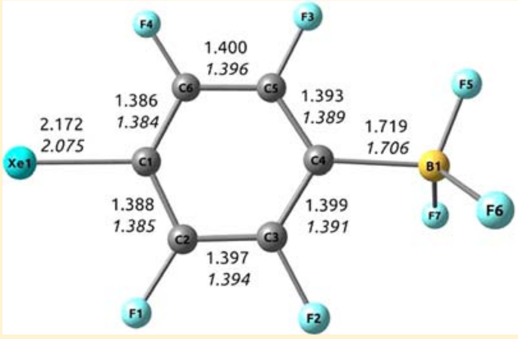
Inorganic Chemistry
Article
pubs.acs.org/IC

Spacer Separated Donor−Acceptor Complexes [D→C_6F_4→BF_3] (D = Xe, CO, N_2) and the Dication $[Xe→C_6F_4←Xe]^{2+}$. A Theoretical Study

Catharina Goedecke,[†] René Sitt,[†] and Gernot Frenking*,[†]

[†]Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerweinstrasse, D-35043 Marburg, Germany

ABSTRACT: Quantum chemical calculations using density functional theory at the BP86/TZ2P+ level and ab initio calculations at MP2/def2-TZVPP have been carried out for the donor−acceptor complexes [D→C_6F_4→BF_3] (D = Xe, CO, N_2,) and the dication $[Xe→C_6F_4←Xe]^{2+}$. The calculations predict rather short D→C_6F_4(BF_3) and (D)C_6F_4→BF_3 bonds in the neutral systems which indicate rather strong binding interactions. The calculated partial charges which give large positive values for the donor moieties and negative values for the acceptor fragments and the large bond indices also suggest very strong donor−acceptor interactions D→C_6F_4→BF_3 and Xe→$C_6F_4^{2+}$←Xe. An energy decomposition analysis suggests very strong intrinsic interactions for both systems. The donor−acceptor bonds in [D→C_6F_4→BF_3] are much stronger than the direct donor−acceptor interactions D→BF_3 which are only weakly bonded van der Waals complexes. The calculated donor−acceptor interactions D→C_6F_4(BF_3) are 26.1 kcal/mol for D = Xe, 121.5 kcal/mol for D = CO, and 86.9 kcal/mol for D = N_2. The strength of the intrinsic (D)C_6F_4→BF_3 interactions are calculated to be between 51.1−51.6 kcal/mol. The theoretical bond dissociation energies for the decomposition of [D→C_6F_4→BF_3] yielding D + C_6F_4 + BF_3 suggests that the xenon compound [Xe→C_6F_4→BF_3] is metastable but may become stabilized in the condensed phase by intermolecular interactions. The complexes [OC→C_6F_4→BF_3] and [N_2→C_6F_4→BF_3] are predicted to be thermodynamically stable. It is suggested that the above adducts are examples of spacer-separated donor−acceptor complexes [D→S→A] which are a hitherto unrecognized class of molecules.



■ INTRODUCTION

In 2009, Frohn reported in a lecture at the 19th International Symposium on Fluorine Chemistry at Jackson Hole, Wyoming about the synthesis of the xenon compound Xe−C_6F_4−BF_3 which was identified by NMR spectroscopy.[1] Although the author could not obtain crystals which are suitable for X-ray structure analysis, the spectroscopic evidence made it clear that the compound is a rare example of a molecule which has a xenon−carbon bond. We were intrigued by the finding, because the direct donor−acceptor bond between the Lewis acid/base pair BF_3 and Xe yields only a very weakly bonded complex Xe→BF_3. The observation by Frohn let us speculate that the spacer moiety 2,3,5,6-C_6F_4 effectively enhances the donor−acceptor interactions between the Lewis base Xe and the Lewis acid BF_3. Quantum chemical calculations supported our assumption, and they revealed astonishingly strong Xe→C_6F_4→BF_3 binding in the molecule. We extended the investigation to complexes with the donor species CO and N_2. Here we report about our theoretical investigation of spacer-separated donor−acceptor complexes [D→C_6F_4→BF_3] (D = Xe, N_2, CO). We also report about quantum chemical calculations of the dication $[Xe→C_6F_4←Xe]^{2+}$. The latter molecule has also been observed by Frohn who reports about his experimental findings in the preceding paper in this issue.[2]

■ COMPUTATIONAL METHODS

All geometries were optimized under C_s-symmetry constraint using density functional theory at the BP86 level of theory[3] in conjunction with uncontracted Slater-type orbitals (STOs) as basis functions for the SCF calculations.[4] The basis sets for all elements are triple-ζ quality augmented by two sets of polarization functions and one set of diffuse functions. Core electrons were treated by the frozen-core approximation. This level of theory is denoted BP86/TZ2P+. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[5] Scalar relativistic effects have been incorporated by applying the zeroth-order regular approximation (ZORA).[6] The nature of the stationary points on the potential energy surface was determined by calculating the vibrational frequencies at BP86/TZ2P+. All structures are minima on the potential energy surface (PES) unless otherwise noted. Thermodynamic corrections for calculating free energies were taken from the latter calculations. All energy values in this work have been calculated at BP86/TZ2P+, unless otherwise specified. These calculations were done with the program package ADF.[7] Additional geometry optimizations have been carried out using the Møller−Plesset perturbation theory terminated at second order (MP2)[8] in conjunction with def2-TZVPP[9] basis sets using Gaussian 09.[10] This level of theory is denoted MP2/TZVPP. Atomic partial charges have been taken from the latter calculations using the NBO method.[11] The analysis of the electron density with the Atoms-in-Molecules (AIM) method[12] was performed at the (BP86/

