Myths and Reality of Hypervalent Molecules. The Electronic Structure of FClO$_x$, x = 1−3, Cl$_3$PO, Cl$_3$PCH$_2$, Cl$_3$CClO, and C(ClO)$_4$

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ABSTRACT: In the present work we examine a series of hypervalent molecules, namely, FClO$_x$ (x = 1−3), Cl$_3$PO, Cl$_3$PCH$_2$, Cl$_3$CClO, and C(ClO)$_4$, through single-reference [CCSD(T)] and multireference (MRCI) ab initio methods, the principal aim being the deciphering of their binding pattern. Our electronic structure calculations consistently show that the bonding occurs through an electron pair transfer from the Cl or P atoms of the molecules considered to the ^{1}D state of the O atom(s). We strongly believe that the term "hypervalency" when viewed from an unbiased side and with a critical eye reveals a simple chemical bonding situation that is in conformity with a scientific parsimony that dissolves the mythology of an enormous class of molecular systems that are categorized under the term hypervalent .
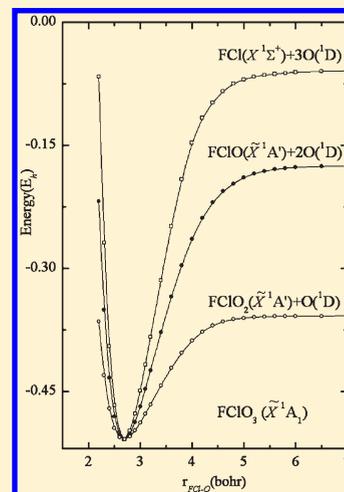
1. INTRODUCTION

The term "hypervalent" was introduced in 1969 by Musher in an effort to describe and classify molecular systems that do not obey "traditional" rules of valency;[1] see also ref 2 and references cited therein. Musher writes:

"We classify as "hypervalent" molecules and ions all these molecules and ions formed by elements in Groups V−VIII of the periodic table in any of their valences other than their lowest stable chemical valence of 3, 2, 1, and 0, respectively. We refer to these molecules as *hypervalent* (or HV) since they involve atoms, called donor atoms, which exceed the number of valences allowed them by traditional theory, and thus utilize more electron-pairs of bonding than provide stability in the Lewis− Langmuir theory."

Needless to say, the term hypervalency by itself does not explain the binding mechanism in such systems; nevertheless, when it is used by chemists it is, somehow, considered as self-explanatory. See a typical modern textbook in relation, for instance, to the hypervalent molecule of H$_2$SO$_4$.[3] It is also interesting and amusing what is stated by Cooper et al.[4] about the preconceptions on hypervalent molecules deeply rooted in the chemical community:

"Nevertheless, the existence of PF$_5$, but not of NF$_5$, is still often rationalized to high school students, and to many under-graduates, in terms of the availability of d orbitals and the possibility of obtaining "an expanded octet". Indeed, models based on d^{2}sp^3, dsp^2, and dsp^3 hybrid orbitals are still in

widespread use among professional chemists and are described in many of the most widely used textbooks. It is tempting to speculate as to why such models continue to survive when there is so much theoretical evidence which does not support them."

The motivation of the present article is to offer a rational answer as to the nebulous bonding nature of hypervalent molecules by examining a series of hypervalent systems, namely, the oxide fluorides of chlorine (FClO$_x$, x = 1, 2, 3), phosphoryl chloride (Cl$_3$PO), Cl$_3$PCH$_2$, and C(ClO)$_4$.

Recently we clarified the electronic structure of the common, but hypervalent, acids (HO)$_2$SO$_2$, HOClO$_3$, and HONO$_2$.[5] It was shown that the X$_2$S($\rightarrow$O)$_2$, XCl($\rightarrow$O)$_3$, and XN($\rightarrow$O)$_2$ bonds (X = OH) naturally arise from the first excited ^{1}D state of the O atom, 1.956 eV (=45.1 kcal/mol) above the ^{3}P term. This means that the hydroxyl oxygen atoms (^{3}P) are different from the non-hydroxyl ones (^{1}D). The interplay between the excitation energy O(^{1}D$\leftarrow^3$P) and the bond strength of the non-hydroxyl oxygen atom(s) defines the stability of the particular molecule.

In a series of recent articles, the Dunning group examined a different class of hypervalent molecules, namely, SF$_n$ (n = 1−6),[6a] ClF$_n$ (n = 1−7),[6b] and PF$_n$ (n = 1−5).[6c] They interpreted hypervalency in terms of decoupling electron pairs followed by coupling the decoupled electrons into (recoupled) pair bonds,

