A Theoretical Study of Chlorine Atom and Methyl Radical Addition to Nitrogen Bases: Why Do Cl Atoms Form Two-Center−Three-Electron Bonds Whereas CH_3 Radicals Form Two-Center−Two-Electron Bonds?

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Abstract: Ab initio molecular orbital calculations have been carried out on a series of adducts between chlorine atom and NH_3, NMe_3, NCl_3, $HN{=}CH_2$, and pyridine, and between methyl radical and $HN{=}CH_2$ and pyridine. A two-center−three-electron (2c−3e) bond is predicted for all the chlorine adducts, whereas the CH_3 adducts with the unsaturated systems form two-center−two-electron (2c−2e) bonds following promotion of one of the nitrogen lone pair electrons into a π^* orbital. For chlorine adducts, the greater strength of the 2c−2e N−Cl bond compared with the 2c−3e N−Cl bond is not sufficient to compensate for the required promotion energy in both the saturated and unsaturated amines. On the other hand, for CH_3 adducts of the unsaturated nitrogen bases, $HN{=}CH_2$ and pyridine, the C−N and C−C bond energies are sufficiently high and the promotion energy is sufficiently low that adducts to both N and C with 2c−2e bonds can be formed. Adducts between CH_3 and saturated nitrogen centers are less stable than the separated species because of the inability of CH_3 to form effective 2c−3e bonds in neutral systems (due to its low electron affinity), and because of the high excitation energy required to promote an electron from the nitrogen lone pair (due to the absence of suitable low-lying empty orbitals in these systems).

Introduction

Understanding the interaction of radicals with neutral molecules is a crucial prerequisite for many areas of chemistry as well as biology.[2] In this connection, there have been extensive recent studies of radical addition complexes formed between chlorine atoms and various nitrogen bases including amines[3−5] and pyridine.[3,6−8]

A study of $Cl{\therefore}NR_3$ complexes was carried out by Symons and co-workers.[4] They subjected ammonium chloride samples to γ radiation at 77 K. Initially only $Cl_2^{\bullet-}$ was observed by ESR, but after annealing to 180 K and recooling to 77 K more complex spectra were obtained, attributed in part to chlorine−amine 2c−3e complexes.[4] It is perhaps surprising that irradiation of trimethylammonium chloride did not result in a $Cl{\therefore}NMe_3$ complex, given that such a complex is predicted by ab initio calculations to be quite stable (see below).

Breslow and co-workers have used the chlorine−pyridine complex to direct selective steroid chlorinations.[6a] The selective behavior has been rationalized in terms of the weak nature of the 2c−3e Cl−N bond, which was estimated with the help of ab initio calculations to have a binding energy of 21.3 kJ mol^{-1}.[6b] Abu-Raqabah and Symons[7] studied the *N*-chloropyridinyl radical using ESR spectroscopy and established that the chlorine atom is in the plane of the ring and is bound to nitrogen by a 2c−3e bond, in agreement with previous calculations.[6b] Similarly, the experimental data for the complex of chlorine atom with quinoline are consistent with the formation of a 2c−3e bond.[8]

It is interesting that a 2c−3e $Cl{\therefore}N$ bond involving pyridine cation can be obtained by a completely different mechanism.[9] From an analysis of the ESR spectrum, it has been determined that ionization of pyridine leads to a Σ state rather than a Π state.[10] Therefore, if a solution of pyridine in a chlorine-containing solvent (such as $CFCl_3$) is irradiated with a γ-ray source, electron transfer from pyridine to an ionized solvent molecule will generate the Σ pyridinyl radical cation. The cation can then associate with a neutral solvent molecule in a 2c−3e interaction (e.g. $C_5H_5N^{\bullet+}...{:}ClCFCl_2$).[9b]

We have used ab initio molecular orbital calculations in the present study to examine the adducts formed between the chlorine atom and NH_3, NMe_3, NCl_3, $HN{=}CH_2$, and pyridine and between the methyl radical and $HN{=}CH_2$ and pyridine. Our aim is to try to obtain a better understanding of the important interactions that might take place between a radical and a nitrogen base.