Received: August 6, 2012
Published: October 15, 2012

dx.doi.org/10.1021/ic301722q | *Inorg. Chem.* 2012, 51, 11259−11265

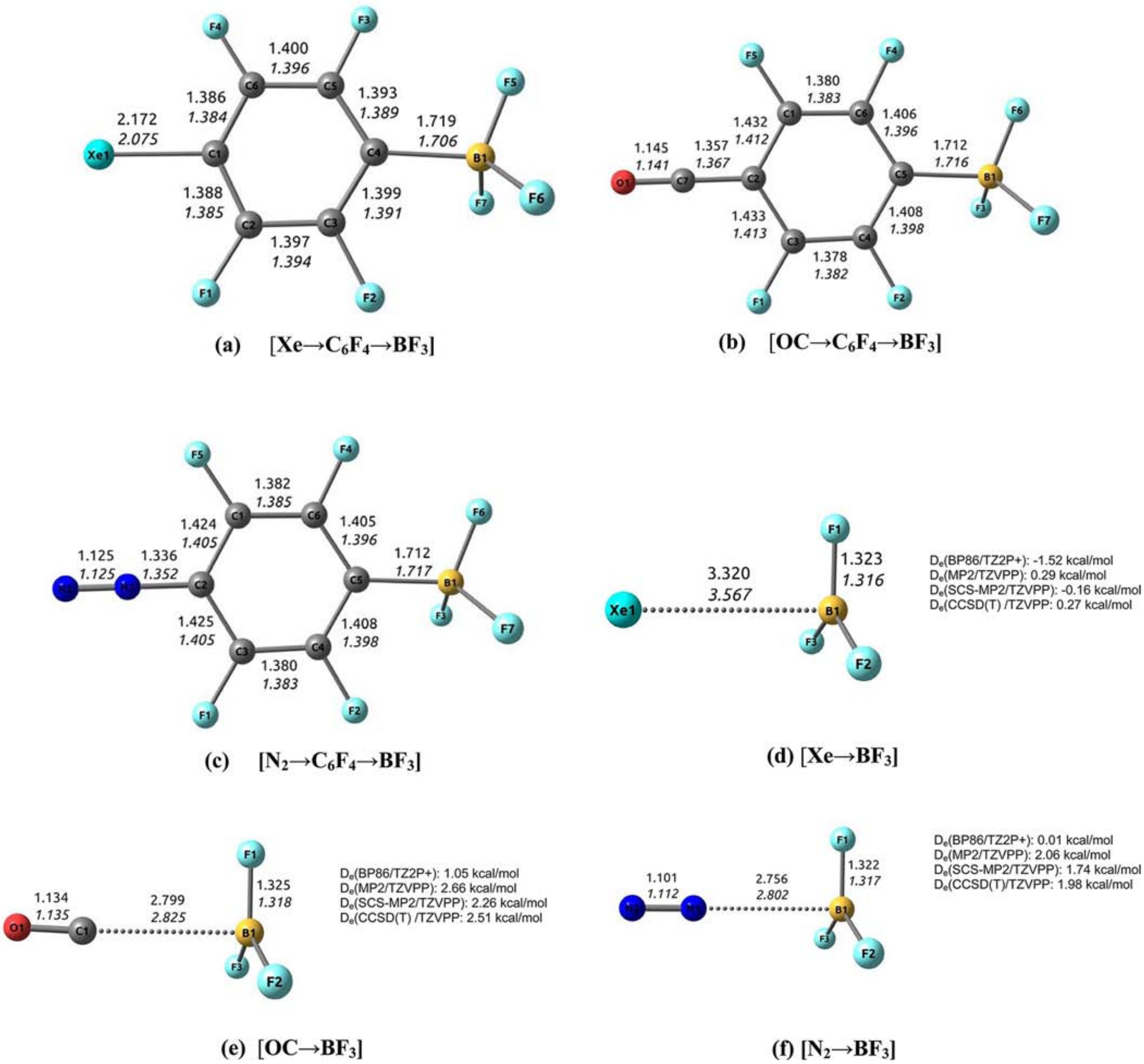


Figure 1. Optimized geometries of (a–c) [D→C_6F_4→BF_3] and (d–f) [D-→BF_3] (D = Xe, CO, N_2) at BP86/TZ2P+ (*MP2/TZVPP*). Bond distances are given in Å. Calculated bond dissociation energies D_e for structures D-BF_3 at different levels of theory.

def2-TZVPP// BP86/TZ2P+ level with the AIMAll program package.[13]

The bonding situation of the donor−acceptor bonds was investigated by an energy decomposition analysis (EDA) which was developed by Morokuma[14] and by Ziegler and Rauk.[15,16] The bonding analysis focuses on the instantaneous interaction energy ΔE_{int} of a bond A−B between two fragments A and B in the particular electronic reference state and in the frozen geometry of AB. This interaction energy is divided into three main components [eq 1a].

$$\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{orb}} \tag{1a}$$

The term $\Delta E_{\mathrm{elstat}}$ corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the prepared atoms and is usually attractive. The Pauli repulsion $\Delta E_{\mathrm{Pauli}}$ is the energy change associated with the transformation from the superposition of the unperturbed electron densities $\rho_A + \rho_B$ of the isolated fragments to the wave function $\Psi^0 = N\hat{A}[\Psi_A\Psi_B]$, which properly obeys the Pauli principle through explicit antisymmetrization ($\hat{A}$ operator) and renormalization of the product wave function. It comprises the destabilizing interactions between electrons of the same spin on either fragment. The orbital interaction ΔE_{orb} accounts for charge transfer and polarization effects.[17] The ΔE_{orb} term can be decomposed into contributions from each irreducible representation of the point group of the interacting system. This makes it possible to estimate the intrinsic strength of orbital interactions from orbitals having a′ (σ) and a″ (π) symmetry quantitatively. To obtain the bond dissociation energy (BDE) D_e the preparation energy ΔE_{prep} which gives the relaxation of the fragments into their electronic and geometrical ground states must be added to ΔE_{int} [eq 2a].

$$\Delta E(= -D_e) = \Delta E_{\mathrm{int}} + \Delta E_{\mathrm{prep}} \tag{2a}$$