Scheme 1

$F(^2P; M_L=0)$ $Cl(^2P; M_L=0)$ $(X^1\Sigma^+)$

$= :\ddot{F}—\ddot{C}l:$

$F(^2P; M_L=\pm1)$ $Cl(^2P; M_L=0)$ $F(^2P; M_L=0)$ $Cl(^2P; M_L=\pm1)$

$= (\dot{F}: \cdot\ddot{C}l) + (\ddot{F}\cdot :\dot{C}l)$ $(B^3\Pi)$

Scheme 2

FCl $(X^1\Sigma^+)$

O $(\sim^1D)$

FClO $(\tilde{X}^1A')$
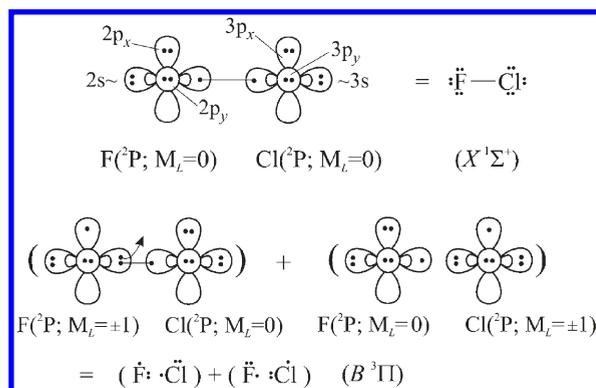
(see also ref 1, p 60). In the same spirit, Cooper et al.[4] introduced the "democracy principle" which states that "almost all valence electrons can participate in chemical bonding if provided with sufficient energetic incentives."[7]

The conviction of the present authors is that the bonding in all hypervalent molecules can be naturally rationalized by taking into account the excited states of the appropriate moieties, molecular or atomic, of the system at hand. To our knowledge this has not been explicitly stated in the literature, although, indirectly, it seems to be implied by the decoupling—recoupling[1,6] and democracy principle[4,7] models. For a short historical account of the evolution and confusion on the bonding of hypervalent systems, see Jensen.[8]

Presently we investigate the hypervalent molecules $FClO_x$ ($x = 1, 2, 3$), Cl_3PO, Cl_3PCH_2, Cl_3CClO, and $C(ClO)_4$ through multireference (complete active space self-consistent field + single + double replacements CASSCF + 1 + 2 = MRCI) and coupled-cluster $[CCSD(T)]^9$ calculations. For all atoms we employed the cc−pVTZ basis set generally contracted to $[3s2p1d/_H{}^{10}\ 4s3p2d1f/_{C,O,F}{}^{10}\ 5s4p2d1f/_{P,Cl}{}^{11}]$. Although the cc−pVTZ ($=3\zeta$) basis is rather limited for obtaining accurate numerical results, it is more than adequate for the purpose of this report which is focused on the bonding scenario of these systems. All calculations were performed by the MOLPRO package.[12]

2. RESULTS AND DISCUSSION

A. FClO. The ground states of both $FCl(X^1\Sigma^+)$ and $FClO(\tilde{X}^1A')$ have been examined at the MRCI and CCSD(T) levels. The zeroth order multireference wave functions of FCl and FClO were constructed by distributing all valence electrons to the corresponding valence orbitals, 14 e^- to 8 orbitals and 20 e^- to 12 orbitals, respectively. Correlation with respect to the reference function was accounted for by single and double replacements out of the active space, resulting in (internally contracted) icMRCI expansions of $\sim23\,000$ (FCl) and 530 000 (FClO) configuration functions (CF). The ground state atoms of F and $Cl(^2P)$ give rise to 12 $\Lambda-\Sigma$ states, namely,[1,3] ($\Sigma^+[2]$, Σ^-, $\Pi[2]$, Δ), one of which ($X^1\Sigma^+$) forms a genuine covalent σ bond bound by $D_e{}^0 = 61.5$ kcal/mol at $r_e = 1.628$ Å, and a weakly bound van der Waals-type $B^3\Pi_{0+}$ state located 18 826.4 cm^{-1} higher with $D_e{}^0 = 7.6$ kcal/mol at $r_e = 2.031$ Å.[13] The remaining 10 states are of repulsive character; see also ref 14. The structures of $X^1\Sigma^+$ and $B^3\Pi$ states are clearly captured by the valence-bond Lewis (vbL) diagrams shown in Scheme 1.
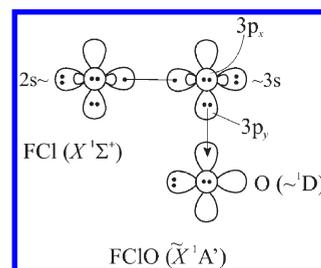
The diagrams of Scheme 1 (bottom) represent a very weak two center—three electron (2c−3e$^-$) σ and π interactions per vbL diagram. The leading MRCI configurations of the $B^3\Pi$ state are (counting valence electrons only)

$$|B^3\Pi\rangle \approx 0.84|1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 1\pi_x^2 2\pi_x^1 1\pi_y^2 2\pi_y^2\rangle$$
$$+ 0.50|1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^2 1\pi_x^1 2\pi_x^2 1\pi_y^2 2\pi_y^2\rangle$$

Notwithstanding the small basis set employed here, our numerical results concerning the $X^1\Sigma^+$ state of FCl are of acceptable quality: at the MRCI(MRCI+Q)[CCSD(T)]/3ζ level we obtain $r_e = 1.645(1.647)[1.645]$ Å and $D_e{}^0 = 52.1(54.4)[55.3]$ kcal/mol, 0.02 Å and ~7 kcal/mol smaller than the experimental values.[13]