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Methods and Results

Standard ab initio molecular orbital calculations[11] were carried out using the GAUSSIAN 92,[12a] GAUSSIAN 94,[12b] and ACES II[13] programs. Initial geometry optimizations were carried out at the UHF/6-31G(d) level of theory, and the nature of the stationary points was determined through frequency calculations. The geometries of the minimum energy structures were further optimized at the UMP2/6-31G(d) level of theory, and in certain cases at the UMP2(fc)/6-311+G(2df,p) and QCISD(T)(full)/6-31G(d) levels as well. Selected structural characteristics for systems **4**−**18** are displayed in Figure 1. Total energies for **1**−**18** at the UHF/6-31G(d), PMP4/6-31G(d)//UMP2(fc)/6-31G(d), and G2(MP2,SVP)[14,15] levels of theory are presented as supporting information (Table S1). Spin-squared expectation values ($\langle S^2 \rangle$) (to give an indication of the extent of spin contamination), zero-point energies (ZPE) calculated from scaled (by 0.8929)[16] UHF/6-31G(d) harmonic frequencies, and heats of formation ($\Delta H_{f\ 298}$) calculated from the G2(MP2,SVP) total energies using the atomization reaction are presented in Table 1. Triplet−singlet splittings (T − S) and binding energies of the Cl and CH_3 adducts are included in Table 2. Unless otherwise noted, the relative energies quoted in the text correspond to G2(MP2,SVP) values at 298 K. In the case of **10**, the more rigorous G2[17] and G2(MP2)[18] methods were also applied.

Discussion

In this study, we consider the adducts formed with nitrogen bases by two quite different radicals, the chlorine atom and the methyl radical. The stability of the addition products is determined by (1) the strength of the newly formed bond and (2) the electronic reorganization required to prepare the substrate for this bond. In the case of formation of a two-center−three-electron (2c−3e) adduct,[19−23] little electronic reorganization is required but the resultant 2c−3e bond is relatively weak. On the other hand, a 2c−2e bond is generally significantly stronger but it requires considerable electronic reorganization through a formal promotion of one of the nitrogen lone pair electrons to an empty low-lying orbital. The form of the preferred adduct will depend on the balance between these effects.

We find that the Cl and CH_3 radicals both form adducts with unsaturated nitrogen compounds (Table 2) but through very different mechanisms. The chlorine atom forms a 2c−3e bond directly with the nitrogen lone pair in all cases. The resulting 2c−3e bond in the $(\sigma)^2(\sigma^*)^1$ complex is much weaker than a conventional 2c−2e bond but has the advantage of not requiring any promotion energy. On the other hand, the methyl radical forms a 2c−2e bond at an unsaturated nitrogen center following the promotion of an electron from the nitrogen lone pair to a π^* empty orbital. It is important to understand the factors that determine the relative merits of the 2c−3e mechanism versus the promotion/2c−2e mechanism.

Structural Aspects. A comparison of calculated (MP2(full)/6-31G(d)) and experimental bond lengths for NMe_3 (**4**),[24a] NCl_3 (**5**),[24b] $HN{=}CH_2$ (**6**),[24a] and pyridine (**8**)[24c] shows uniformly good agreement (Figure 1).