To calculate the dissociation energies, we calculated each fragment in its optimized geometry and derived ΔE by eq 2a. Further details on the EDA can be found in the literature.[7b,18] The EDA has been used by us for a comprehensive study of donor−acceptor interactions in main-group and transition-metal complexes.[19,20]

Donor–Acceptor Complexes [D→C_6F_4→BF_3]. Figure 1a–c shows the optimized geometries of the complexes [D→C_6F_4→BF_3] (D = Xe, N_2, CO) at BP86/TZ2P+ and MP2/TZVPP. The calculated bond lengths and angles which were obtained at the two levels of theory are very similar to each other. The calculated Xe–C distances at BP86/TZ2P+ (2.172 Å) and MP2/TZVPP (2.075 Å) are close to the value for a standard Xe–C single bond (2.06 Å).[21] Very short distances are also predicted for the C–C bond in [OC→C_6F_4→BF_3] (1.357 Å at BP86/TZVPP and 1.367 Å at MP2/TZVPP) and for the N–C bond in [N_2→C_6F_4→BF_3] (1.336 Å at BP86/TZVPP and 1.352 Å at MP2/TZVPP). The C–B bond lengths in the complexes [D→C_6F_4→BF_3] are in a narrow range between 1.706–1.719 Å which means that they are somewhat longer than in donor–acceptor complexes NHC→BF_3 (NHC = N-Heterocyclic Carbene) which have been isolated (1.635–1.668 Å).[22] The calculated bond lengths suggest that the donor–acceptor interactions D→C_6F_4→BF_3 are rather strong.

The very short distances of the donor–acceptor bonds in [D→C_6F_4→BF_3] are in striking contrast to the direct donor–acceptor interactions D→BF_3 which are very weak. Figure 1d–e shows the optimized geometries of the complexes [D→BF_3]. The donor–acceptor bonds are very long, and the BDEs of the D→BF_3 bonds are quite small. The calculations suggest that the complexes D→BF_3 are weakly bonded adducts, while the spacer separated complexes [D→C_6F_4→BF_3] have genuine chemical bonds.

We calculated the bond dissociation energies (BDEs) of the complexes [D→C_6F_4→BF_3] into the closed-shell fragments[23] according to the following equations:

$$[\mathrm{Xe}\to \mathrm{C_6F_4}\to \mathrm{BF_3}] \to \mathrm{Xe} + \mathrm{C_6F_4} + \mathrm{BF_3}$$
$$\Delta E = -5.2\ \mathrm{kcal/mol};\quad \Delta G^{298} = -24.5\ \mathrm{kcal/mol} \qquad (1)$$

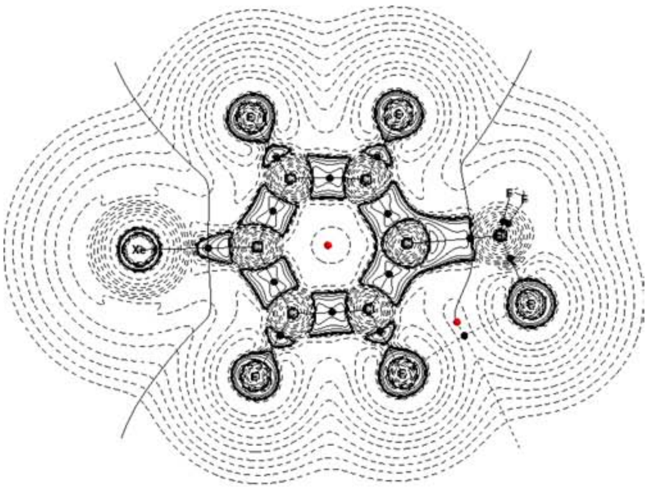
$$[\mathrm{OC}\to \mathrm{C_6F_4}\to \mathrm{BF_3}] \to \mathrm{CO} + \mathrm{C_6F_4} + \mathrm{BF_3}$$
$$\Delta E = 67.0\ \mathrm{kcal/mol};\quad \Delta G^{298} = 47.0\ \mathrm{kcal/mol} \qquad (2)$$

$$[\mathrm{N_2}\to \mathrm{C_6F_4}\to \mathrm{BF_3}] \to \mathrm{N_2} + \mathrm{C_6F_4} + \mathrm{BF_3}$$
$$\Delta E = 28.3\ \mathrm{kcal/mol};\quad \Delta G^{298} = 8.3\ \mathrm{kcal/mol} \qquad (3)$$

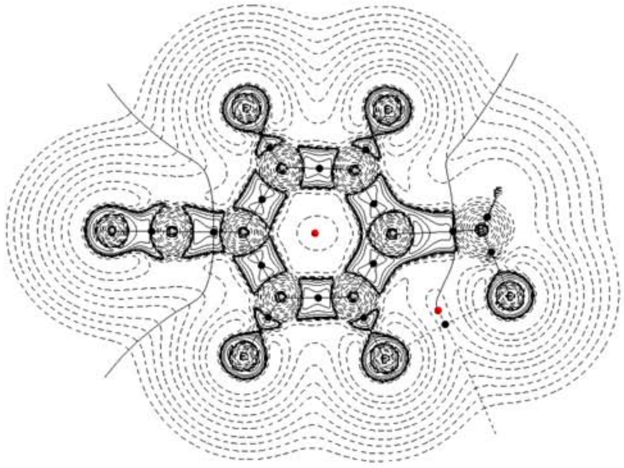
The calculations suggest that, in spite of the short donor–acceptor bonds, free [Xe→C_6F_4→BF_3] is thermodynamically unstable with respect to fragmentation into the donor, spacer, and acceptor fragments Xe + C_6F_4 + BF_3. The experimental results indicate that intermolecular interactions in the solid state are strong enough to make [Xe→C_6F_4→BF_3] an observable species which can be investigated with spectroscopic methods.[2] In contrast, the complexes [OC→C_6F_4→BF_3] and [N_2→C_6F_4→BF_3] are predicted to be stable at room temperature for dissociation into the fragments even as free molecules.

