

Is cyanogen chloride (fluoride) a source of C N(+)?

Henry Rzepa 

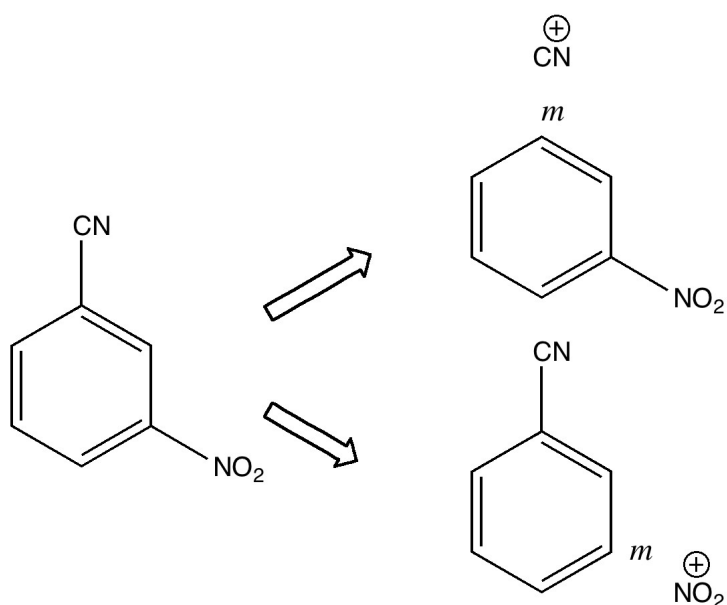
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Keywords