In methanimine (**6**), excitation to the n−π^* triplet (**7**) is accompanied by a lengthening of the C−N bond and a twisting of the methylene group. A recent study[25] using electron spin-echo (ESE) spectroscopy found that the lowest triplet state of pyridine (**9**) is nonplanar, and that it is a mixture of the $^3B_1$ (n−π^*) and $^3A_1$ (π−π^*) states. This is supported by ab initio calculations[26−28] which find the planar triplet ($^3B_1$ in C_{2v} symmetry) to be a transition structure connecting two equivalent $^3A'$ states. We find a barrier to this interconversion of 23.8 kJ mol^{-1} at the G2(MP2,SVP) level of theory. The calculated flap angles at nitrogen and carbon (141.6° and 166.3°, respectively) in **9** (Figure 1) are in very good agreement with those proposed on the basis of the ESE data (139° and 169°, respectively).[25b]

Chlorine addition to amines to form 2c−3e adducts does not significantly affect the internal distances to nitrogen (N−X). In contrast, the ∠XNX angle opens up upon 2c−3e bond formation with chlorine in $ClNH_3$ (**10**) (106.3° → 110.8°), $ClNCl_3$ (**12**) (107.6° → 108.3°), and $ClNMe_3$ (**11**) (110.4° → 113.9°), which is consistent with a greater p-orbital contribution to the Cl-directed orbital and a decreased p-orbital contribution to other bond-directed orbitals. The preferred structure of $ClNCl_3$ (**12**) has C_{3v} symmetry with one long 2c−3e Cl−N bond and three shorter 2c−2e bonds.

Two possible adducts between chlorine and methanimine are the planar 2c−3e complex **13a** and the "twisted" 2c−2e isomer **13b**, which corresponds to the (chloroamino)methyl radical, $ClNH{-}CH_2^{\bullet}$. It is interesting that as the N═C bond is broken in going from **13a** to **13b**, the N−Cl distance shortens significantly (2.509 Å in **13a** → 1.753 Å in **13b**), indicating an increase in the N−Cl bond order as the description of the N−Cl interaction changes from 2c−3e to 2c−2e.

The pyridine fragment in the *N*-chloropyridinyl radical **14** has a geometry very similar to that of neutral pyridine itself, consistent with the fact that little electronic reorganization takes

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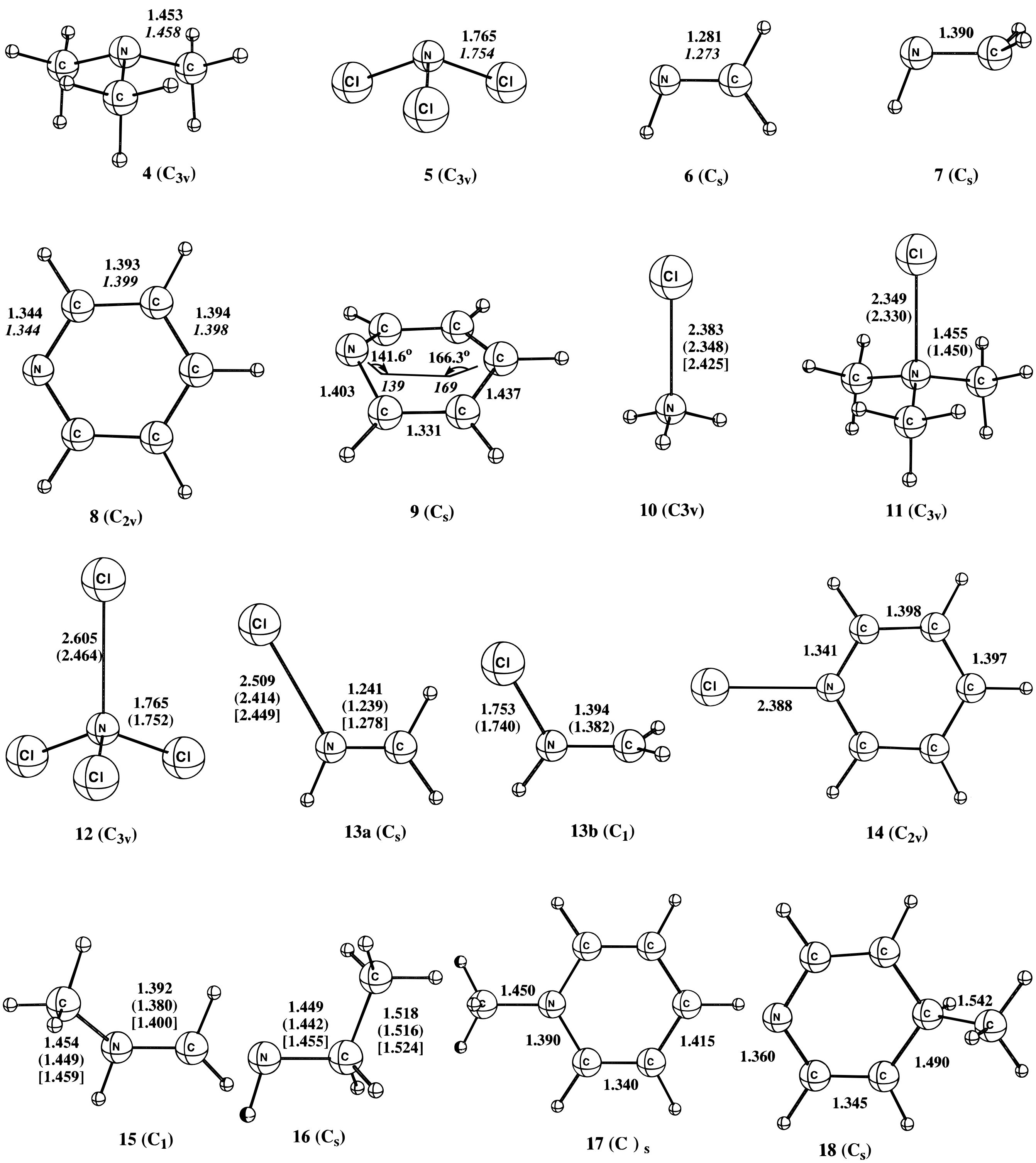