Figure 2 shows the Laplacian of the electron density $\nabla^2\rho(r)$ of the complexes [D→C_6F_4→BF_3]. There is an area of charge concentration from the donor species toward the spacer fragment D→C_6F_4 which indicates signifcant charge donation particularly from xenon. The Xe–C bond in [Xe→C_6F_4→BF_3] is strongly polarized toward the carbon end, and the xenon atom is surrounded by an area of charge depletion ($\nabla^2\rho(r) > 0$, dashed lines). This is in agreement with the calculated partial charge at Xe (+0.72 e) which is given by the NBO calculations (Table 1). The partial charges at CO (+0.56) and N_2 (+0.34) exhibit a decreasing order which should not be confused with the strength of the D→C_6F_4(BF_3) interactions. This will be discussed further below.

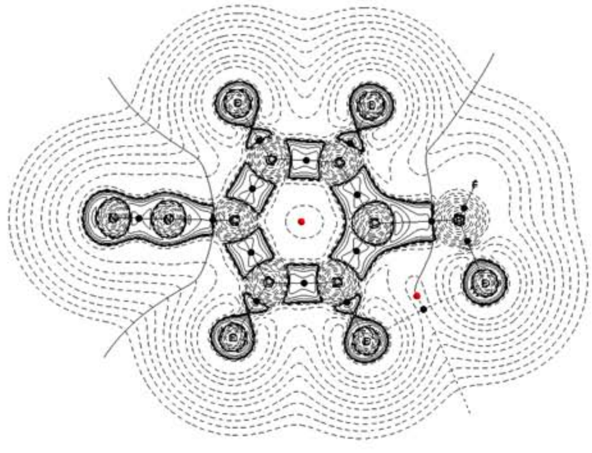
The shape of the Lapacian indicates also an area of charge concentration at the carbon donor atom which is bonded to boron (Figure 2). The calculated partial charges at the BF_3 moiety which have values between 0.39–0.41 e are nearly the same for all complexes [D→C_6F_4→BF_3]. This finding suggests that the DC_6F_4→BF_3 donation is not much influenced by the nature of the donor species D. The calculated partial charge for the space fragment C_6F_4 varies between −0.31 e in [Xe→C_6F_4→BF_3] and +0.05 e [N_2→C_6F_4→BF_3]. The AIM analysis gives a bond critical point between one fluorine atom of the BF_3 group and one fluorine atom of the benzene ring as well as a ring critical point which indicates weak fluorine–fluorine



(a) [Xe→C_6F_4→BF_3]



(b) [OC→C_6F_4→BF_3]



(c) [N_2→C_6F_4→BF_3]

Figure 2. Contour line diagram showing the Laplacian of the electron density $\nabla^2\rho(r)$ of (a–c) [D→C_6F_4→BF_3] (D = Xe, CO, N_2) at BP86/def2-TZVPP// BP86/TZ2P+. Dashed lines indicate areas of charge depletion ($\nabla^2\rho(r) > 0$), solid lines indicate areas of charge

Figure 2. continued

accumulation ($\nabla^2\rho(r) < 0$). Bond critical points are shown in black, ring critical points are shown in red. Solid lines which connect the atomic nuclei are the bond paths, while the solid lines which cross the bond paths indicate the zero-flux surfaces in the molecular plane. Only the zero-flux surface lines which separate the donor and acceptor moieties from C_6F_4 are shown.

Table 1. Calculated NBO Partial Charges q and Wiberg Bond Indices P

$[D \rightarrow C_6F_4 \rightarrow BF_3]$	q(D)	q(C_6F_4)	q(BF_3)	P(D−C)	P(C−B)
D = Xe	0.72	−0.31	−0.41	0.84	0.65
D = CO	0.56	−0.17	−0.39	1.38	0.66
D = N_2	0.34	0.05	−0.39	1.20	0.66
$[Xe \rightarrow C_6F_4 \leftarrow Xe]^{2+}$.	0.45	1.10	-	0.41	-

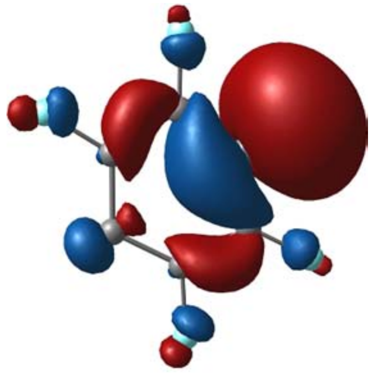
interactions. The calculated bond orders (Table 1) suggest that the $D \rightarrow C_6F_4(BF_3)$ bonds can be considered single bonds which in case of D = CO, N_2 have some contributions from π bonding. This is in agreement with the EDA results which are discussed below that show a significant π bonding character for the $OC \rightarrow C_6F_4(BF_3)$ and $N_2 \rightarrow C_6F_4(BF_3)$ bonds. The bond order for the $(D)C_6F_4 \rightarrow BF_3$ bonds has a rather uniform value of 0.65 for all three complexes.

Figure 3 shows the shape of the lowest lying vacant orbital (LUMO) and the highest lying occupied orbital (HOMO) of C_6F_4 in the frozen geometry of $Xe{-}C_6F_4{-}BF_3$.[24] It becomes clear that the LUMO and the HOMO are perfectly suited for strong donor−acceptor interactions with the HOMO of D = Xe, CO, N_2 and the LUMO of BF_3, respectively. It is thus reasonable to analyze the bonding situation in the compounds in terms of dative bonds $[D \rightarrow C_6F_4 \rightarrow BF_3]$. A quantitative account of the strength of the donor−acceptor interactions is given by the energy decomposition analysis.