Reaction Mechanism

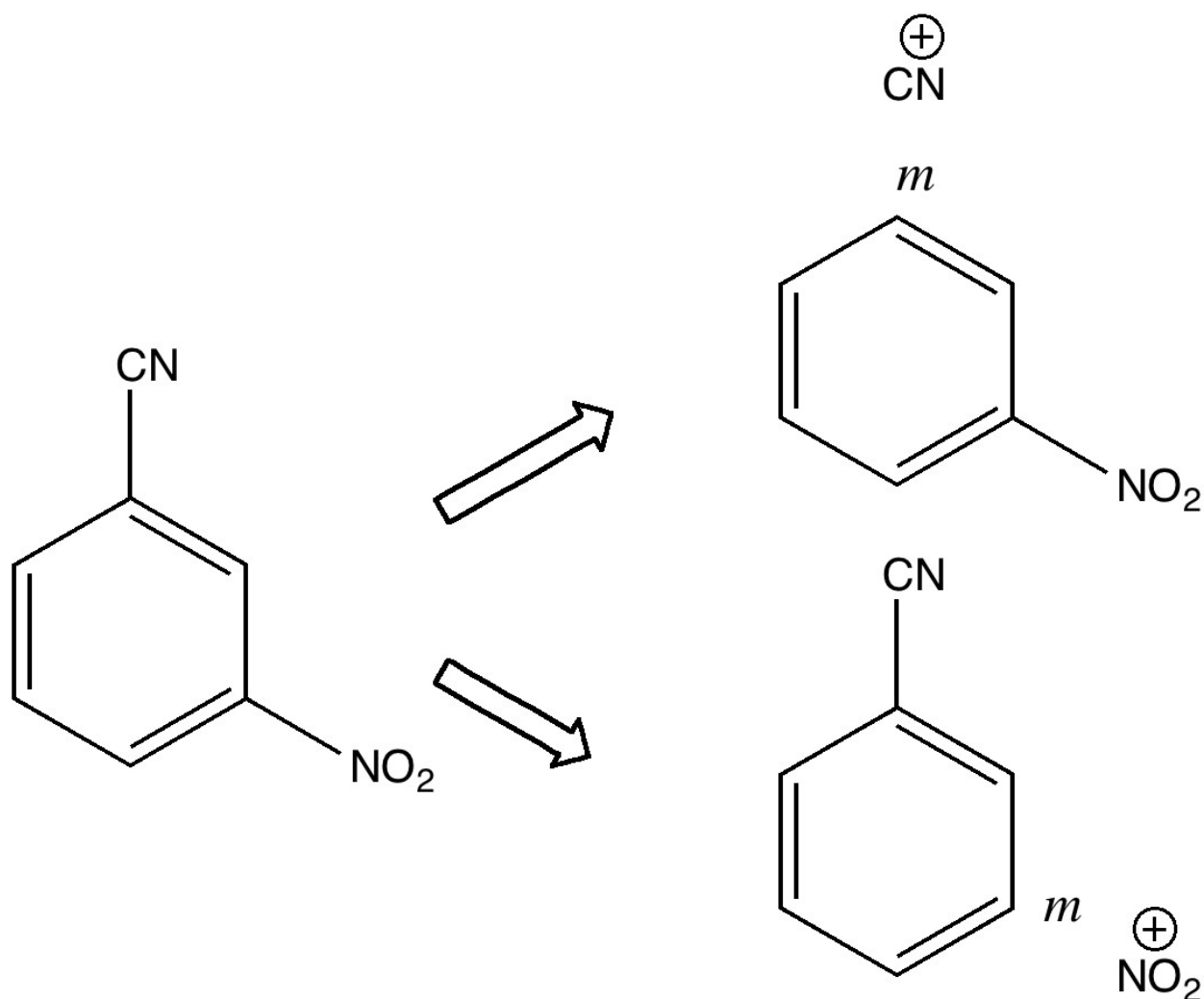


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In 2010 I [recounted the story](#) of an organic chemistry tutorial, in which I asked the students the question “how would you synthesize 3-nitrobenzonitrile”.

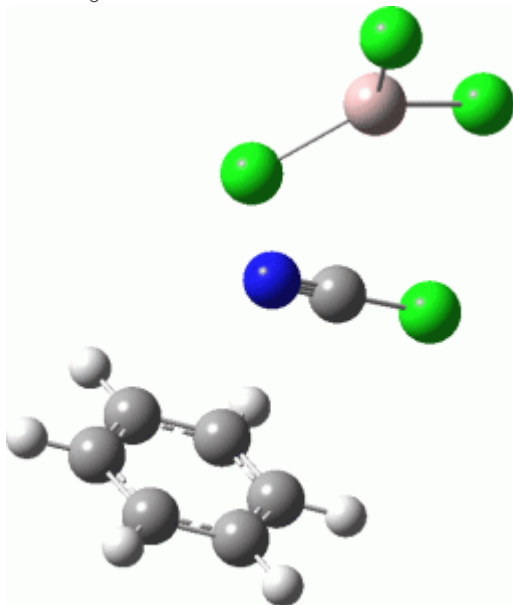


The expected answer was to generate a nitronium ion to nitrate benzonitrile, but can one invert this by generating a C N⁺ ion to cyanate nitrobenzene? The students were then invited to generate a valence bond structure for C N⁺ and I showed them the possibility that it might contain a quadruple bond to the carbon. Ten years later, Mike Turner [in a comment on that post](#) revealed an article dating from 1960[cite]10.1021/ja01491a064[/cite] in which cyanogen fluoride was studied. There, in an innocuous comment, they state “**Cyanogen fluoride, like cyanogen chloride, re-acted with benzene in the presence of aluminum chloride to form benzonitrile in 20% conversion**”. Here I explore whether this reagent really can be a source of free C N⁺.