4 (C_{3v}) **5** (C_{3v}) **6** (C_s) **7** (C_s)

8 (C_{2v}) **9** (C_s) **10** (C3v) **11** (C_{3v})

12 (C_{3v}) **13a** (C_s) **13b** (C_1) **14** (C_{2v})

15 (C_1) **16** (C_s) **17** (C) s **18** (C_s)

Figure 1. Molecular display of UMP2(full)/6-31G(d) optimized structures. Values in italics are from experiment (see text), parameters in parentheses are calculated at the MP2(fc)/6-311+G(2df,p) level, while those in square brackets are from QCISD(T)(full)/6-31G(d) calculations. Bond distances are given in angstroms and angles in degrees.

place for 2c−3e bond formation. The Cl−N distance in **14** is somewhat shorter than the corresponding bond length in **13a**.

With the exception of **11**, the lengths of the 2c−3e Cl−N bonds are grossly overestimated at the UHF/6-31G(d) level of theory as compared with MP2(full)/6-31G(d).[29,30] At the QCISD(T)(full)/6-31G(d) level of theory, the 2c−3e bonds can be longer (as in **10**) or shorter (as in **13a**) than the MP2(full)/6-31G(d) values (Figure 1). The choice of the basis set is also quite important. At the MP2 level, the larger 6-311+G(2df,p) basis set tends to contract the bond length as compared with the 6-31G(d) basis set. This effect is larger for the longer Cl−N bonds, with the result that the range of Cl−N bond lengths is reduced at the MP2(fc)/6-311+G(2df,p) level. We note that, at least in the cases of $ClNH_3$ and $ClNCl_3$, the G2(MP2,SVP) heats of formation calculated at the different geometries differ by less than 1 kJ mol^{-1}.

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(29) The UHF/6-31G(d) Cl−N bond lengths are 2.684 (**10**), 2.402 (**11**), 3.276 (**12**), 2.837 (**13a**), and 2.838 (**14**) Å.