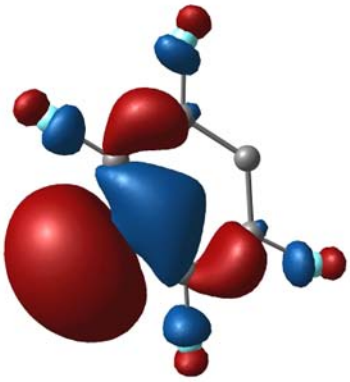
Table 2 shows the results of the EDA calculations for the complexes $[D \rightarrow C_6F_4 \rightarrow BF_3]$ (D = Xe, CO, N_2,). Each complex has been analyzed using three different fragmentation schemes. We first calculated the donor−acceptor bonds $D \rightarrow C_6F_4(BF_3)$ and $(D)C_6F_4 \rightarrow BF_3$ separately, but we also calculated the strength of both bonds $D \rightarrow C_6F_4 \rightarrow BF_3$ using the fragments C_6F_4 and $D \cdots BF_3$.

The EDA data reveal that the instantaneous interactions $D \rightarrow C_6F_4(BF_3)$ and $(D)C_6F_4 \rightarrow BF_3$ are very strong. The ΔE_{int} values of the donor moieties where D is Xe (−26.1 kcal/mol), CO (−121.5 kcal/mol), or N_2 (−86.9 kcal/mol) are much higher than the interaction energies when D is a ligand in transition-metal complexes $(CO)_5W{-}D$.[19a,25] The ΔE_{int} values for the Lewis acid BF_3 are nearly the same in the three complexes. The calculated data which are between −51.1 kcal/mol for $(Xe)C_6F_4 \rightarrow BF_3$ and −51.6 kcal/mol for $(N_2)C_6F_4 \rightarrow BF_3$ are larger than the ΔE_{int} values for other strongly bonded complexes like $Me_3P \rightarrow BF_3$ (−45.4 kcal/mol) and $H_3N \rightarrow BF_3$ (−46.6 kcal/mol).[19,26] The ΔE_{int} values for the simultaneous interactions of both donor−acceptor bonds $D \rightarrow C_6F_4 \rightarrow BF_3$ are a bit higher than the sum of the two separately calculated values. The theoretical values for the interactions energies support the assessment that the instantaneous interactions $D \rightarrow C_6F_4 \rightarrow BF_3$ are very strong. The calculated preparation energies ΔE_{prep} for the interacting fragments predict that the free complex $[Xe \rightarrow C_6F_4 \rightarrow BF_3]$ is thermodynamically unstable with respect to dissociation into the three fragments (Table 2). The level of theory which is employed in this study is not sufficient to give a highly accurate estimate of the BDE of the complexes. However, the calculated data agree with the experimental observation[2] that the compound $[Xe \rightarrow C_6F_4 \rightarrow BF_3]$ is not very stable. Intermolecular forces contribute somewhat to the stability of the xenon compound which makes it possible that it can be studied with spectroscopic methods.

The calculated data in Table 2 predict that the CO and N_2 complexes $[OC \rightarrow C_6F_4 \rightarrow BF_3]$ and $[N_2 \rightarrow C_6F_4 \rightarrow BF_3]$ do not only possess stronger bonds between $C_6F_4{-}BF_3$ and the diatomic donor species CO and N_2 but that they are also much more stable with regard to dissociation into the donor and acceptor fragments. The BDEs of the weakest bonds $(OC)C_6F_4 \rightarrow BF_3$ (D_e = 20.2 kcal/mol) and $(N_2)C_6F_4 \rightarrow BF_3$ (D_e = 20.1 kcal/mol) are ca. 25 kcal/mol larger than the BDE of the $(Xe)C_6F_4 \rightarrow BF_3$ bond. Since the latter molecule could be observed, we think that the former species should also be stable enough to be isolated.



LUMO
(-0.128 eV)



HOMO
(-0.356 eV)

Figure 3. Plot of the lowest lying vacant orbital (LUMO) and the highest lying occupied orbital (HOMO) of C_6F_4 in the frozen geometry of $Xe{-}C_6F_4{-}BF_3$.

The finding that the chemical bonding in the complexes $[D \rightarrow C_6F_4 \rightarrow BF_3]$ is much stronger than the direct donor−acceptor interactions $D \rightarrow BF_3$ leads to the question if there are other spacer moieties S and acceptors A which yields adducts $[D \rightarrow S \rightarrow A]$ that are more strongly bonded than $D \rightarrow A$. We searched the literature and found that related complexes with the spacer moieties CO_2, P_4, and N_2O which are bonded with one atom to the Lewis bases phosphines PR_3 and NHCs and with another atom to Lewis acids boranes BR_3 have been reported. The bonding situation in these complexes has not been analyzed, and no comparison has been made with the directly bonded complexes $R_3P \rightarrow BR_3$ and $NHC \rightarrow BR_3$. What is the common feature of C_6F_4, CO_2, P_4, and N_2O which enables them to engage in concerted donor−acceptor interaction? We think that spacer-separated donor−acceptor complexes are an unrecognized class of molecules which exhibits an interesting bonding situation that is worthwhile to become studied. We will address this topic in forthcoming theoretical studies.[27]

Dication $[Xe \rightarrow C_6F_4 \leftarrow Xe]^{2+}$. Figure 4 shows the optimized geometry and the Laplacian of the electron density $\nabla^2\rho(r)$ of the