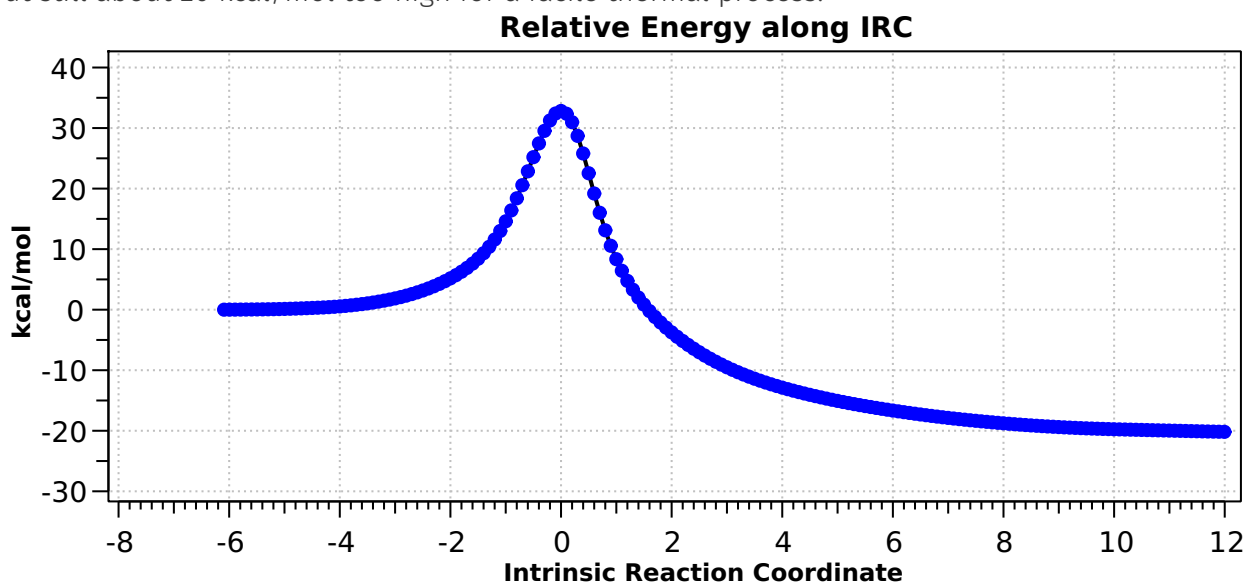
Calculations at the ω B97XD/Def2-TZVPP/SCRF=water level (FAIR Data DOI: [10.14469/hpc/7584](https://doi.org/10.14469/hpc/7584)) were conducted to explore the possible energetics of using ClCN to electrophilically cyanate benzene. Firstly, the energy of the separated ion pair AlCl₄⁻.C N⁺ is 190.9 kcal/mol higher than the neutral reagents AlCl₃.ClCN, which makes the formation of free C N⁺ unlikely. So what about a concerted process, in which benzene as a nucleophile attacks ClCN with the help