(30) This is a counterexample to the statement that UHF (fortuitously) predicts correct geometries for odd-electron species.[23]

Table 1. Calculated Spin-Squared Expectation Values (⟨S^2⟩), Zero-Point Energies (ZPE, kJ mol^{-1}), and Heats of Formation (kJ mol^{-1}) at 298 K[a]

	sym	state	⟨S^2⟩[b]	ZPE[c]	$\Delta H_{f\ 298}$ (G2(MP2,SVP))
components					
1 Cl	K_h	^2P	0.75	0.0	121.3
2 CH_3	D_{3h}	$^2A_2''$	0.76	81.3	149.5
3 NH_3	C_{3v}	$^1A_1$	0.00	97.2	−42.3
4 NMe_3	C_{3v}	$^1A_1$	0.00	340.0	−27.7
5 NCl_3	C_{3v}	$^1A_1$	0.00	20.1	203.7
6 HN═CH_2	C_s	$^1A'$	0.00	113.6	85.6
7 HN−CH_2	C_s	$^3A''$	2.01	101.2	378.3
8 pyridine	C_{2v}	$^1A_1$	0.00	250.6	130.4
9 pyridine	C_s	$^3A'$	2.42	231.6	504.0
Cl adducts					
10 $ClNH_3$	C_{3v}	$^2A_1$	0.76	101.1	41.0
11 $ClNMe_3$	C_{3v}	$^2A_1$	0.77	345.0	2.0
12 $ClNCl_3$	C_{3v}	$^2A_1$	0.76	20.7	304.7
13a ClNH═CH_2	C_s	$^2A'$	0.78	114.5	175.1
13b ClNH−CH_2	C_1	^2A	0.77	114.9	233.6
14 *N*-chloropyridinyl	C_{2v}	$^2A_1$	0.76	251.8	204.5
Me adducts					
15 MeNH−CH_2	C_1	^2A	0.76	221.8	158.9
16 $MeCH_2$−NH	C_s	$^2A''$	0.76	219.9	155.2
17 *N*-methylpyridinyl	C_s	$^2A'$	1.12	350.5	223.4
18 4-methylpyridinyl	C_s	$^2A'$	1.23	349.8	242.4

[a] Calculated UHF/6-31G(d), PMP4/6-31G(d), G2(MP2,SVP) (0 K), and G2(MP2,SVP) (298 K) total energies are listed in the supporting information (Table S1). [b] Calculated from the UHF/6-31G(d) wave function at the UHF/6-31G(d) optimized geometries. [c] Calculated from scaled UHF/6-31G(d) harmonic vibrational frequencies.

Table 2. Triplet−Singlet (T−S) Splittings (kJ mol^{-1}) of Components and Bond Dissociation Energies (kJ mol^{-1}) of the Cl− and CH_3− Adducts

	PMP4 0 K[a]	G2(MP2,SVP) 0 K	G2(MP2,SVP) 298 K
T−S Splittings			
HN═CH_2	275.4	292.0	292.7
pyridine	400.0	371.5	373.6
Bond Dissociation Energies			
Cl-adducts			
10 $ClNH_3$	38.0	36.3	38.0
11 $ClNMe_3$	76.6	90.2	91.6
12 $ClNCl_3$	12.0	21.0	20.3
13a ClNH═CH_2	24.8	31.5	31.8
13b ClNH−CH_2	−58.3	−30.0	−26.7
14 *N*-chloropyridinyl	41.6	47.5	47.2
Me adducts			
15 MeNH−CH_2	58.5	69.0	76.1
16 $MeCH_2$−NH	78.9	72.5	79.8
17 *N*-methylpyridinyl	24.6	51.5	56.5
18 4-methylpyridinyl	32.9	32.1	37.5

[a] Including ZPE corrections calculated from scaled UHF/6-31G(d) frequencies.

