al–equatorial interactions ((1)–(3)), the equatorial–equatorial interaction ((4)) is less favored in energy than expected on the basis of electrostatic attraction (more negative charge is localized on the equatorial phosphoryl oxygens) as well as the linearity of the $O–H\cdots O^-$ interactions;[27] the bond angles of $O–H\cdots O_{axial}$ and $O–H\cdots O_{equatorial}$ are 131.8° and 153.8°, respectively, in structure (1); on the other hand, the corresponding bond angles $O–H\cdots O_{equatorial}$ in structure (4) are 143.5° and 146.4°. The water molecule in structure (4) could have come closer to the phosphoryl oxygens to achieve more linear hydrogen bonds. This, however, did not occur despite the more spherical electron distribution about the anionic oxygens as compared to the electrons of a lone pair. As a result, axial attack and/or axial departure is further stabilized by the preferred axial–equatorial hydrations. Overall there is nearly a 6.0 kcal/mol range in stabilization energies reported in this study.

In summary, we have identified seven predominant monohydrations of a newly identified pentacoordinated oxyphosphorane intermediate (**2a**) found in the reaction of methoxide with tetracovalent ethylene phosphate monoanion. These results together with ongoing calculations[7] support our earlier conclusion[5] that the pentacoordinated intermediate is formed in a very rapid equilibrium and only a small fraction of 2′-alkoxide attack on the phosphate backbone results in productive 5′ cleavage under basic conditions.[28] The recent report by Lim and Karplus[6] suggesting the nonexistence of the dianionic intermediate of cyclic oxyphosphorane system **2b** is in contrast to our oxyphosphorane **2a** presented here. The cause of this discrepancy can be reconciled by the ability of the axial OMe group in **2a** to better delocalize the dianionic charges than OH in **2b**. In strong alkaline solution, in fact, **2a** does exist as an intermediate since the hydrolysis of methyl ethylene phosphate yields 2–4% exocyclic products, which can only be formed after pseudorotation of the intermediate **2a**.[29,30] Nevertheless, the overall transition-state structure is independent of the mechanism (stepwise vs concerted), and it has an extended P–O(5′) bond-breaking character (TS2 structure in ref 5). Location of the mechanistically relevant pentacoordinated oxyphosphorane intermediate together with the dominant monohydrations will now be applied to a theoretical evaluation of the effect of solvent on this potential energy surface.

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Singlet Nitrene Insertion into H_2O, H_2S, HF, and HCl

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Abstract: The insertion of singlet nitrene, ^{1}NH, into the O–H bond of water, the S–H bond of H_2S, and the F–H and Cl–H bonds has been studied by means of ab initio molecular orbital theory including electron correlation and zero-point corrections. Nitrene forms initial donor–acceptor complexes, with the exception of HF, after which hydrogen migration leads to the more stable tautomers H_2NX (X = OH, SH, F, Cl). Bader's charge density analysis has been used to delineate bonding properties. The ^{1}NH complexes with the second-row hydrides have very short N–S and N–Cl bonds. Correlation effects are important in the description of the complexes.

Diradicals are reactive, electron-deficient intermediates that lend themselves to addition and insertion reactions. They have been the subject of numerous studies that focus on the mechanistic pathways of their reactions.[1] In contrast to the wealth of experimental and theoretical information on carbene and silylene insertion reactions, relatively little is known about the corresponding nitrene reaction.[1-3] Theoretical studies concerning the insertion of carbenes[3h] and silylenes[3d,f] have suggested the formation of intermediate complexes. These are generally unstable in the case of carbenes with little or no barrier for hydrogen migration or fragmentation, but silylene complexes are thought to be spectroscopically observable.[3f] The objective of the present study is (a) to shed more light on the related singlet nitrene insertions into X–H bonds (X = O, S, F, Cl) by means of theoretical analyses and (b) to analyze possible intermediate complexes along the reaction pathway.