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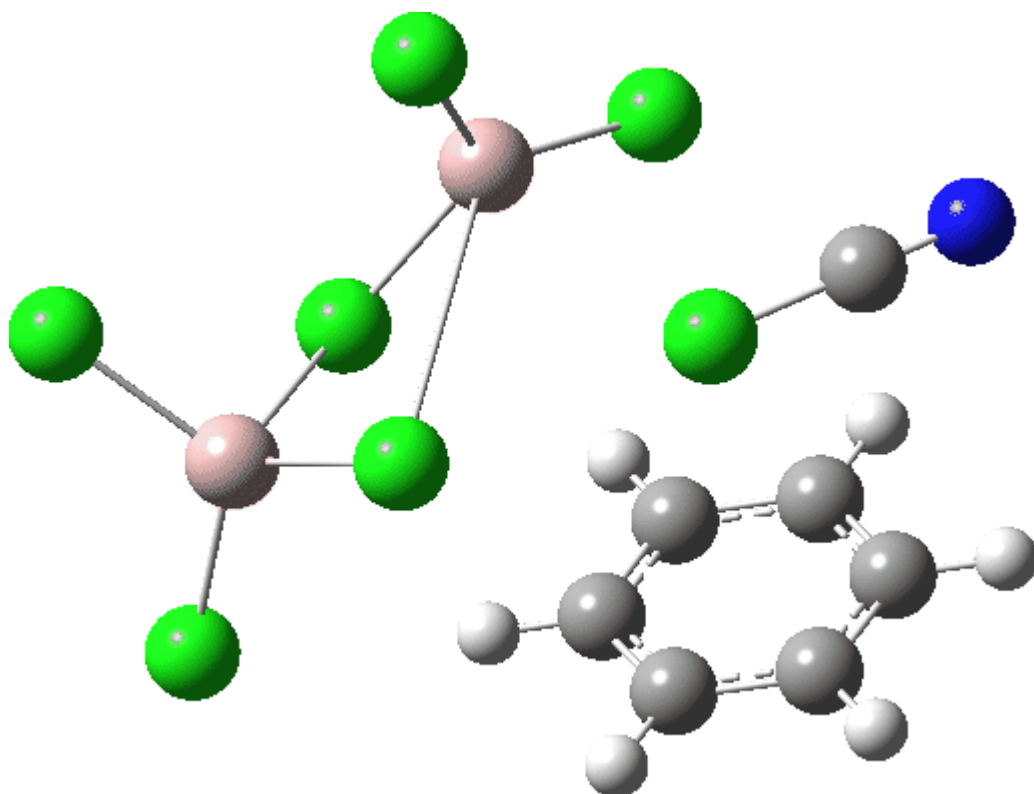
of AlCl_3 ? This would be a 1,1-substitution reaction at an sp-carbon centre.



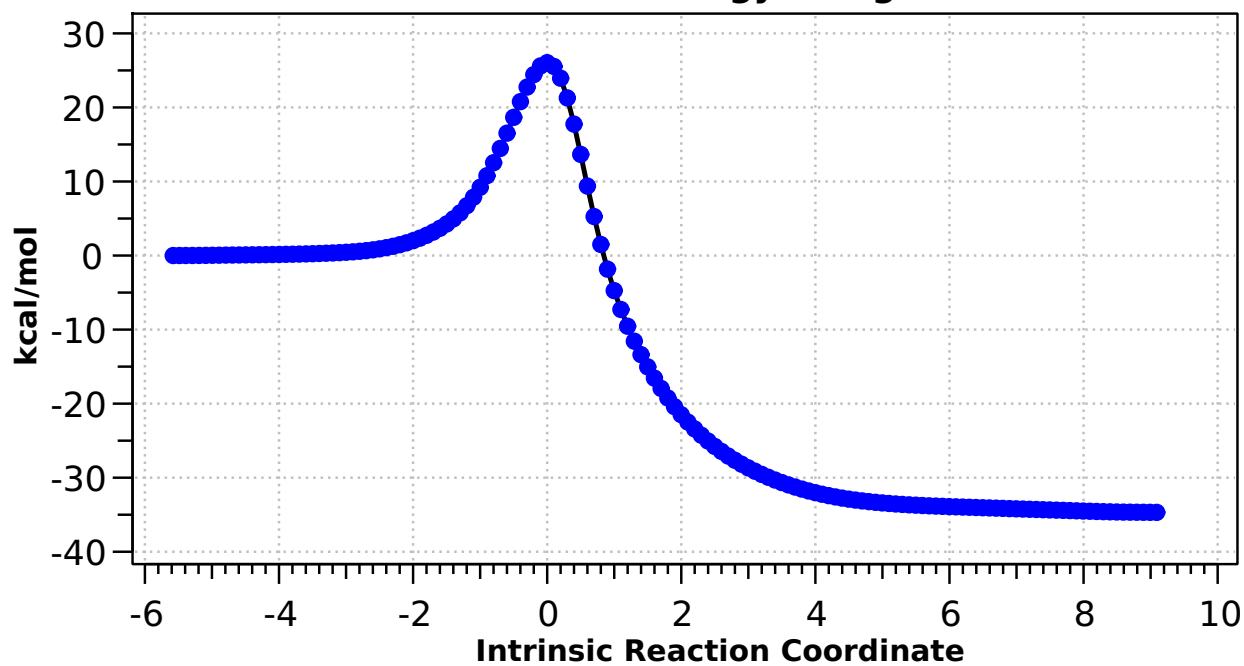
The free energy barrier for this bimolecular process is 46.4 kcal/mol. It is along the right lines, but still about 20 kcal/mol too high for a facile thermal process.

