. The ratio of 1-trifluoromethylcyclopentadiene and 2-trifluorometh-

ylcyclopentadiene was similar to that reported by Olsson and Wennerström (2.4:1, respectively), and as previously noted, 5-trifluoromethylcyclopentadiene is not observed.

Tetramethyl(trifluoromethyl)cyclopentadiene 1

An isomeric mixture of 1,2,3,4-tetramethyl-5-(trifluoromethyl)-cyclopentadiene x, 2,3,4,5-tetramethyl-1-(trifluoromethyl)-cyclopentadiene y and 1,3,4,5-tetramethyl-2-(trifluoromethyl)-cyclopentadiene z was prepared, using a previously reported procedure, in a relative ratio of 1:16:2.4, respectively.[4a,c] The relative amount of each isomer was determined by integration of the ^{1}H NMR resonance of the proton bound to the C-5 position: δ_H 3.26 (q, J_{HF} 10.0 Hz, 1x), 2.99 (q, J_{HH} 6.6 Hz, 1y) and 2.66 (q, J_{HH} 6.6. Hz, 1z) (assignments were based on the proximity of the proton to the CF_3 group).

Trimethylbis(trifluoromethyl)cyclopentadiene 3

An isomeric mixture of 1,3,4-trimethyl-2,5-bis(trifluoromethyl)cyclopentadiene x and 2,3,5-trimethyl-1,4-bis(trifluoromethyl)cyclopentadiene y or 2,4,5-trimethyl-1,3-bis(trifluoromethyl)cyclopentadiene z was prepared in a relative ratio of 9.8:1, respectively using a previously reported procedure.[6] The relative amount of each isomer was determined by integration of the proton bound to the C-5 carbon in the ^{1}H NMR spectrum. The assignment of the major isomer 3x is based on the downfield chemical shift and the J_{HF} coupling constant of the proton at C-5 (δ 3.42, q, J_{HF} 10.5 Hz) while the minor species (3y or 3z) has a broad resonance at δ 3.16.

Acknowledgements

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