The $B^3\Pi$ state of FCl is of small importance to the purpose of this work (vide infra). However, it is an interesting state, well-defined experimentally[13] but not thoroughly explored theoretically. At the MRCI/3ζ level it is practically unbound; increasing the basis set to sextuple cardinality (cc-pV6Z),[10] we get $D_e{}^0 = 1.64(4.1)$ kcal/mol and $r_e = 2.288(2.086)$ Å at the MRCI(+Q) level, as compared to the experimental values of 7.6 kcal/mol and 2.031 Å, respectively.[13] Results at the CCSD(T) level are questionable because $B^3\Pi$ is a two configuration state (vide supra); see also refs 6b and 14. It should be said though that the vbL diagram of Figure 1 of ref 6b is not compatible with the MRCI description as pictured in Scheme 1 (bottom) of the present work.

We turn now to the FClO molecule. Clearly, the approach of a ^3P oxygen atom to FCl ($X^1\Sigma^+$) along any direction cannot result in a covalent bonding interaction with the chlorine atom of FCl. The first excited state ^1D of the oxygen atom located experimentally (MRCI/3ζ) 1.956(2.033) eV above the ground state, however, can easily form a covalent "dative" or a harpoonlike σ bond with either the $3p_y$ or $3p_x$ lone pairs of Cl, predicting at the same time a strongly bent molecule and a significant electron transfer to the O (^1D) atom; see Scheme 2. Our findings completely corroborate this picture.

The microwave Fourier transform[15] structural parameters of the $\tilde{X}^1A'$ state of FClO are $r_{FCl} = 1.6865$ Å, $r_{ClO} = 1.4843$ Å, $\theta_{FClO} = 110.56°$, and $\mu = 1.926$ D, as contrasted to the MRCI/3ζ [identical to CCSD(T)] results 1.709 Å, 1.507 Å, and 111.4°, respectively. The MRCI dipole moment calculated as expectation value is 1.987 D, whereas the finite-field CCSD(T) value is 2.16 D. The MRCI Mulliken charges on the atoms are $F^{-0.27}-Cl^{+0.63}-O^{-0.36}$, comparing interestingly with the corresponding distributions of the $X^1\Sigma^+$ of FCl, $F^{-0.20}-Cl^{+0.20}$, indicating an in situ increased electron affinity of the oxygen atom in FClO (O atom in ^1D). Observe that the negative charge on the O atom is larger than that on the F atom. It is interesting to mention at this point that the Mulliken MRCI/3ζ charge on the O atom of $ClO(X^2\Pi)$, where the bond is of regular covalent character, is ~-0.20.

2379

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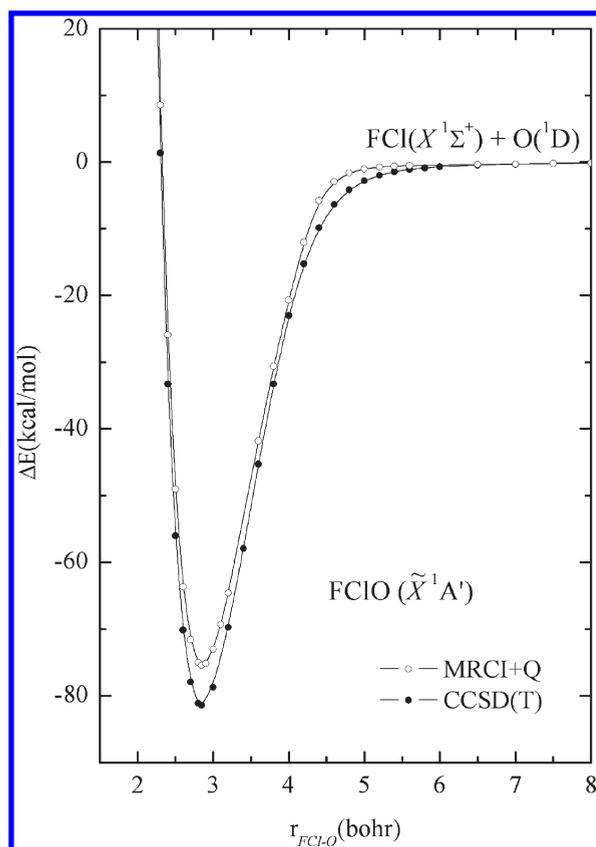
Figure 1. Dissociation curve of the FCl—O($\tilde{X}^1A_1$) system at the MRCI+Q/3ζ and CCSD(T)/3ζ computational levels.

Figure 2. Experimental geometrical (theoretical CCSD(T)/3ζ) parameters of the ground $\tilde{X}^1A'$ state of FClO$_2$ (distances in Å, angles in deg).

Figure 3. Dissociation curve of the FClO—O($\tilde{X}^1A'$) system at the MRCI+Q/3ζ and CCSD(T)/3ζ computational levels.