Nitrene (NH) has a triplet ground state that is an estimated 36 kcal/mol more stable than the singlet form;[4] a value of 41 kcal/mol was reported in a study using a large CI calculation.[5] Triplet nitrenes are well-known experimentally,[1a-d,6] and excited nitrene radicals have been implicated in the two-photon dissociation of ammonia.[7] However, the nitrenes generated from azides and isocyanates[1a-d,6,8] are in most instances singlets. This is also the case in many organic rearrangements involving nitrene centers as well as in the photochemistry of aroylnitrenes.[9] Even the

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Table I. Total (au) and Relative (kcal/mol) Energies of Singlet Nitrene Complexes with XH Bonds (X = O, S, F, Cl)

structure		state	HF/3-21G		HF/6-31G*		MP2(Full)/6-31G*			MP4(FC)/6-311G**[a]		
			tot.	rel	tot.	rel	tot.	rel	NIMAG	tot.	rel	final[b]
1	C_s	$^1A'$	−130.256 44	0.0	−130.978 84	0.0	−131.324 52	0.0	(0)	−131.446 27	0.0	0.0
2	C_s	$^1A'$	−130.170 86	53.7	−130.880 98	61.4	−131.216 56	67.8	(0)	−131.340 69	62.3	60.4
3	C_1	^1A	−130.145 28	69.8	−130.854 47	78.0	−131.209 34	72.3	(1)	−131.336 56	68.8	66.9
4	C_s	$^1A'$	−451.409 81	0.0	−453.673 84	0.0	−453.973 94	0.0	(0)	−454.081 70	0.0	0.0
5	C_s	$^1A'$	−451.271 90	86.6	−453.576 14	61.3	−453.884 12	56.4	(0)	−453.996 53	53.5	49.3
6	C_1	^1A	−451.258 36	95.0	−453.517 92	97.9	−453.825 06	93.4	(1)	−453.940 95	88.3	84.1
7	C_s	$^1A'$	−154.119 21	0.0	−154.955 78	0.0	−155.298 11	0.0	(0)	−155.423 28	0.0	0.0
8	C_1	^1A	−154.028 86	56.7	−154.862 43	58.6	−155.172 14	79.1	(0)	−155.310 08	71.0	66.9
9	C_1	^1A	−154.012 20	67.2	−154.838 80	73.4	−155.171 86	79.2	(1)	−155.310 52	70.8	66.7
10	C_s	$^1A'$	−512.549 27	0.0	−515.041 56	0.0	−515.350 82	0.0	(0)	−515.444 50	0.0	0.0
11	C_1	^1A	−512.424 70	78.2	−514.914 23	79.9	−515.208 12	89.6	(0)	−515.311 93	83.2	80.0
12	C_1	^1A	−512.420 58	80.8	−514.902 70	87.1	−515.187 79	102.3	(1)	−515.300 32	90.5	87.3

[a] Based on MP2/6-31G* optimized geometries. [b] Corrected for zero-point energies scaled by 0.95.[30]

gas-phase[10] and solution-phase[11] insertions into the paraffin C–C bonds are thought to involve a reactive singlet nitrene. Likewise, the near-diffusion-controlled insertion into C–H bonds involves a singlet phosphorylnitrene, which is believed to undergo complex formation with perfluoro hydrocarbon solvents.[12] Nitrene complexes are known in organometallic structures as imido ligands,[13] and recently, a nitrene transfer in a tungsten complex was reported to yield a Staudinger complex.[14] Nitrene insertion into symmetrical bonds has been studied theoretically. Fueno et al.[5] reported that both the ^{1}NH insertion into the hydrogen molecule and its addition to ethylene to yield ammonia and aziridine, respectively, occur essentially without barrier. These authors used multireference configuration interaction (MRCI) and also considered low-lying excited states in their study.

Derivatives of the nitrene–hydrogen sulfide complex, the sulfilimines, are experimentally well-known synthons.[15] The bond rotation and S-pyramidal inversion of H_2SNH has been studied at HF/4-31G.[16] The sulfilimines are isoelectronic with the *N*-oxides and the sulfoxides,[17] which are of interest in the context of sulfur hypervalency.[18] The sulfilimines are related to the nitrene complexes of phosphines, known as iminophosphoranes or Staudinger complexes, which are also widely applied synthons.[13,19] The nature of the N–P interaction in these complexes has attracted theoretical interest.[20] Recently, we addressed the complexation of ^{1}NH with PH_3 as well as that of the alternate addition of ^{1}PH to NH_3.[21] The resulting isomeric "ylides", the Staudinger complex H_3PNH (containing a very polar partial triple bond) and the tight van der Waals complex H_3NPH, are both ca. 30 kcal/mol less stable than the insertion product H_2PNH_2. In the present study, we explore whether singlet nitrenes yield addition complexes with XH_n (X = O, S, F, Cl) before undergoing hydrogen migration to the thermodynamically more stable tautomeric insertion products.