Table 2. Results of the EDA Calculations of $D-C_6F_4-BF_3$ (D = Xe, CO, N_2) at BP86/TZ2P+[c]

fragments	$F_3B(C_6F_4)$ + Xe		F_3B + (C_6F_4)Xe		$[F_3B\cdots Xe]$ + C_6F_4	
ΔE_{int}	−26.1		−51.1		−95.2	
ΔE_{Pauli}	147.0		130.5		250.1	
ΔE_{elstat}[a]	−66.5	(38.4%)	−78.1	(43.0%)	−141.8	(41.1%)
ΔE_{orb}[a]	−106.6	(61.6%)	−103.5	(57.0%)	−203.6	(59.0%)
ΔE_{orb} (σ)[b]	−97.0	(91.0%)	−99.6	(96.3%)	−190.5	(93.6%)
ΔE_{orb} (π)[b]	−9.6	(9.0%)	−3.8	(3.7%)	−13.0	(6.4%)
ΔE_{prep}	26.3		55.7		100.4	
ΔE (= $-D_e$)	0.2		4.5		5.2	
fragments	$F_3B(C_6F_4)$ + CO		F_3B + (C_6F_4)CO		$[F_3B\cdots CO]$ + C_6F_4	
ΔE_{int}	−121.5		−51.5		−179.3	
ΔE_{Pauli}	364.9		148.4		478.9	
ΔE_{elstat}[a]	−162.6	(33.4%)	−101.3	(50.7%)	−252.7	(38.4%)
ΔE_{orb}[a]	−323.9	(66.6%)	−98.5	(49.3%)	−405.4	(61.6%)
ΔE_{orb} (σ)[b]	−271.9	(83.9%)	−90.3	(91.7%)	−351.1	(86.6%)
ΔE_{orb} (π)[b]	−52.0	(16.1%)	−8.2	(8.3%)	−54.3	(13.4%)
ΔE_{prep}	49.6		31.3		112.3	
ΔE (= $-D_e$)	−71.9		−20.2		−67.0	
fragments	$F_3B(C_6F_4)$ + N_2		F_3B + $(C_6F_4)N_2$		$[F_3B\cdots N_2]$ + C_6F_4	
ΔE_{int}	−86.9		−51.6		−139.3	
ΔE_{Pauli}	308.6		147.6		458.9	
ΔE_{elstat}[a]	−124.1	(31.4%)	−110.6	(50.5%)	−230.8	(38.6%)
ΔE_{orb}[a]	−271.4	(68.6%)	−98.6	(49.5%)	−367.4	(61.4%)
ΔE_{orb} (σ)[b]	−225.9	(83.2%)	−90.5	(91.8%)	−316.8	(86.2%)
ΔE_{orb} (π)[b]	−45.6	(16.8%)	−8.1	(8.2%)	−50.6	(13.8%)
ΔE_{prep}	53.5		31.5		111.0	
ΔE (= $-D_e$)	−33.5		−20.1		−28.3	

[a] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$. [b] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}. [c] Energy values are given in kcal/mol.

dication $[Xe{\rightarrow}C_6F_4{\leftarrow}Xe]^{2+}$. The calculated Xe−C bond length (2.134 Å) is a bit shorter than in $[Xe{\rightarrow}C_6F_4{\rightarrow}BF_3]$ (2.172 Å). The dication $[Xe{\rightarrow}C_6F_4{\leftarrow}Xe]^{2+}$ can formally be considered as a donor−acceptor complex between the acceptor moiety $C_6F_4^{2+}$ in the electronic singlet state and two xenon atoms as donors. The doubly charged $C_6F_4^{2+}$ fragment is a stronger acceptor than neutral $C_6F_4{\rightarrow}BF_3$ which explains the shorter Xe−C bonds in the dication. The shape of the Laplacian $\nabla^2\rho(r)$ of $[Xe{\rightarrow}C_6F_4{\leftarrow}Xe]^{2+}$ shows similar features for the Xe−C bonds as in $[Xe{\rightarrow}C_6F_4{\rightarrow}BF_3]$. Table 1 shows that the partial charge at the xenon atoms in the dication (+0.45 e) is smaller than in the neutral complex (+0.72 e).

The Xe−C bonds of the dication $[Xe{\rightarrow}C_6F_4{\leftarrow}Xe]^{2+}$ are not only shorter, they are also stronger than in $[Xe{\rightarrow}C_6F_4{\rightarrow}BF_3]$. We calculated the bond dissociation energies of the dication according to the following fragmentation schemes:

$$[Xe-C_6F_4-Xe]^{2+} \rightarrow 2Xe + C_6F_4^{2+} \; \Delta E = 75.3 \text{ kcal/mol}; \quad \Delta G^{298} = 57.1 \text{ kcal/mol} \qquad (4)$$

$$[Xe-C_6F_4-Xe]^{2+} \rightarrow Xe + C_6F_4^{+} + Xe^{+} \quad \Delta E = 30.0 \text{ kcal/mol}; \quad \Delta G^{298} = 10.5 \text{ kcal/mol} \qquad (5)$$

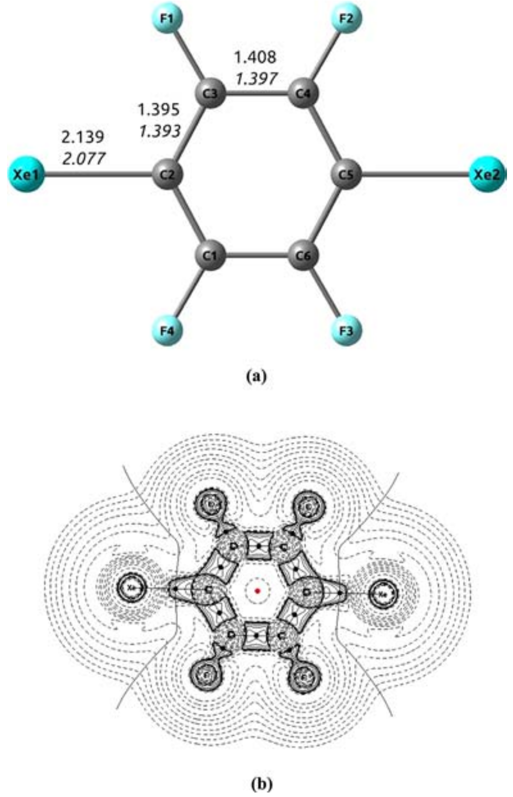


Figure 4. (a) Optimized geometry of $[Xe{\rightarrow}C_6F_4{\leftarrow}Xe]^{2+}$ at BP86/TZ2P+. Bond distances are given in Å. (b) Contour line diagram showing the Laplacian of the electron density of $[Xe{\rightarrow}C_6F_4{\leftarrow}Xe]^{2+}$ at BP86/def2-TZVPP// BP86/TZ2P+. Dashed lines indicate areas of charge depletion, solid lines indicate areas of charge accumulation. Bond critical points are shown in black, ring critical points are shown in red. Solid lines which connect the atomic nuclei are the bond paths, while the solid lines which cross the bond paths indicate the zero-flux surfaces in the molecular plane. Only the zero-flux surface lines which separate xenon from C_6F_4 are shown.