There are no experimental or theoretical results on the dissociation energy of the FCl—O bond. With respect to FCl-($X^1\Sigma^+$) + O(^{1}D) at the MRCI(+Q)[CCSD(T)]/3ζ level, we calculate D_e(FCl—O) = 72.0(75.4)[80.1] kcal/mol, or 25.1(24.7)[29.4] kcal/mol with respect to FCl + O(^{3}P), employing MRCI(+Q) and CCSD(T) ^{3}P—^{1}D splittings 46.9(46.9) and 50.7 kcal/mol, respectively.

Our thoughts above as to the FCl—O bonding have been completely confirmed through the construction of MRCI+Q and CCSD(T) potential energy curves (cuts through the potential energy surfaces), by pulling apart the O atom; see Figure 1.

Along the FCl—O PECs the interatomic distance of the FCl moiety was maintained constant at the equilibrium value of FClO. The CCSD(T) (and the Hartree—Fock) curve opens smoothly to singlet *neutral* fragments, FCl($X^1\Sigma^+$) + O($\sim^1$D), indicating the singlet character of the oxygen atom within the FClO molecule. The same fragments, FCl($X^1\Sigma^+$) + O(^{1}D), are observed in the MRCI+Q curve, although, potentially, the two fragments could also dissociate to FCl($B^3\Pi$) + O(^{3}P) as far as the spin symmetry is concerned. However, the previous discussion on the electronic structure and stability of the B$^3\Pi$ state of FCl precludes this triplet—triplet path. Therefore a correct picture of the FCl—O bond is FC1:$\rightarrow\ddot{O}$:, with the understanding that the in situ O atom is in the ^{1}D state.

B. FClO$_2$. Chloryl fluoride, FClO$_2$, was first prepared by Schmitz and Schumacher in 1942 in the thermal reaction between F$_2$ and ClO$_2$.[16] Equilibrium geometries and the dipole moment were first reported by Parent and Gerry in 1974 through microwave spectroscopy in the frequency region 8—37 GHz.[17]

In 1981 Robiette et al.[18] refit the previous published microwave data of Parent and Gerry in order to extract refined structural parameters. Their results are depicted in Figure 2 along with our CCSD(T)/3ζ values (in parentheses).

The $\tilde{X}^1A'$ state of FClO$_2$ was optimized at the CCSD(T)/3ζ level. The PECs of FClO—O and FCl—(O)$_2$ have been calculated at both the CCSD(T) and MRCI//CCSD(T)/3ζ levels of theory. To make the MRCI calculations feasible, we were forced to keep doubly occupied the 2s and 3s orbitals of the O, F, and Cl atoms. The CASSCF reference function was created by allotting 18 e$^-$ to 12 orbitals resulting in 15 730 CFs; the corresponding length of the *ic*MRCI expansion is ~6.4 × 10^6 CFs.

The bonding of the two O atoms on the Cl of FCl($X^1\Sigma^+$) is identical to that of FCl—O($\tilde{X}^1A'$) as discussed previously; i.e., the Cl 3p$_x$ and 3p$_y$ lone pairs form dative bonds with two excited ^{1}D O atoms; see Scheme 2. Figure 3 displays the MRCI+Q and CCSD(T) FClO—O PECs, corroborating the dative bond scenario outlined above: both MRCI+Q and CCSD(T) curves dissociate to singlet neutral fragments FClO($\tilde{X}^1A'$) + O(^{1}D).
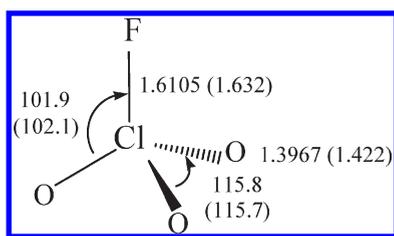
Figure 4. Experimental geometrical (theoretical CCSD(T)/3ζ) parameters of the ground state $\tilde{X}^1A_1$ of FClO$_3$ (distances in Å, angles in deg).
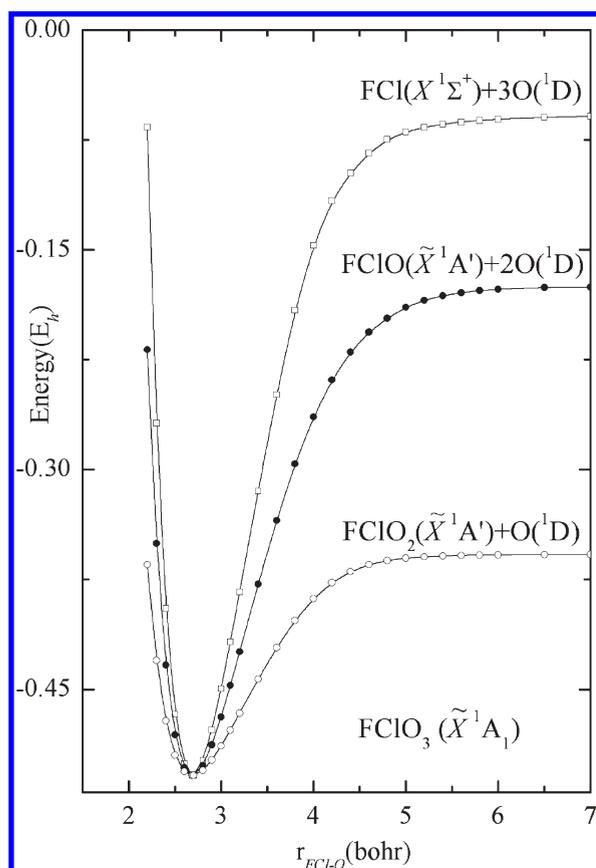
Figure 5. CCSD(T)/3ζ dissociation PECs of one, two, and three O atoms from the equilibrium geometry of the $\tilde{X}^1A_1$ FClO$_3$ state. Energies have been shifted by +784.0 E_h.