Table III. MP4/6-31G** Binding Energies (kcal/mol) of NXH_n (X = O, S, F, Cl) toward ^{1}NH and XH_{n-1}[a]

2	→	$OH_2 + {}^1NH$	21.5
5	→	$SH_2 + {}^1NH$	59.1
8	→	$FH + {}^1NH$	6.1
11	→	$ClH + {}^1NH$	15.5
1	→	$OH_2 + {}^1NH$	85.9
4	→	$SH_2 + {}^1NH$	110.6
7	→	$FH + {}^1NH$	73.2
10	→	$ClH + {}^1NH$	92.6

[a] Corrected for 0.95-scaled ZPEs.

Methods

Ab initio molecular orbital calculations[22] were carried out with the GAUSSIAN 88[23] suite of programs. Geometries were optimized within specified symmetries by use of the split-valence 3-21G[24] and polarized 6-31G*[25] basis sets within the restricted Hartree–Fock approximation. Electron correlation effects in the geometry optimization were evaluated by using the all-electron (Full) Møller–Plesset perturbation theory[26] at second order (MP2), since it is well-known that correlation effects become important when electronegative elements are involved in weak bonding interactions. Energy evaluations were performed at MP4/6-311G** + scaled zero-point energies (ZPE), which includes valence electron (FC, frozen core) correlation up to fourth-order terms and uses an essentially triply split valence basis set with p- and d-polarization functions for hydrogen and the heavy elements,[27] respectively.

The nature of bonding in the MP2(Full)/6-31G* optimized geometries was investigated by using the topological one-electron density distributions of Bader's theory of atoms in molecules.[28,29] The gradient

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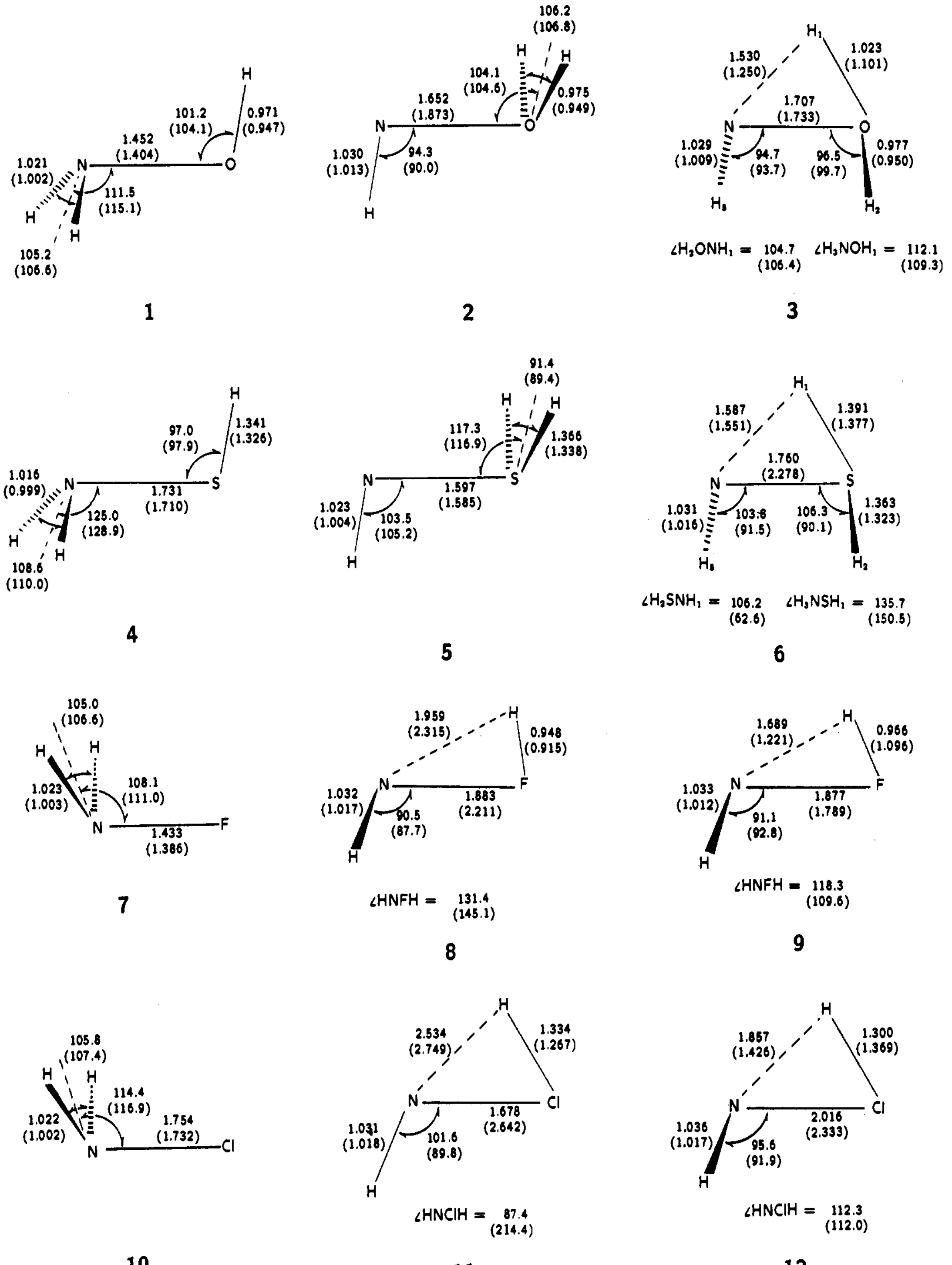