$$[Xe-C_6F_4-Xe]^{2+} \rightarrow Xe_2^{+} + C_6F_4^{+} \quad \Delta E = -5.7 \text{ kcal/mol}; \quad \Delta G^{298} = -15.5 \text{ kcal/mol} \qquad (6)$$

The calculated energy for reaction 4 shows that the dissociation of two xenon atoms from the dication $[Xe-C_6F_4-Xe]^{2+}$ is endergonic by 57.1 kcal/mol, which gives an average BDE for a Xe−C bond of 28.6 kcal/mol. However, reaction 4 is not the most favorable fragmentation pathway of $[Xe-C_6F_4-Xe]^{2+}$. The calculations predict that the dissociation into Xe + $C_6F_4^+$ + Xe^+ (reaction 5) is still endergonic by 10.5 kcal/mol. However, the dissociation reaction becomes exergonic by 15.5 kcal/mol with respect to formation of Xe_2^+ + $C_6F_4^+$ (reaction 6). We want to point out that the choice of 2 Xe + $C_6F_4^{2+}$ as interacting species for discussing the bonding situation in $[Xe-C_6F_4-Xe]^{2+}$ is valid even in cases where the actual dissociation products are singly charged species. It has been shown in a systematic study of dications that the electronic structure and the unusual geometries in doubly charged species is best described in terms of donor−acceptor interactions.[28]

SUMMARY

The results of this work can be summarized as follows. The insertion of the spacer moiety C_6F_4 into the weakly bonded van der Waals complexes $[D{\rightarrow}BF_3]$ yields spacer separated adducts $[D{\rightarrow}C_6F_4{\rightarrow}BF_3]$ which possess very strong donor−acceptor bonds. This is because the spacer fragment 2,3,5,6-C_6F_4 possess an energetically low-lying LUMO and high-lying HOMO which lead to much stronger donor−acceptor interactions than in [$D\rightarrow BF_3$]. The calculations suggest that the relaxation of the bonded fragments of the xenon complex [$Xe\rightarrow C_6F_4\rightarrow BF_3$] nearly cancel the energy gain of the donor−acceptor bonds which yields a metastable complex that in the solid state becomes stabilized by intermolecular interactions. The complexes [$OC\rightarrow C_6F_4\rightarrow BF_3$] and [$N_2\rightarrow C_6F_4\rightarrow BF_3$] have significantly stronger donor−acceptor bonds which make the adducts to be thermodynamically stable. It is suggested that the above adducts are examples of spacer-separated donor−acceptor complexes [$D\rightarrow S\rightarrow A$] which are a hitherto unrecognized class of molecules. Very strong donor−acceptor bonds are also calculated for the dication [$Xe-C_6F_4-Xe$]$^{2+}$. The calculations suggest that the latter dication is stable toward breaking the Xe−C bonds.

AUTHOR INFORMATION

Corresponding Author

*Fax (+49)-6424-282-5566. E-mail: frenking@chemie.uni-marburg.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the Deutsche Forschungsgemeinschaft.

REFERENCES

(1) Frohn, H.-J. *Chem. Eng. News* **2009**, *87* (41), 45.

(2) Frohn, H.-J.; Bilir, V.; Westphal, U. *Inorg. Chem.* **2012**, DOI: 10.1021/ic3017112.

(3) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.

(4) Van Lenthe, E.; Baerends, E. J. *J. Comput. Chem.* **2003**, *24*, 1142.

(5) Krijn, J.; Baerends, E. J. *Fit Functions in the HFS-Method*; Internal Report (in Dutch); Vrije Universiteit: Amsterdam, The Netherlands, 1984.

(6) Van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597.

(7) Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; Van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.

(8) (a) Møller, C.; Plesset, M. S. *Phys. Rev. A* **1934**, *46*, 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9S*, 229.

(9) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K, N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A. L.*; Gaussian, Inc.: Wallingford, CT, 2009.

(11) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(12) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford University Press: Oxford, 1990.

(13) AIMAll (Version 12.06.03), Todd A. Keith, TK Gristmill Software, Overland Park KS, USA, 2012. aim.tkgristmill.com (accessed October 3, 2012).

(14) Morokuma, K. *J. Chem. Phys.* **1971**, *55*, 1236.

(15) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1755.

(16) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558.

(17) Bickelhaupt, F. M.; Nibbering, N. M. M.; Van Wezenbeek, E. M.; Baerends, E. J. *J. Phys. Chem.* **1992**, *96*, 4864.

(18) Bickelhaupt, F. M.; Baerends, E. J. In *Reviews In Computational Chemistry, Vol 15, Vol. 15*; Wiley-Vch, Inc.: New York, 2000; p 1.