Table 3. IE−EA Stability Index for 2c−3e Bonds

X∴Y		EA(X)[a]	IE(Y)[a]	IE − EA[a]	BDE[b]	*r*(X−Y)[c]
11	$ClNMe_3$	3.62	7.82	4.20	91.6	2.349
14	Clpy	3.62	9.25	5.63	47.2	2.388
13a	ClNH═CH_2	3.62	9.88[d]	6.26	31.8	2.509
12	$ClNCl_3$	3.62	10.12	6.50	20.3	2.605
10	$ClNH_3$	3.62	10.16	6.54	38.0	2.383

[a] Experimental electron affinities and ionization energies (in eV) for components X and Y from ref 33, unless otherwise noted. [b] Bond dissocation energies in kJ mol^{-1} from Table 2. [c] UMP2(full)/6-31G(d) bond distances in Å from Figure 1. [d] Reference 50.

The addition products of CH_3 to both the nitrogen (**15**) and carbon (**16**) atoms of HN═CH_2 were examined, with the latter found to be slightly more stable. In both cases, 2c−2e bonds are formed. **15** has C_1 symmetry and the geometry at the pyramidalized nitrogen is similar to that found in the NH_2CH_2 radical, consistent with its description as the (methylamino)methyl radical.[31]

The pyridine moiety in the CH_3−pyridine complexes is nearly planar and its bond lengths resemble those of triplet pyridine, in agreement with the notion of promotion (electronic reorganization) accompanying bond formation in the CH_3 complexes. In this respect, the difference between the *N*-chloro (**14**) and *N*-methyl (**17**) complexes is very striking. Two alternative conformations were considered for the methyl group in the *N*-methylpyridinyl radical. In the lower-energy conformation (**17**), one of the C−H bonds is oriented perpendicular to the ring, allowing a hyperconjugative interaction with the unpaired electron density of the ring ($^2A'$ state). Only 1.6 kJ mol^{-1} higher in energy[32] is the structure with a C−H bond in the plane of the pyridine ring ($^2A''$ state). The latter corresponds to the transition structure that interconverts two equivalent structures of type **17**, via the methyl group rotation. The geometries of the C (**18**) and N adducts (**17**) are similar, indicating similar extents of electronic reorganization.

Formation of Adducts with Two-Center−Three-Electron Bonding. Clark has found that the stability of 2c−3e complexes $X\therefore Y^{\bullet+}$ drops off exponentially with the difference in ionization energies (IE) of X and Y (Δ(IE)).[21] The latter quantity is equivalent to the energy required to transfer an electron from Y to $X^{\bullet+}$ in reaction 1:

$$X^{\bullet+} + Y \rightarrow X + Y^{\bullet+} \tag{1}$$

and reflects the contributions of the valence-bond structures $\overset{+}{X}{\cdot}{:}Y$ and $X{:}{\cdot}\overset{+}{Y}$.

In the case of 2c−3e bonded systems formed by a neutral radical $X^{\bullet}$ (e.g. $Cl^{\bullet}$ or $CH_3^{\bullet}$), an equivalent index would be the IE of Y minus the electron affinity (EA) of X, i.e. the energy change in reaction 2:

$$X^{\bullet} + Y \rightarrow X^{-} + Y^{\bullet+} \tag{2}$$

reflecting in this case the contributions of the valence-bond structures $X{\cdot}{:}Y$ and $\overset{-}{X}{:}{\cdot}\overset{+}{Y}$. Thus, 2c−3e bond formation in such situations is most favorable for radicals $X^{\bullet}$ with high electron affinities (e.g. $Cl^{\bullet}$, EA = 3.62 eV[33]) and molecules Y with low ionization energies (e.g. $N(CH_3)_3$, IE = 7.82 eV[33]). The values of IE − EA for all the chlorine complexes investigated in this study are presented in Table 3.

As expected from the above qualitative considerations, we generally observe an inverse relationship between IE − EA and the strength of the 2c−3e bond (BDE) and a direct relationship between IE − EA and the length of the 2c−3e bond (*r*(X−Y)) (Table 3). The strongest complex (**11**) is formed between Cl and trimethylamine, and the weakest complex (**12**) is formed between Cl and NCl_3, in both cases consistent with considerations based on IE − EA values. On the other hand, we note that the Cl∴N bond in $ClNH_3$ (**10**) is considerably stronger and shorter than expected on the basis of IE − EA alone.