1 **2** **3** **4** **5** **6** **7** **8** **9** **10** **11** **12**

Figure 1. Optimized structures for the ylides, their conventional isomers, and their transitions for H-transfer. The top values are at MP2/6-31G*, and the values in parentheses are the geometrical parameters at HF/6-31G*.

vector field $\nabla\rho(r)$ and the (3,−1) or "bond critical points" r_b, which have a minimum value in $\rho(r)$ along the maximum electron density path connecting two nuclei, were located. The magnitude of the soft curvature $\lambda_2(r)$ of the three eigenvalues of the Hessian of $\rho(r)$ at a critical point characterizes the topological stability of a structure. The Laplacian of $\rho(r)$ determines regions in space wherein charge is concentrated ($\nabla^2\rho(r) < 0$) or depleted ($\nabla^2\rho(r) > 0$). The sign of $H(r_b)$, which is the sum of the local potential and kinetic energy density at a bond critical point, determines whether a bond is covalent ($H(r) < 0$) or ionic ($H(r) > 0$).[28d]

Results and Discussion

The ab initio total and relative energies at various levels of theory used for the singlet ^{1}NH complexes of OH_2, SH_2, HF, and HCl and their transition structures for hydrogen migration, whose geometries are shown in Figure 1, are given in Table I. The number of imaginary frequencies (NIMAG) are indicated in parentheses to identify minima (i.e., 0) and transition structures (i.e., 1). The final column in Table I gives the relative energies at MP4/6-311G** corrected for 0.95-scaled[30] ZPE, obtained at

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Table IV. Bond Critical Point Data for NXH_n (X = O, S, F, Cl) Species at MP2/6-31G*[a]

