The reportedly unprotonatable pentacyano-cyclo-pentadienide ion, C₅(CN)₅⁻, can be protonated and silylated at the cyano N atom using electrophilic reagents derived from weakly coordinating carborane anions.

The 1966 report by Webster¹ that the pentacyano-cyclo-pentadienide ion, C₅(CN)₅⁻, cannot be protonated by perchloric acid has led to the belief that its conjugate acid cannot be prepared. If true, the C₅(CN)₅⁺ anion should at least find uses in the field of weakly coordinating anions.²⁻⁴ Indeed, lithium battery applications have been explored.⁵ On the other hand, the preparation of the conjugate acid, H(C₅(CN)₅), presents a long standing synthetic challenge. Would protonation occur at the carbanionic C atom or the cyano N atom? N-Protonation has been suggested by comparison to cyanomethanes⁶ but C-protonation to give a cyclo-pentadienyl is the basis of the calculated gas phase acidity.⁷

Having recently developed silylation methodology to prepare carborane superacids (e.g. H(CB₁₁H₆Cl₆)⁸ which are stronger than oxyacids (perchloric, triflic, etc.),⁹ we decided to explore silylation of C₅(CN)₅⁻ as a possible route to its conjugate acid. Silylation also provides a method of assessing the Lewis basicity of the C₅(CN)₅⁻ anion using a ranking for weakly coordinating anions based on downfield ²⁹Si NMR shifts in i-Pr₃Si(Anion) compounds.²

The C₅(CN)₅⁻ anion was prepared in multigram quantities as a trimethylammonium salt from tetracyano-1,4-dithiin ¹⁰ via the method of Simmons.¹¹ [HMMe₃][C₅(CN)₅] was converted to the silver salt by simple metathesis. Treatment of triphenylmethyltrimethylammonium salt from tetracyano-1,4-dithiin ¹⁰ etc.

As illustrated in Fig. 1, X-ray crystallography shows that the C₅(CN)₅⁻ anion is coordinated to silicon via a cyano N atom. The anion retains near planarity and bond length differences between the coordinated and non-coordinated CN groups are small (< 0.04 Å). The Si–N distances in ¹ and ² are 1.843 (2) and 1.834 (2) Å respectively, quite close to that observed in the acetonitrile cation [i-Pr₃Si(MeCN)]⁺ (1.82 (2) Å).¹² This similarity to a neutral nitrile extends to the degree of pyramidalization at Si which lies between sp³ and sp² ideals. Increasing angle is taken as a measure of developing R₃Si⁺ silyl cation character.¹³ The average C–Si–C bond angle is 114.9° in ¹, 115.3° in ², and 115.6° in [i-Pr₃Si(MeCN)⁺]. The values in ¹ and ² are not as large as those in the more nearly ionic i-Pr₃Si⁺(carborane⁻)⁺ species (> 117°)¹³ indicating that the C₅(CN)₅⁻ anion ranks as a moderately weakly coordinating anion towards Si.

The same conclusion is reached by consideration of ²⁹Si NMR shifts. As compared in Table 1, the downfield shifts of ¹ (35 ppm) and ² (40 ppm) lie in the range of common oxy and halo weakly coordinating anions. This parallel indicates that C₅(CN)₅⁻ has a place in the chemistry of weakly coordinating anions but not at the least coordinating extreme. Its advantages include ease of synthesis, a convenient IR handle in vCN, non-explosiveness of its salts (compared to oxanions such as ClO₄⁻), and good crystallizing properties (π-π anion stacking is observed in all three X-ray crystal structures). Disadvantages include the aforementioned moderate Lewis basicity, cathodic electrochemical instability,⁵ and the tendency of the cyanogroup to hydrolyze to an amide in aqueous base. The potential of the anion to become coloured when coordinated can be considered an advantage or a disadvantage depending on the application, but coloured weakly coordinating anions are quite rare.

In spite of the moderately good Lewis basicity of the C₅(CN)₅⁻ anion towards the R₃Si⁺ moiety, the silyl derivatives ¹ and ² nevertheless have enough silylium ion character to abstract anions from HCl and triflic acid (HOTf) to produce the desired conjugate acid, H(C₅(CN)₅) (eqn. (1)).

\[ \text{Et}_3\text{Si}(\text{C}_5\text{C}_5) + \text{HOTf} \rightarrow \text{H(C}_5\text{C}_5) + \text{Et}_3\text{Si(OTf)} \] (1)

The acid precipitates instantly from toluene solution as an amorphous black-brown powder. The IR spectrum in the vCN region is similar in band shape to the silver and silyl species except for the approx. 1720 cm⁻¹ absorption at 1770 cm⁻¹ for the free anion.