(19) (a) Diefenbach, A.; Bickelhaupt, F. M.; Frenking, G. *J. Am. Chem. Soc.* **2000**, *122*, 6449. (b) Frenking, G.; Wichmann, K.; Fröhlich, N.; Grobe, J.; Golla, W.; Le Van, D.; Krebs, B.; Läge, M. *Organometallics* **2002**, *21*, 2921. (c) Cases, M.; Frenking, G.; Duran, M.; Solà, M. *Organometallics* **2002**, *21*, 4182. (d) Uddin, J.; Frenking, G. *J. Am. Chem. Soc.* **2001**, *123*, 1683. (e) Massera, C.; Frenking, G. *Organometallics* **2003**, *22*, 2758. (f) Nechaev, M. S.; Rayón, V. M.; Frenking, G. *J. Phys. Chem. A* **2004**, *108*, 3134. (g) Rayón, V. M.; Frenking, G. *Organometallics* **2003**, *22*, 3304. (h) Frunzke, J.; Lein, M.; Frenking, G. *Organometallics* **2002**, *21*, 3351. (i) Lein, M.; Frunzke, J.; Frenking, G. *Inorg. Chem.* **2003**, *42*, 2504. (j) Nemcsok, D. S.; Kovács, A.; Rayón, V. M.; Frenking, G. *Organometallics* **2002**, *21*, 5803. (k) Kovács, A.; Frenking, G. *Organometallics* **2001**, *20*, 2510. (l) Pandey, K. K.; Lein, M.; Frenking, G. *J. Am. Chem. Soc.* **2003**, *125*, 1660. (m) Dietz, O.; Rayón, V. M.; Frenking, G. *Inorg. Chem.* **2003**, *42*, 4977. (n) Loschen, C.; Frenking, G. *Inorg. Chem.* **2004**, *43*, 778. (o) Nemcsok, D.; Wichmann, K.; Frenking, G *Organometallics* **2004**, *23*, 3640. (p) Bessac, F.; Frenking, G. *Inorg. Chem.* **2006**, *45*, 6956. (q) Krapp, A.; Pandey, K. K.; Frenking, G. *J. Am. Chem. Soc.* **2007**, *129*, 7596. (r) Caramori, G. F.; Frenking, G. *Organometallics* **2007**, *26*, 5815. (s) Gamez, J. A.; Tonner, R.; Frenking, G. *Organometallics* **2010**, *29*, 5676. (t) Suresh, C. H.; Frenking, G. *Organometallics* **2010**, *29*, 4766. (u) Petz, W.; Neumüller, B.; Klein, S.; Frenking, G. *Organometallics* **2011**, *30*, 3330. (v) Goedecke, C.; Leibold, M.; Siemeling, U.; Frenking, G. *J. Am. Chem. Soc.* **2011**, *133*, 3557. (w) Molon, M.; Gemel, C.; von Hopffgarten, M.; Frenking, G.; Fischer, R. A. *Inorg. Chem.* **2011**, *50*, 12296. (x) Bollermann, T.; Freitag, K.; Gemel, C.; Molon, M.; Seidel, R. W.; von Hopffgarten, M.; Jerabek, P.; Frenking, G.; Fischer, R. A. *Inorg. Chem.* **2011**, *50*, 10486. (y) Dias, R. M. V.; Dash, C.; Yousufuddin, M.; Celik, M. A.; Frenking, G *Inorg. Chem.* **2011**, *50*, 4253. (z) Takagi, N.; Krapp, A.; Frenking, G. *Inorg. Chem. Inorg. Chem.* **2011**, *50*, 819.

(20) (a) Frenking, G.; Wichmann, K.; Fröhlich, N.; Loschen, C.; Lein, M.; Frunzke, J.; Rayón, V. R. *Coord. Chem. Rev.* **2003**, *238*−*239*, 55. (b) Lein, M.; Frenking, G. In *Theory and Applications of Computational Chemistry: The First 40 Years*; Dykstra, C. E., Frenking, G., Kim, K. S., Scuseria, G. E., Eds.; Elsevier: Amsterdam, 2005; p 367.

(21) Pyykkö, P.; Atsumi, M. *Chem.—Eur. J.* **2009**, *15*, 186.

(22) (a) Arduengo, A. J., III; Davidson, F.; Krafczyk, R.; Marshall, W. J.; Schmutzler, R. *Monatsh. Chem.* **2000**, *131*, 251. (b) Nielsen, D. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2003**, *352*, 143. (c) Kuhn, N.; Fawzi, R.; Kotowski, H.; Steimann, M. *Z. Kristallogr.* **1997**, *212*, 259.

(23) The spacer fragment C_6F_4 has a singlet ground state which is slightly (2.2 kcal/mol at (BP86/TZVPP) lower than the triplet. This is in agreement with multireference ab initio calculations at the CASPT2/cc-pVDZ level which predict that the singlet state is 0.5 kcal/mol lower than the triplet: Henk, H. H.; Balster, A.; Sander, W.; Hrovat, D. A.; Borden, W. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 2295 . Note that the reference state of C_6F_4 for the present study is the singlet state, irrespective of the nature of the ground state..

(24) The plots of the HOMO and LUMO which are shown in Figure 2 have been taken from calculations at HF/6-31G(d). The HOMO and LUMO of the DFT calculations have a similar shape, but the energy level of the LUMO is below the highest lying occupied orbitals. This is not because the DFT calculations give an electronically excited state. Rather, the energy levels of the Kohn−Sham orbitals do not necessarily follow the aufbau principle.

(25) (a) Ehlers, A. W.; Frenking, G.; Baerends, E. J. *Organometallics* **1997**, *16*, 4896. (b) Esterhuysen, C.; Frenking, G. *Chem.—Eur. J.* **2003**, *9*, 3518.

(26) Loschen, C.; Voigt, K.; Frunzke, J.; Diefenbach, A.; Diedenhofen, M.; Frenking, G. *Z. Allg. Anorg. Chem.* **2002**, *628*, 1294.

(27) (a) Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124. (b) Holschumacher, D.; Bannenberg, T.; Ibrom, K.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Dalton Trans.* **2010**, *39*, 10590. (c) Otten, E.; Neu, R. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 9918. (d) Ménard, G.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, *132*, 1796.

(28) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D. *J. Am. Chem. Soc.* **1986**, *108*, 5808.