struct	X-Y	d_X	d_Y	λ_1	λ_2	λ_3	ϵ	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$
1	N-O	0.670	0.783	-0.593	-0.580	0.888	0.022	1.882	-6.858	-1.648
	O-H	0.777	0.194	-1.704	-1.647	1.549	0.035	2.322	-43.400	-3.519
	N-H	0.765	0.256	-1.243	-1.189	0.788	0.045	2.233	-39.594	-3.142
2	N-O	0.717	0.936	-0.225	-0.163	0.657	0.379	0.978	6.464	-0.469
	O-H	0.791	0.185	-1.720	-1.700	1.586	0.011	2.244	-44.201	-3.503
	N-H	0.759	0.272	-1.184	-1.073	0.721	0.104	2.181	-37.010	-3.011
3	N-O	0.763	0.946	-0.208	-0.141	0.608	0.478	0.902	6.227	-0.384
	O-H_1	0.833	0.190	-1.349	-1.309	1.366	0.031	1.854	-31.124	-2.648
	O-H_2	0.790	0.187	-1.678	-1.672	1.559	0.003	2.234	-43.142	-3.440
	N-H_3	0.765	0.265	-1.200	-1.104	0.742	0.087	2.179	-37.653	-3.030
4	N-S	1.023	0.710	-0.249	-0.197	0.167	0.262	1.279	-6.725	-1.366
	S-H	0.871	0.470	-0.441	-0.390	0.304	0.131	1.411	-12.699	-1.176
	N-H	0.764	0.252	-1.220	-1.171	0.792	0.042	2.200	-38.528	-3.075
5	N-S	0.970	0.627	-0.333	-0.280	0.444	0.192	1.666	-4.068	-2.174
	S-H	0.897	0.469	-0.441	-0.415	0.341	0.062	1.394	-12.456	-1.117
	N-H	0.760	0.263	-1.133	-1.098	0.729	0.032	2.142	-36.201	-2.959
6	N-S	0.876	0.887	-0.259	-0.234	0.276	0.108	1.245	-5.207	-0.966
	S-H_1	0.976	0.417	-0.392	-0.359	0.400	0.092	1.182	-8.451	-0.853
	S-H_2	0.900	0.463	-0.424	-0.409	0.346	0.037	1.362	-11.730	-1.068
	N-H_3	0.762	0.269	-1.114	-1.064	0.710	0.047	2.117	-35.358	-2.893
7	N-F	0.632	0.801	-0.563	-0.514	1.033	0.095	1.769	-1.037	-1.394
	N-H	0.769	0.255	-1.263	-1.206	0.804	0.047	2.239	-40.134	-3.163
8	N-F	0.860	1.029	-0.082	-0.057	0.417	0.434	0.451	6.716	-0.050
	F-H	0.792	0.156	-1.937	-1.933	1.797	0.002	2.101	-49.961	-3.982
	N-H	0.770	0.263	-1.238	-1.120	0.760	0.106	2.189	-38.511	-3.064
9	N-F	0.874	1.020	-0.089	-0.059	0.450	0.506	0.488	7.288	-0.060
	F-H	0.806	0.160	-1.738	-1.731	1.714	0.004	1.958	-42.303	-3.471
	N-H	0.773	0.260	-1.244	-1.131	0.770	0.100	2.187	-38.677	-3.068
10	N-Cl	0.849	0.905	-0.314	-0.295	0.430	0.062	1.309	-4.311	-0.907
	N-H	0.769	0.252	-1.226	-1.183	0.794	0.037	2.202	-38.926	-3.089
11	N-Cl	0.738	0.939	-0.345	-0.271	0.527	0.270	1.456	-2.140	-1.104
	Cl-H	0.943	0.392	-0.543	-0.516	0.566	0.052	1.424	-11.864	-1.144
	N-H	0.762	0.269	-1.153	-1.083	0.721	0.065	2.157	-36.493	-2.971
12	N-Cl	0.875	1.142	-0.116	-0.089	0.358	0.302	0.627	3.671	-0.189
	Cl-H	0.952	0.348	-0.587	-0.585	0.515	0.003	1.472	-15.864	-1.402
	N-H	0.767	0.269	-1.171	-1.070	0.724	0.094	2.145	-36.574	-2.958

[a] d_X (d_Y) is the distance from the critical point to atom X (Y); λ's are in $e{\cdot}a_0^{-5}$; $\rho(r)$ is in e-Å^{-3}; $\nabla^2\rho(r)$ is in e·Å^{-5}; $H(r)$ is in hartrees·Å^{-3}.

MP2/6-31G*. The conventional tautomers of this study have been included to make the comparisons convenient and consistent. The MP2/6-31G* geometrical parameters and the MP4/6-311G** + scaled ZPE energies are used throughout the text unless otherwise noted. The harmonic vibrational MP2/6-31G* frequencies of **1**–**12** are listed in Table II (supplementary material) to assist experimental verification of the minimum-energy structure of the present study.