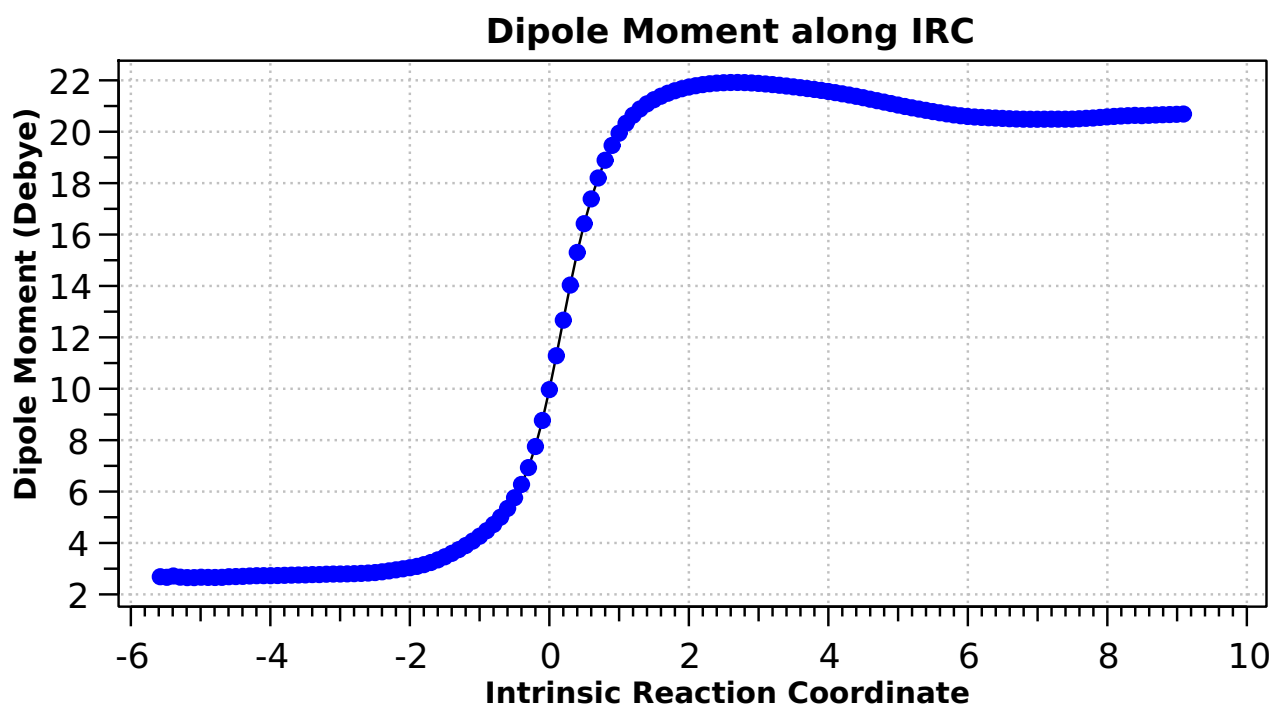


In an effort to improve the model and hence reduce this barrier, the dimeric reagent Al_2Cl_6 was tried instead. The final free energy barrier was 48.5 kcal/mol.



Relative energy along IRC





So to conclude, generating free $C N^+$ is very unlikely. But cyanogen chloride can act as a $C N^+$ “delivery agent” *via* a bimolecular route. There remains a mystery however. The free energy barriers for our two models are too high to accomplish facile cyanation of benzene. There must be another mechanism, as of yet unexplored, which must be found to finish off this study!

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