The binding energy of FClO–O with respect to FClO-($\tilde{X}^1A'$) + O(^1D)[^3P] is D_e = 110.1 [59.4] kcal/mol. Notice that the CCSD(T)/3ζ FCl–O and FClO–O binding energies are considerably different, being 80.1 and 110.1 kcal/mol, respectively, with a mean binding energy $\overline{D}_e$ = 95.1 kcal/mol, or 44.4 kcal/mol with respect to O(^3P). The Mulliken MRCI charges on the F and O atoms are quite similar to those of FClO, while the charge on the Cl atom increases by ~+0.40, equal to the differential charge increase from FCl to FClO, F$^{-0.28}$–Cl$^{+1.00}$–(O$^{-0.36}$)$_2$. The CCSD(T)/3ζ finite-field dipole moment μ_{FF} = 2.00 D compares favorably with the experimental value of 1.722 ± 0.03 D.[17] It should be said at this point that by pulling apart both O atoms in a C_s fashion at the CASSCF/3ζ level, we are led to the lowest adiabatic channel FCl($X^1\Sigma^+$) + 2 O(^3P), after encountering, as expected, a barrier due to the avoiding crossing of the incoming FCl + 2 O(^1D) PEC.
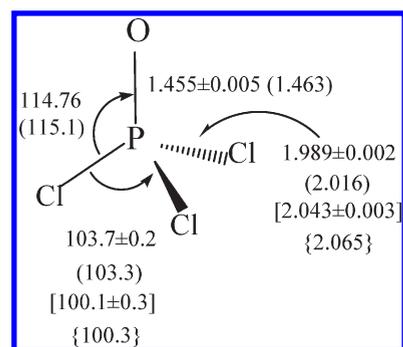
Figure 6. Experimental structure of $\tilde{X}^1A_1$ Cl$_3$PO and $\tilde{X}^1A_1$ PCl$_3$ (in square brackets) and corresponding CCSD(T)/3ζ values (in parentheses for Cl$_3$PO and curly brackets for PCl$_3$). Distances in Å and angles in deg.

C. FClO$_3$. A nice introduction on the history of perchloryl fluoride molecule (FClO$_3$), a prolate symmetric rotor of C_{3v} symmetry, can be found in ref 19. The accurate microwave geometrical structure obtained by Müller and Gerry[19] is reproduced in Figure 4 (theoretical CC results in parentheses); see also ref 20.

At the valence CCSD(T)/3ζ level, bond distances are shorter than experiment by ~0.02 Å; see Figure 4. The inclusion of core–valence correlation effects of the Cl atom at the same level of theory brings into practical coincidence the experimental and theoretical geometry.[21] As in the previous two cases of FClO and FClO$_2$, the three O atoms of FClO$_3$ are "datively" bonded to the ~3p$_x$, ~3p$_y$, and ~3s electron pairs of the Cl atom of FCl, involving the first excited ^1D state of the three O atoms; see Scheme 2. Figure 5 displays dissociation CCSD(T)/3ζ PECs of FClO$_3$ → FClO$_2$($\tilde{X}^1A'$) + O(^1D), FClO$_3$ → FClO($\tilde{X}^1A'$) + 2 O(^1D), and FClO$_3$ → FCl($X^1\Sigma^+$) + 3 O(^1D). All PECs are constructed by pulling apart one, two, and three O atoms simultaneously, while keeping the fragments FClO$_2$, FClO, and FCl, respectively, frozen to the FClO$_3$ equilibrium geometry.

With respect to the optimized end channels, the mean binding energies $\overline{D}_e$ are 92.3 (FClO$_2$–O), 101.2 (FClO–(O)$_2$), and 94.2 (FCl–(O)$_3$) kcal/mol, or 41.6, 50.5, and 43.5 kcal/mol with respect to O(^3P). The $\overline{D}_e$ of 94.2 kcal/mol is the same as the $\overline{D}_e$ value of FClO$_2$ (95.1 kcal/mol, vide supra). The similarity between FClO$_3$ and the (hypervalent) isoelectronic perchloric acid (HO)ClO$_3$ is worth mentioning, concerning both geometrical and energetic parameters.[5] For instance, the $\overline{D}_e$ of (HO)Cl–(O)$_3$ calculated at the same level is 99 kcal/mol, and the Cl–O distance ~1.40 Å. The Hartree–Fock Mulliken charges on FClO$_3$ are F$^{-0.25}$–Cl$^{+1.46}$–(O)$_3^{-0.40}$. From FCl to FClO$_3$ the negative charges on F remain essentially the same (0.20–0.30 e$^-$), while the positive charge on Cl increases in steps of ~0.4 per oxygen atom added. Finally, our calculated CCSD(T)/3ζ dipole moment μ_{FF} = 0.016 D is in affordable agreement with the experimental value of 0.027 D[22] taking into consideration its remarkably small value.

