Bond Theory

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Hypervalent Carbon Atom: “Freezing” the S_N2 Transition State**

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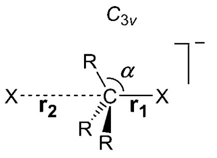
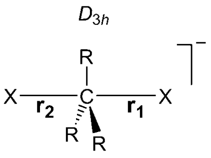
The quest for hypervalent molecules, in particular ones involving pentavalent carbon atoms, has challenged chemists for about a century.[1] Over the decades, the non-hypervalence (e.g., **A**; $\mathbf{r_1}$ and $\mathbf{r_2}$ are bond distances) or hypervalence (e.g., **B**) of various atoms in both molecular as well as extended structures has been investigated.[2,3] Recently, we have addressed the issue of why silicon is hypervalent (i.e., pentavalent) in $[Cl{-}SiH_3{-}Cl]^-$, whereas the carbon atom in $[Cl{-}CH_3{-}Cl]^-$ is not.[4] In terms of this ball-in-a-box model, silicon fits perfectly into the box constituted of five substituents. Carbon, in contrast, is too small and, in a sense, “drops to the bottom” of the box leading, consequently, to a $Cl^-{-}H_3CCl$ species having one long C–Cl bond, one localized C–Cl contact, and a pyramidalized CH_3 unit. The validity of this model was extended to heavier central group-14 atoms (Ge, Sn, Pb) as well as to other axial substituents (F).[4]



A



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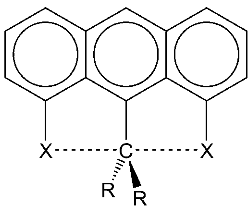

C

Herein, we present computational evidence that, under certain conditions, a carbon atom can become hypervalent as the central atom in a D_{3h}-symmetric, trigonal-bipyramidal $[X{-}CR_3{-}X]^-$ species. This hypervalence comes down to “freezing” the S_N2 transition state,[5] that is, converting it from a labile first-order saddle point into a stable equilibrium structure. Note, however, that in the present work, at variance with previous reports on hypervalent carbon atoms, the axial substituents are not geometrically confined by a molecular scaffold such as **C**.[6] Our evidence is based on relativistic density functional theory (DFT) computations with the ADF program at ZORA-OLYP/TZ2P.[7]

The idea is that if the CR_3 moiety in $[X{-}CR_3{-}X]^-$ is sufficiently rigid, the ball-in-a-box model (central atom moving within a box of substituents) will break down and the system rather behaves as one planar CR_3 unit between two X groups (see disk-between-balls model[8]). The behavior is then identical to that of the isoelectronic (3-center-4-electron) trihalides which form perfectly hypervalent, $D_{\infty h}$-symmetric $[X{-}Y{-}X]^-$ structures.[4,9] We have previously found such behavior for the noble gas (Ng)–methyl cation complexes $[Ng{-}CH_3{-}Ng]^+$ (with Ng = He, Ne), which are isoelectronic with $[Cl{-}CH_3{-}Cl]^-$ but, at variance to the latter, adopt perfectly hypervalent equilibrium structures **B**.[8,10]

The question now is: can we can extend the behavior of CR_3, which serves as a rigid disk between two axial substituents in the weakly bound noblegas complexes, to the anionic $[X{-}CR_3{-}X]^-$ species which feature significantly more stable axial bonds. The answer turns out to be yes. An interesting first indication for this was that by making CH_3 rigid in an artificial manner, $[Cl{-}CH_3{-}Cl]^-$ became hypervalent. Therefore, by freezing the CH_3 umbrella motion (by keeping only α fixed at 90°; see **A**), the imaginary frequency of $i337\ \mathrm{cm}^{-1}$, associated with an asymmetric Cl-C-Cl stretch vibration, becomes positive. In other words, the C–Cl bonds in $[Cl{-}CH_3{-}Cl]^-$ lose there tendency to localize.