Insertion into O–H and S–H Bonds. The first question to be asked is whether nitrene ^1NH gives a complex with OH_2. For example, the CH_2 carbene gives only a very modest interaction with water (i.e., the C–O bond length is 1.805 Å at MP2/6-31G*), but the CH_2–NH_3 complex is stronger (d_{CN} = 1.559 Å),[3h] as are the silylene complexes with water, ammonia, HF, and HCl.[3f] The nitrene–water complex **2**, which can be considered as an ylide-like species, is at a minimum at MP2/6-31G*. Its relatively long N–O bond of 1.652 Å and near-orthogonal HNO angle (see Figure 1, which also illustrates the strong geometrical dependency on the level of theory employed) suggest that the interaction is predominantly between the nitrogen and an oxygen lone pair. The estimated binding energy amounts to 21.5 kcal/mol (see Table III). Hydrogen migration of the $NHOH_2$ complex **2** via **3** yields the thermodynamically 60.4 kcal/mol more stable tautomer, hydroxylamine (**1**). This well-studied species has a much shorter N–O bond length of 1.452 Å. Transition structure **3**, which is nonsymmetric (C_1) to circumvent in-plane bond pair repulsions, represents a three-center two-electron complex between the nitrene and an O–H bond of water. Its geometrical parameters are indicative of an early transition for the HN–OH_2 → H_2N–OH process. This is in line with the estimated small rearrangement barrier for this process of 6.5 kcal/mol, which is larger than the corresponding $CH_2{\cdots}OH_2$ barrier for proton transfer of ca. 1 kcal/mol[3h] but much smaller than the 38 kcal/mol estimated for that of the silylene–water complex.[3f] For comparison, the HN–NH_3 → H_2N–NH_2[21] and H_2C–NH_3 → H_3C–NH_2[3h] barriers at MP2/6-31G* + ZPE amount to 19.0 and 14.8 kcal/mol, respectively.

The nitrene interaction with H_2S differs from that with water. The addition or "ylide" complex HN–SH_2 (**5**) has a significant kinetic barrier of 34.8 kcal/mol for rearrangement via **6** (C_1) to the thermodynamically 49.3 kcal/mol more stable thiohydroxylamine (**4**). In contrast to the case of the nitrene–water adduct, the effects of correlation are modest on both the geometries and the energies of **4**–**6**, except for the large NS bond shortening in the transition structure. The important distinction between the NSH_3 and NOH_3 isomers is that the NS bond in the complex HN–SH_2 (**5**) of only 1.597 Å is significantly shorter than that in the conventional isomer H_2N–SH (**4**). Similar short bonds to nitrogen have been noted in imido complexes of organometallic systems[13] and in Staudinger complexes.[20,21]

Insertion into F–H and Cl–H Bonds. The singlet nitrene insertion into group 17 hydrides is anticipated to be less favorable than the discussed insertion into group 16 hydrides. This is because the higher electronegativities of the halogens, in particular fluorine, restrict the lone-pair donation to the empty nitrogen p orbital. The calculational data support this qualitative picture. While between ^1NH and HF an addition complex (i.e., HN–FH (**8**)) is characterized at MP2/6-31G*, inclusion of zero-point energy corrections and single-point MP4/6-311G** calculations show a destabilization of this species relative to the MP2 transition structure **9**. Consequently, the HN–FH complex **8**, with a binding energy of 6.1 kcal/mol, is likely to convert without barrier into the 66.7 kcal/mol more stable fluoramine (**7**).

The interaction of nitrene with hydrogen chloride results in the NH–ClH complex **11**, which has a barrier (**12**, C_1) of 7.3 kcal/mol for hydrogen transfer to the 80.0 kcal/mol more stable chloramine (**10**). Similar to the nitrene–SH_2 complex, NH–ClH has also an N–X bond that is shorter in the addition complex than in the more

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(30) DeFrees, D. J.; McLean, A. D. *J. Chem. Phys.* **1985**, *82*, 333.

stable tautomer. Evidently, the nitrene complexes of the second-row hydrides are relatively stabilized with bond properties that differ from those of the first-row analogues.

Electron Density Analysis

The MP2/6-31G* bond critical point ($\mathbf{r}_b$) data for structures **1**–**12** are listed in Table IV. The electron density ρ at $\mathbf{r}_b$(NO) has a much larger value for hydroxylamine than for the $HNOH_2$ complex **2**. The higher ellipticity ϵ, the relative depletion of electron density ($\nabla^2\rho(\mathbf{r}_{b1}) > 0$), and the relatively small value for the total energy density H suggest that the N–O interaction in $HNOH_2$ represents only a partial bond that is highly polarized; i.e., **2** is a weak donor–acceptor complex. The same applies to the ^{1}NH complex with F–H, **8**, which exhibits a near-ionic interaction ($H = -0.050$).