D. Cl$_3$PO and Cl$_3$P(CH$_2$). The geometrical structure of the symmetric top molecule phosphorus oxytrichloride, Cl$_3$PO, was first investigated through electron diffraction[23] and then by microwave spectroscopy.[24] However, the first unbiased and accurate microwave geometry of Cl$_3$PO was reported by Li et al. in 1972.[25] The structure of ref 25 along with the microwave structure of PCl$_3$[26] (in square brackets), and the CCSD(T)/3ζ
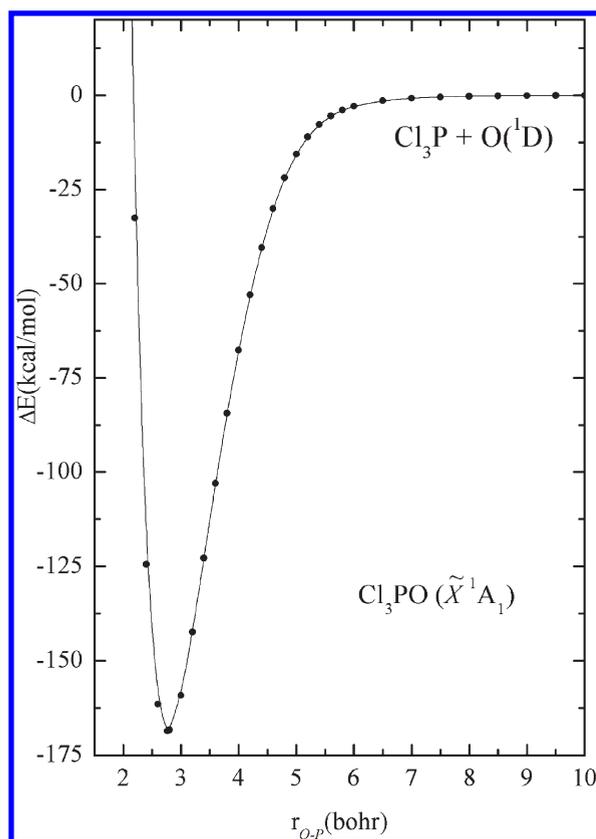
Figure 7. CCSD(T)/3ζ Cl_3P-O dissociation curve of the $\tilde{X}^1A_1$ Cl_3PO state.
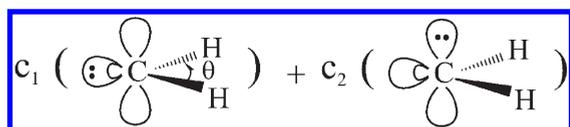
Figure 8. $\tilde{a}^1A_1$ ($c_1 = 0.97$, $c_2 = -0.21$, $\theta = 102.2°$) and $\tilde{c}^1A_1$ ($c_1 = 0.67$, $c_2 = 0.73$, $\theta = 172.0°$) structures of CH_2.
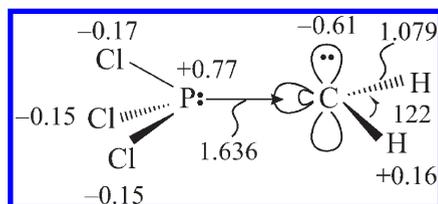
Figure 9. CCSD(T)/3ζ geometry and HF Mulliken charges of Cl_3PCH_2 (distances in Å, angles in deg).

structure of Cl_3PO (in parentheses and curly brackets for PCl_3) calculated presently, are depicted in Figure 6.

From the Stark effect transitions, the dipole moments of Cl_3PO and PCl_3 are 2.54 ± 0.04 and 0.56 ± 0.02 D, respectively;[27] the present theoretical finite-field CCSD(T)/3ζ values are 2.34 and 0.61 D. Notice that upon bonding of the O atom to the PCl_3 moiety, the geometry of the latter changes only slightly: the $OPCl_2-Cl$ distance decreases by about 0.05 Å, whereas the angle remains practically the same.

Figure 7 displays the dissociation CCSD(T)/3ζ PEC of the Cl_3P-O bond, with adiabatic fragments $PCl_3(\tilde{X}^1A_1)$ +
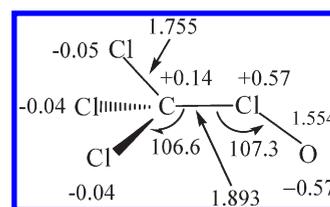
Figure 10. Equilibrium geometry at the CCSD(T)/ 3ζ level and Mulliken HF charges of $Cl_3CCl-O(\tilde{X}^1A')$. The Cl (trans to the O atom), C, Cl, and O atoms are in a plane bisecting the $\angle ClCCl$ angle. Distances in Å, angles in deg.