Similarly, the reason why methyl groups do not form 2c−3e bonds can be attributed to the very low electron affinity of CH_3

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[32] At the G2(MP2,SVP) level at 0 K excluding the ZPE correction terms. If the latter are included, then the energy ordering is reversed but the energies of the two structures differ by less than 0.1 kJ mol^{-1}.

(0.08 eV).[33] An ab initio study of CH_3NH_3 and CH_3NMe_3 has indicated an interesting alternative to adding an electron to the σ^* orbital.[34] A metastable molecule results when an electron enters a Rydberg orbital and the core can be described as a cationic system which includes a 2c−2e bond to the CH_3 group (e.g. $CH_3NH_3^+$) while the outer electron then occupies a very diffuse orbital. However, the energy required for the promotion to the Rydberg orbital is very high, and therefore the energy of the metastable species lies significantly above the energy of the separated methyl radical and amine.

The G2(MP2,SVP) binding energy (Table 2) of the simplest Cl adduct ($ClNH_3$) is within 0.6 kJ mol^{-1} of the G2(MP2) and G2 values[35] lending confidence to the G2(MP2,SVP) energies of the other systems. The PMP4/6-31G(d) binding energies (Table 2) are in good agreement with the corresponding QCISD(T)6-31G(d) values and in reasonable agreement with G2(MP2, SVP) values, in accordance with previous experience.[23,36] The differences between the PMP4/6-31G(d) and G2(MP2,SVP) binding energies are mainly due to the basis set correction that is included in the latter method, but not in the former.

Formation of Adducts with Two-Center−Two-Electron Bonding. The strength of a 2c−2e bond in the adduct will depend in part on the promotion energy required to excite one electron from the nitrogen lone pair to an acceptor orbital. Thus, a requirement for a stable 2c−2e radical adduct is a low-energy acceptor orbital. We have chosen methanimine ($HN{=}CH_2$) and pyridine (NC_5H_5) as examples of unsaturated nitrogen compounds with low-lying π^* orbitals. The promotion energies for both molecules can be estimated as the lowest-energy adiabatic S−T excitations.

In methanimine (**6**), at our standard G2(MP2,SVP) level, the T−S splitting is 292.7 kJ mol^{-1} (3.03 eV). By analogy with ethylene, the T−S gap in methanimine should be a reasonable approximation to the bond strength of the C═N π bond. Our value (292.7 kJ mol^{-1}) is in agreement with the expectation that the more polar C═N π bond in methanimine should be stronger than the C═C π bond in ethylene (270 kJ mol^{-1}). Since the promotion energy is estimated to be lower than the energy of a 2c−2e C−N bond,[37] the formation of a stable adduct between CH_3 and methanimine is predicted.

The two lowest vertical triplet states of pyridine lie close in energy and cannot be distinguished experimentally, but they are thought to strongly interact through vibronic coupling.[38,39] Experiments place these two states 4.1 eV higher than the ground state.[40,41] The onset for phosphorescence was determined by Baba and co-workers[42] to be near 340 nm (3.65 eV or 352 kJ mol^{-1}), while other determinations of the adiabatic T−S gap range between 3.5 and 3.8 eV.[40,41,43,44]

A variety of *ab initio* methods have been used to study the vertical (CIS (CI singles),[26] GVB,[45] SAC-CI,[46] and MRCI[47,48]) and adiabatic (CISD[27] and CASPT2[49]) T−S gap in pyridine, with the best estimates ranging between 3.9 and 4.3 eV for the former and 3.6 and 4.1 eV for the latter. At the G2(MP2,SVP) level, the adiabatic excitation energy to the nonplanar triplet **9** is calculated to be 373.6 kJ mol^{-1} (3.87 eV). Regardless of whether the experimental or computational numbers are used, the energy required for the lowest triplet excitation is seen to be comparable to the strength of a 2c−2e C−N bond.[37] This makes it difficult to predict a priori whether or not an *N*-methylpyridinyl adduct is likely to be stable. The calculations indicate that such a species (**17**) is bound with respect to *singlet* pyridine plus methyl radical by 56.5 kJ mol^{-1}, a quantity smaller than the binding energy for **15**.

