Stable NCNgNSi (Ng=Kr, Xe, Rn) Compounds with Covalently Bound C-Ng-N Unit: Possible Isomerization of NCNSi through the Release of the Noble Gas Atom

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Although the noble gas (Ng) compounds with either Ng?C or Ng?N bonds have been reported in the literature, compounds containing both bonds are not known. The first set of systems having a C-Ng-N bonding unit is predicted herein through the analysis of stability and bonding in the NCNgNSi (Ng=Kr?Rn) family. While the Xe and Rn inserted analogues are thermochemically stable with respect to all dissociation channels, but for the one producing CNSiN and free Ng, NCKrNSi has another additional three-body dissociation channel, NCKrNSi?CN+Kr+NSi, which is exergonic by ?9.8 kcal mol?1 at 298 K. This latter dissociation can be hindered by lowering the temperature. Moreover, the NCNgNSi?Ng+CNSiN dissociation is also kinetically prohibited by a quite high free energy barrier ranging from 25.2 to 39.3 kcal mol?1, with a gradual increase in going from Kr to Rn. Therefore, these compounds are appropriate candidates for experimental realization. A detailed bonding analysis by employing natural bond orbital, electron density, energy decomposition, and adaptive natural density partitioning analyses indicates that both Ng?N and C?Ng bonds in the title compounds are covalent in nature. In fact, the latter analysis indicates the presence of delocalized 3c?3e ?-bond within the C-Ng-N moiety and a totally delocalized 5c?2e ?-bond in these compounds. This is an unprecedented bonding characteristic in the sense that the bonding pattern in Ng inserted compounds is generally represented as the presence of covalent bond in one side of Ng, and the ionic interaction in the other side. Further, the dissociation of Ng from NCNgNSi facilitates the formation of a higher energy isomer of NCNSi, CNSiN, which cannot be formed from bare NCNSi as such, because of the very high free energy barrier associated with the isomeric transformation. Therefore, in the presence of Ng atoms it might be possible to detect the high energy isomer.

bonding

energy decomposition analysis

isomerization

noble gas insertion

stability

Bonding

Convergence of numerical methods

Dissociation

Energy barriers

Free energy

Inert gases

Isomerization

Isomers

Krypton

Radon

Xenon

Analysis of stability

Bonding characteristics

Dissociation channels

Energy decomposition

Energy decomposition analysis

Experimental realizations

Isomeric transformation

Natural bond orbital

Silicon compounds