$O(\sim^1D)$. The three equivalent $P-Cl$ σ bonds in PCl_3 are obviously formed by coupling the ^4S state of the P atom into a singlet with three ^2P Cl atoms.

As previously discussed, the Cl_3P-O bond is formed by the dative interaction of the phosphorus $\sim 3s^2$ pair to the ^1D state of the O atom: schematically, $Cl_3P:\rightarrow O$. The Mulliken Hartree–Fock charges are calculated to be $(Cl)_3{}^{-0.15}-P^{+0.95}-O^{-0.50}$, while the corresponding charges on PCl_3 are $(Cl)_3{}^{-0.20}-P^{+0.60}$. Notice again the very large difference of the negative charges on Cl and O atoms, -0.15 vs -0.50, despite the fact that their electronegativity differs by less than 0.5 units in the Pauling scale. The CCSD(T)/3ζ Cl_3P-O dissociation energy with respect to $PCl_3(\tilde{X}^1A_1$, equilibrium geometry) + $O(^1D)[^3P]$ is $D_e =$ 166.1[115.4] kcal/mol, indeed remarkably high.

Our ideas expressed in the previous subsections can be applied on a completely different hypervalent system, namely, the interaction of PCl_3 with the parent carbene CH_2. The latter is isoelectronic to the O atom, with a ground state of $^3B_1$ symmetry while its first excited state, $\tilde{a}^1A_1$, lies 9.0 kcal/mol higher.[28] The $\tilde{X}^3B_1$ and $\tilde{a}^1A_1$ states of CH_2 can be considered "isomorphic" to the ^3P and ^1D terms of the O atom under C_{2v} symmetry; see also ref 29. Obviously, the interaction of $PCl_3(\tilde{X}^1A_1)$ with the $\tilde{X}^3B_1$ state of CH_2 is repulsive. Considering, however, the $\tilde{a}^1A_1$ state of CH_2 whose electronic structure[28] is given in Figure 8, an attractive interaction is predicted similar to that of Cl_3P + $O(^1D)$.

Indeed, a perpendicular attack to the CH_2 plane by PCl_3 from its P side leads to a barrierless attractive interaction of about 50 kcal/mol at the CCSD(T)/3ζ level. Upon partial optimization of the Cl_3P-CH_2 singlet complex keeping the PCl_3 in its free equilibrium geometry, we obtain $D_e \approx 70.0$ kcal/mol with respect to $PCl_3 + CH_2(\tilde{a}^1A_1)$. Figure 9 displays the equilibrium geometry and Mulliken Hartree–Fock charges of Cl_3PCH_2.

The angle between the $P-C$ axis and the bisector of the CH_2 angle is $\sim 173°$. With an identical binding mode, the dinitrogen $N_2(X^1\Sigma_g^+)$ binds to $CH_2(\tilde{a}^1A_1)$ leading to the well-known diazomethane molecule, CH_2N_2, with a binding energy of ~ 40 kcal/mol.[30] Observe that the Mulliken Hartree–Fock charges shown in Figure 9 are consistent with the binding mode suggested. The charges on the atoms of the free $CH_2(\tilde{a}^1A_1)$ at the same level of theory are close to zero. To our knowledge the Cl_3PCH_2 complex has not been observed but certainly should exist according to our calculations.

E. Cl_3CClO and $C(Cl-O)_4$. By pushing further the binding scenario previously discussed to the extreme, we investigated at the CCSD(T)/3ζ level the interaction of carbon tetrachloride, CCl_4, a rather chemically inert molecule, with oxygen atom(s). The experimental $C-Cl$ bond distance is 1.767 Å,[31] and the $\angle ClCCl$ angle 109.47° by symmetry. We first calculated the interaction of CCl_4 with one O atom (Cl_3CClO) and then with

four atoms $[C(ClO)_4]$, both species in a singlet state. The CCl_4 + $O(^3P)$ channel leads, obviously, to a repulsive interaction. At the $CCSD(T)/3\zeta$ level the binding energy of $Cl_3CCl−O$ with respect to $CCl_4(\tilde{X}^1A_1)$ + $O(\sim^1D)$ is D_e = 57.0 kcal/mol, or 6.3 kcal/mol with respect to $O(^3P)$. Equilibrium geometry and Mulliken Hartree−Fock charges for the Cl_3CClO molecule are depicted in Figure 10.

The C−Cl distance and charges on C and Cl atoms in CCl_4 calculated at the $CCSD(T)/3\zeta$ level are 1.777 Å, +0.20, and −0.05, respectively. It is important to emphasize at this point that the charge transfer to the O atom(s) bonded to Cl and P atoms in all five species $FClO$, $FClO_2$, $FClO_3$, Cl_3PO, and Cl_3CClO is similar, ranging from ∼0.4 to 0.5 electrons, whereas the $\angle XClO$ (X = F, C) angle is bracketed between 102 and 110° degrees. With no doubt the bonding of the O atom to the Cl of CCl_4 is rationalized by the scheme $Cl_3CCl:→O(\sim^1D)$.