The bonding picture for the ^{1}NH complexes of the second-row hydrides differs significantly from those of the first-row congeners. The addition complex $HNSH_2$ (**5**) has a stronger and 0.135 Å shorter N–S bond than that of thiohydroxylamine (**4**), which is reflected in its higher values of both $\rho(\mathbf{r}_b)$ and $H(\mathbf{r}_b)$. Hence, the lower ϵ of the N–S bond of $HNSH_2$ may suggest partial triple-bond character (instead of double-bond behavior).[21] The net atomic charges, obtained from integrating the total electron densities of the atomic basins of $HNSH_2$, indicate a polarized N–S bond; the charges are −1.35e for N, +0.99e for S, 0.00e for H_S, and +0.37e for H_N. This polarization is less than that in the parent Staudinger complex H_3P–NH (i.e., −1.73e for N and +2.96e for P),[21] because sulfur is a more electronegative element than phosphorus. The short N–P bond in the Staudinger complex, like the short P–O bond in phosphine oxide and the P–C bond in the Wittig reagent H_3PCH_2, has been attributed to mainly Coulombic interactions augmented with some triple-bond character.[21] The electrostatic force in $HNSH_2$ is less and may suggest a stronger electronic interaction. The same phenomenon observed in $HNSH_2$ is also present in the ^{1}NH complex with HCl (**11**) but is less pronounced. The slightly higher values of $\rho(\mathbf{r}_b)$ and $H(\mathbf{r}_b)$ for structure **11** as compared to those of chloramine (**10**) are in line with the 0.076 Å shorter N–Cl bond length for HNClH and emphasize the strong interaction within this halo ylide.

Molecular Orbitals. If $NHSH_2$ (**5**) and HNClH (**11**) contain partial multiple bonds with the nitrene nitrogen, they might also be considered to contain a hypervalent sulfur and chlorine atom, respectively. In fact, the molecular orbitals of these species lend some support for partial triple NS and NCl bonds. As might have been anticipated from Reed and Schleyer's recent study[18a] on hypervalency and our own work[21] on phosphinidene complexes, neither of the two species, however, experiences stabilization through d-orbital participation. In the case of $HNSH_2$, the HOMO is composed of a nitrogen lone pair that interacts with the π^* orbital of the SH_2 group to render negative hyperconjugative stabilization. The HOMO-1 and -2 of $HNSH_2$ comprise a set that may be best described as bonding and antibonding combinations of the in-plane N and S lone pairs with additional SH and NH bonding contributions. The LUMO is an NS π^* orbital. The MO's of the NHClH structure **11** and of the well-studied sulfoxide H_2SO,[17] which is isoelectronic with H_2SNH, display similar characteristics. Such stabilizations are much weaker in the first-row congener $HNOH_2$ (**2**) and absent in HNFH (**8**), where the lone pairs are more localized on individual centers.

Conclusions

Singlet nitrene ^{1}NH complexes with the protic solvents OH_2, SH_2, and HCl, but not with HF, to form kinetically stable products, which subsequently undergo H-migration to render the thermodynamically more stable insertion products. Electron correlation effects are important in terms of both geometrical parameters and energies. In the case of SH_2, the primary product is the parent sulfilimine (**5**), of which many derivatives are known to be useful synthons. The barrier for rearrangement of **5** is estimated to be 34.8 kcal/mol, and hence this species is expected to be experimentally observable. This significant kinetic stability of the sulfilimine is also displayed in its 1.597 Å short NS bond, which is of partial triple-bond nature, thereby suggesting sulfur hypervalency. However, the nitrogen and sulfur atoms experience a large electrostatic interaction pointing to an ylide-type structure. This indicates that the interaction between ^{1}NH and SH_2 consists of a very polarized NS σ-bond with additional partial triple-bond stabilization without d-orbital participation. Therefore, the sulfur is of normal valency. The bonding situation is similar for the nitrene–HCl complex **11**, which has a 1.678 Å short NCl bond, but its barrier of 7.3 kcal/mol for H-rearrangement is much smaller, making experimental verification more difficult.

The ^{1}NH–water complex **2** represents only a weak donor–acceptor complex ($d_{NO} = 1.652$ Å) with an estimated 6.5 kcal/mol barrier for H-migration to the 60.4 kcal/mol more stable hydroxylamine. A complex between ^{1}NH and HF is characterized at MP2/6-31G*, but higher levels of theory suggest that the insertion of nitrene into the F–H bond occurs without such an intermediate complex.

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Registry No. NH, 13774-92-0; OH_2, 7732-18-5; SH_2, 7783-06-4; HF, 7664-39-3; HCl, 7647-01-0.

Supplementary Material Available: Table II, listing MP2/6-31G* vibrational harmonic frequencies for NXH_n isomers (1 page). Ordering information is given on any current masthead page.