Next, we undertook a quest for CR_3 radicals ($CR_3^{\cdot}$) which naturally show an increased resistance against pyramidalization as compared to $CH_3^{\cdot}$. This resistance may be achieved by choosing the substituents R which stabilize the radical electron in the carbon $2p_z$ atomic orbital (AO) on $CR_3^{\cdot}$ through π-acceptor orbitals on R (see **D**). This mechanism in favor of keeping a planar $CR_3^{\cdot}$ arrangement would then be active and even more pronounced in the negatively charged $[X{-}CR_3{-}X]^-$ in which the $2p_z$ AO is further populated.[4] Furthermore, substituents that are more bulky than R = H should also prevent pyramidalization for steric reasons, that is, R–R repulsion.[11] Nonetheless, we do not strive for bulkiness because in the five-coordinate species such steric factors work against hypervalency.[4,5e]

Figure 1 shows the energy of various $CR_3^{\cdot}$ species as a function of the angle θ ($\theta = \alpha - 90°$, see **A**) which measures

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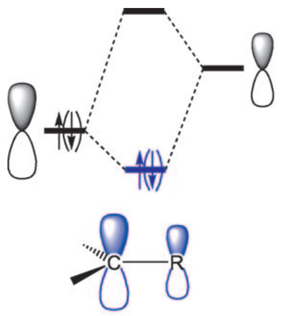

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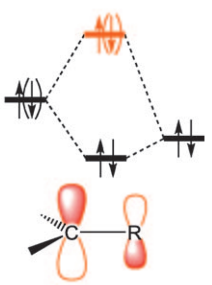

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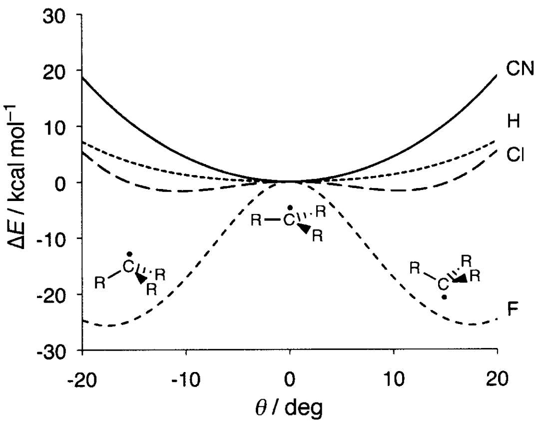

Figure 1. Relative energy, ΔE, of $CR_3^{\cdot}$ as a function of the distortion angle θ ($\theta=\alpha-90°$, see **A**) for R = F, Cl, H, and CN, computed at ZORA-OLYP/TZ2P.

how far the species deviates from planarity. As can be seen, the extent to which the energy goes up on pyramidalization increases indeed from R = H to CN, thus indicating that R = CN would be a good candidate for achieving a hypervalent $[X{-}CR_3{-}X]^-$ species. To probe this principal, we have also introduced π-donating substituents, R = F and Cl, which destabilize the central $2p_z$ electrons of the carbon atom (see **E**). As expected, the tendency to pyramidalize increases in the order of R = H, Cl, and F (see Figure 1).

Finally, we constructed the five-coordinate $[X{-}CR_3{-}X]^-$ species using R = H as a reference, and the substituent that reinforces the rigidity of CR_3, namely, R = CN (see Table 1). For R = H, one can recognize that the tendency of $[X{-}CR_3{-}X]^-$ to localize the axial bonds decreases together with the decreasing axial C–X bond strength in the order of X = F, Cl, Br, I, and At. In the first place, this is reflected by the decreasing height of the central barrier which goes from approximately 9 to 3.9 kcal mol^{-1}. But it also shows up in the systematic weakening of the negative force constant k^{umbrella} of the umbrella mode whithin this series, from -0.0906 to -0.0437 a.u.

This trend within the series of halogens is also reproduced for the substituent R = CN. Importantly, however, the increasing rigidity of $CR_3^{\cdot}$ from R = H to CN additionaly reduces the tendency of $[X{-}CR_3{-}X]^-$ to localize the axial bonds. For X = Br and R = CN, the D_{3h}-symmetric five-coordinate species $[X{-}CR_3{-}X]^-$ is only 0.04 kcal mol^{-1} above the localized C_{3v}-symmetric equilibrium structure $X^-{-}CR_3X$. Note that although the force constant k^{umbrella} of $[Br{-}C(CN)_3{-}Br]^-$ is still negative (i.e., the species is still labile with respect to C–X bond localization), it has dropped in absolute terms to the relatively small value of -0.0047 a.u. This value is more than an order of magnitude smaller than the k^{umbrella} of $[Br{-}CH_3{-}Br]^-$ which amounts to -0.0571 a.u.