It is clear by now that we can append four O atoms to CCl_4 leading to the molecule $C−(ClO)_4$. Employing the geometry of the −C−Cl−O moiety shown in Figure 10, we calculated the total energy of $C(ClO)_4$ at the $CCSD(T)/3\zeta$ level of theory. The $CCSD(T)/3\zeta$ binding energy of $C(Cl−O)_4$ calculated through the relation $D_e = E[C(ClO)_4; \tilde{X}^1A_1] − E(CCl_4; \tilde{X}^1A_1) − 4 \times E[O(\sim^1D)]$ is close to 200 kcal/mol, practically additive with respect to the binding energy of a single $O(^1D)$ atom. The Mulliken Hartree−Fock charges on the C, Cl, and O atoms are ∼0.0, ∼0.5, and ∼ − 0.5, respectively, in conformity with the Cl_3CClO system; see Figure 10.

Our calculations indicate that the hypervalent $C(Cl:→O)_4$ molecule should exist, and in principle, we can speculate the same for the ultra-hypervalent molecular complex $C(ClO_3)_4$, where all 12 O atoms are bound to Cl though the transfer of an electron pair to the ^1D state of the O atom, $Cl:→\ddot{O}:(^1D)$.

3. SYNOPSIS AND FINAL REMARKS

With the purpose of elucidating the binding mode of hypervalent molecules, we calculated a series of selected molecular systems, namely, $FClO_x$ (x = 1, 2, 3), Cl_3PO, $Cl_3P(CH_2)$, $Cl_3C(ClO)$, and $C(ClO)_4$, through MRCI and $CCSD(T)/cc-pVTZ$ methods. The question is, of course, the existence of a large number of molecules whose stability is not in conformity with the "conventional" rules of valency. In the present case FCl $(X^1\Sigma^+)$, $Cl_3P(\tilde{X}^1A_1)$, and $CCl_4(\tilde{X}^1A_1)$ are very stable closed shell systems with, in general, limited propensity for strong attractive interactions to other chemical species. Our calculations consistently demonstrate that the bonding of O atoms to any of the molecules above occurs through an electron pair (on Cl or P) transfer to the first excited ^1D state of the O atoms; see also ref 5. We would like to emphasize in particular the strong binding of CH_2-($\tilde{a}^1A_1$), "isomorphous" to $O(^1D)$, to Cl_3P and the binding of four O atoms to the Cl atoms of CCl_4 leading to a stable $C(ClO)_4$ species.

The thoughts expressed above, that is, the rationalization of bonding in hypervalent systems by invoking the appropriate excited state of the appropriate moiety, can be applied to almost any hypervalent molecule. Common examples of such systems involving the ^1D state of the O atom are the common acids $(HO)_2SO_2$, $HONO_2$, $(HO)_3PO$, and $HOClO_3$,[5] $O(ClO_3)_2$, $FBrO_3$, iodosobenzene $(C_6H_5I−O)$, iodoxybenzene $(C_6H_5−IO)_2$), $CH_3I−O$, etc., and a very large variety of similar systems. Certainly the same approach can be applied to hypervalent molecules of the type $XYS:(→\ddot{O}:)_n$, where X, Y = F, Cl, and Br and n = 1 or 2 (see ref 32). Hypervalent molecules of the type F_3XO_n, X = Cl, Br, I and n = 1 or 2 (see ref 33) can be understood as follows: to a triplet state of $F−\dot{X}−(O)_2$, $F−\dot{X}−(O)_2$, two $F(^2P)$ atoms are bonded through two σ covalent bonds.

Finally we would like to mention the halogen fluorosulfate hypervalent molecule,[33] $F−O−SF(O)_2$. Clearly the in situ O atoms are "different", the two end O atoms being in the ^1D state. To the $F−O−\dot{S}$ doublet a $F(^2P)$ is bonded through a σ covalent bond, whereas two $O(^1D)$ atoms are bound by two dative $S:→O(^1D)$ bonds.

We hope that the present exposition on the ideology of hypervalent molecules would be proven useful to the chemical community. The huge variety of "nonconventional" bonded molecules makes us wondering if the so-called hypervalent molecules are the rule rather than the exception. For example, the simplest of all organic molecules, CH_4, could be clearly considered as of hypervalent nature. Indeed, by bonding two $H(^2S)$ atoms to the ^3P ground state of C, a closed shell species is obtained, namely, $CH_2(^1A_1)$, with no further ability for binding. To add two more $H(^2S)$ atoms we can invoke either the $^3B_1$ state of CH_2 originating from the ^5S state of C atom ∼97 kcal/mol higher, or equivalently, to couple into a singlet four $H(^2S)$ atoms to the C ^5S state, the energy profit for both cases being ∼300 kcal/mol. The latter process is usually called sp^3 hybridization.

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2384

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