| Table 1 Downfield ²⁹Si NMR chemical shifts (ref. TMS)³

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conditions</th>
<th>δ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>[i-Pr₃SiMeCN][CB₄H₄Br₄]</td>
<td>dichloromethane</td>
<td>37</td>
</tr>
<tr>
<td>Et₃Si(C₅(CN)₅)⁺</td>
<td>toluene</td>
<td>35</td>
</tr>
<tr>
<td>i-Pr₃Si(OTf)</td>
<td>toluene</td>
<td>40</td>
</tr>
<tr>
<td>i-Pr₃Si(N(SO₂CF₃)₂)</td>
<td>toluene</td>
<td>53</td>
</tr>
<tr>
<td>i-Pr₃Si(Ph)</td>
<td>toluene</td>
<td>56</td>
</tr>
<tr>
<td>i-Pr₃Si(THF)</td>
<td>solid state</td>
<td>97</td>
</tr>
<tr>
<td>i-Pr₃Si(PO(BF₄)₂)</td>
<td>solid state</td>
<td>107</td>
</tr>
<tr>
<td>i-Pr₃Si(THF)</td>
<td>solid state</td>
<td>110</td>
</tr>
<tr>
<td>i-Pr₃Si(THF)</td>
<td>solid state</td>
<td>115</td>
</tr>
</tbody>
</table>


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that the average frequency is slightly higher (Fig. 2). This indicates that protonation occurs at the cyano N atom and that H\(^+\) binds to the anion somewhat more strongly than does Ag\(^+\) or R\(_3\)Si\(^+\). If H(C\(_5\) (CN)\(_5\)), coordinate 14 so we assign an anion-bridged polymeric structure to are absent.

Strongly acidic protons show a marked tendency to be two-coordinate\(^{14}\) so we assign an anion-bridged polymeric structure to H(C\(_5\) (CN)\(_5\)), 3.

The propagation of bridges within five-fold symmetry and the positional choices amongst different pairs of cyano groups probably explains the formation of non-crystalline structure. Short, strong, low-barrier (SSLB) H-bonds are expected in 3 and the absence of νN–H–H in the IR in the 3000 cm\(^{-1}\) region is consistent with their presence.\(^ {14}\) A broad νN–H–N band is expected at ca. 1000 cm\(^{-1}\) but this region is masked by other vibrations, making deconvolution difficult. Consistent with the polymeric structure, the acid is functionally insoluble in benzene, toluene, m-xylene and even diethyl ether. With the exception of benzene, these solvents are sufficiently basic that they should be protonated by “an acid stronger than perchloric acid.” This indicates that the structure of 3 confers exceptional stability to the solid state, to the extent that insolubility annuls several orders of magnitude of acidity. H(C\(_5\) (CN)\(_5\)) does dissolve in acetonitrile and tetrahydrofuran, the latter with reversible polymerization of the solvent. These are relatively basic solvents but, in light of the insolubility of the acid in diethyl ether, high solvation energies of the dissolved ions must be the important factor for breaking up the polymeric structure. In retrospect, the choice of perchloric acid in acetonitrile for the earlier investigations of the basicity of the C\(_5\) (CN)\(_5\)\(^{-}\) ion,\(^ {15}\) is seen to be unfortunate. We suspect that protonation of C\(_5\) (CN)\(_5\)\(^{-}\) with perchloric acid could be achieved if carried out in toluene with anhydrous HClO\(_4\), but this is not easily done in a safe manner. Acid

3 is extremely sensitive to moisture making it difficult to obtain and store in high purity. Upon recrystallization from acetonitrile or THF it lightens in color as it sequesters water from glassware and solvents. As a solid, it takes up water from air to produce hydronium ion salts (νO–H ~ 3000 cm\(^{-1}\)) which contain H\(_2\)O\(^+\), H\(_2\)O\(_2\)^+ or H\(_2\)O\(_4\)^+ depending on the degree of hydration. This material is a convenient “acid form” of the C\(_5\) (CN)\(_5\)^\(-\) ion for use in metathesis reactions. The loss of colour upon hydration is consistent with electronic communication between anions via the strong H-bond bridges in the polymeric structure of 3.

In summary, these studies reveal the behaviour and possibilities of the C\(_5\) (CN)\(_5\)^\(-\) ion as a weakly coordinating anion and a Brønsted base. H(C\(_5\) (CN)\(_5\)) is the rare example of an acid that should be a superacid but whose functional acidity is significantly attenuated by the high stability of a solid-state polymeric structure. The Lewis basicity of the C\(_5\) (CN)\(_5\)^\(-\) ion towards R\(_3\)Si\(^+\) is similar to that of a neutral nitrile or a weakly basic oxyanion suggesting a general role for C\(_5\) (CN)\(_5\)^\(-\) as a moderately weakly coordinating anion. Given the chemically active role of the cyano group as a Lewis or Brønsted base in this chemistry, cyclo-pentadienidine anions with strongly electron-withdrawing groups that are less basic (e.g. –C\(_6\)F\(_5\)) hold greater promise as carbon-based weakly coordinating anions and non-polymeric carbon superacids.

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Notes and references

5 K. Seppel, Personal communication.