When an electron is promoted from the nitrogen lone pair into a π^* orbital, the methyl radical might be expected to form a 2c−2e σ bond at sites of significant unpaired spin density in the n−π^* triplet state. In the case of pyridine, these sites are the nitrogen atom and the 4-carbon atom. The thermodynamically favored product should be determined by the magnitude of the spin density at the various centers and by the strength of the bond to the methyl group. At the G2(MP2,SVP) level of theory, we find that in the case of pyridine the N adduct (**17**) is preferred over the C adduct (**18**) (by 19 kJ mol^{-1}). On the other hand, for $HN{=}CH_2$, the C adduct (**16**) is slightly more stable than the N adduct (**15**).

In the case of the chlorine adducts, one of the methanimine complexes that we have calculated (**13b**) can clearly be regarded as a 2c−2e system based on its geometrical characteristics (see discussion above). However, this complex is calculated to be less stable than a separated chlorine atom and *singlet* methanimine by 26.7 kJ mol^{-1} and could be regarded as metastable with respect to such a dissociation. This is consistent with our model, the formation of an only moderate strength 2c−2e Cl−N bond failing to compensate for the required promotion energy. The energy difference (58.5 kJ mol^{-1}) between the 2c−2e (**13b**) and 2c−3e (**13a**) complexes is much smaller than the T−S gap in **6** (292.7 kJ mol^{-1}). To the extent that **13b** and **13a** may be viewed as Cl adducts of triplet and singlet methanimine, respectively, then the difference of approximately 230 kJ mol^{-1} may be attributed to the greater intrinsic strength of the 2c−2e Cl−N bond in **13b** as compared with the 2c−3e Cl−N bond in **13a**.

Conclusions

We propose two different mechanisms for bond formation in adducts of radicals with nitrogen bases. The formation of 2c−3e bonds is favored by nitrogen bases with low ionization energies and by radicals with high electron affinities and relatively weak 2c−2e bonds to nitrogen. This is the case for chlorine atoms which are indeed predicted to form 2c−3e complexes with amines and with unsaturated nitrogen bases, the strongest complexes occurring for the nitrogen bases of lowest IE. Formation of 2c−3e bonds would also be expected

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for other radicals which have a high electron affinity but relatively small 2c−2e bond energies (e.g. Br and I atoms). On the other hand, formation of 2c−2e complexes requires a preliminary formal promotion of one of the electrons on nitrogen to an empty molecular orbital. It is only likely to occur for nitrogen bases with low-lying empty π* orbitals. It is favored (relative to 2c−3e bond formation) by radicals with low electron affinities and relatively strong 2c−2e bonds to nitrogen or carbon (e.g. methyl radical). An n−π* promotion in such circumstances can prepare either a nitrogen or carbon center for 2c−2e bond formation, and if the C−N or C−C bond strength is comparable to or greater than the promotion energy, a stable adduct might be anticipated. Adducts between Cl and NH_3, NMe_3, NCl_3, $HN{=}CH_2$ and pyridine, and between CH_3 and $HN{=}CH_2$ and pyridine can all be rationalized on the basis of such considerations.

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Supporting Information Available: Calculated total energies at the UHF/6-31G(d), PMP4/6-31G(d), G2(MP2,SVP) (0 K), and G2(MP2,SVP) (298 K) levels (Table S1) and GAUSSIAN archive entries for UMP2/(full)6-31G(d) optimized geometries for species **1**−**18** and UHF/6-31G(d) frequency calculations for the 2c−3e Cl adducts (**10**−**14**) (Table S2) (13 pages). See any current masthead page for ordering and Internet access instructions.

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