Indeed, as we proceed in this manner, we eventually arrive at a viable hypervalent carbon species $[X{-}CR_3{-}X]^-$ where X = I as well as At and R = CN. Thus, $[I{-}C(CN)_3{-}I]^-$ and $[At{-}C(CN)_3{-}At]^-$ are D_{3h}-symmetric, pentavalent equilibrium structures with positive force constants, k^{umbrella}, of 0.0024 and 0.0026 a.u., respectively. The species $[I{-}C(CN)_3{-}I]^-$ and $[At{-}C(CN)_3{-}At]^-$ were confirmed as stable pentavalent equilibrium structures, even on the zero-point vibrational energy (ΔZPE) corrected potential energy surface (Table 1).[12] Note that the inclusion of ΔZPE corrections also converts $[Br{-}C(CN)_3\text{-}Br]^-$ effectively into a stable pentavalent species.

Table 1: Valence of the central carbon atom in $[X{-}CR_3{-}X]^-$.[a]

$[X{-}CR_3{-}X]^-$ R	X	Rigidity of CR_3[b] k^{umbrella} [a.u.]	C–X$^{\text{ax}}$ [kcal mol^{-1}]	$\lvert r_1-r_2\rvert$ [Å][c]	Complex [kcal mol^{-1}][d]	Barrier [kcal mol^{-1}][e]	Barrier + ΔZPE [kcal mol^{-1}][f]	C Valency
H	F	−0.0906	−45.0	1.25	−15.7	8.03	7.71	non-hypervalent
H	Cl	−0.0717	−31.8	1.55	−9.0	8.77	8.23	non-hypervalent
H	Br	−0.0571	−28.7	1.55	−8.0	6.30	5.78	non-hypervalent
H	I	−0.0501	−25.4	1.53	−7.3	5.34	4.82	non-hypervalent
H	At	−0.0437	−23.7	1.44	−6.6	3.90	3.40	non-hypervalent
CN	F	−0.0537	−83.5	0.69	−53.8	4.26	3.83	non-hypervalent
CN	Cl	−0.0197	−53.3	0.75	−25.5	1.00	0.76	non-hypervalent
CN	Br	−0.0047	−47.9	0.44	−22.8	0.04	0.00	hypervalent
CN	I	0.0024	−43.1	0.00	−21.0	0.00	0.00	hypervalent
CN	At	0.0026	−41.9	0.00	−21.2	0.00	0.00	hypervalent

[a] Computed at ZORA-OLYP/TZ2P. [b] Force constants of umbrella mode k^{umbrella} and heterolytic C–X$^{\text{ax}}$ interaction energies, ΔE_{int}, between the corresponding molecular fragments frozen to the geometry they adopt in the overall D_{3h}-symmetric species. [c] Difference in axial bond distances in equilibrium structure. [d] Complexation energy of X^- + CR_3X. [e] Central S_N2 energy barrier. [f] Central S_N2 energy barrier with zero-point vibrational energy correction.

The results are relatively robust with respect to variations in the methodology which we have explored by further increasing the basis-set flexibility and polarization (using ZORA-OLYP/QZ4P), and replacing the OLYP approach by density functionals that, in general, yield somewhat higher barriers (using ZORA-OPBE/TZ2P and ZORA-M06/TZ2P; see the Supporting Information).[7] All these approaches consistently confirm the decrease of the central S_N2 barrier and the shift of the force constant k^{umbrella} towards the positive domain, as one goes from R = H to CN (quite pronounced effect) and as X varies along F, Cl, Br, I, and At (smaller steps). The exact point at which hypervalence is achieved varies somewhat with the approach. On the ZPE-corrected potential energy surface, ZORA-OLYP/TZ2P yields hypervalence for $[Br{-}C(CN)_3{-}Br]^-$, whereas ZORA-OLYP/QZ4P and ZORA-OPBE/TZ2P arrive at hypervalence starting from $[I{-}C(CN)_3{-}I]^-$. However, $[At{-}C(CN)_3{-}At]^-$ is hypervalent at all levels of theory, including ZORA-M06/TZ2P. Our proof of principal may inspire the quest for hypervalent carbon in trigonal bipyramidal configurations.

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