

more readily approached. The basicity of the substituted π bond, however, is somewhat greater, as indicated by the greater ν_s displacement for structure **8**; the ν_s value for this structure, in fact, is only 13.7 cm⁻¹ greater than that of 2-methylpropene-HF,²¹ and the difference may reflect electrostatic repulsions from an allenic proton in the plane of the hydrogen bond. Unlike structure **8**, no hyperconjugation with the methyl groups is available to structure **7**, but this complex undergoes greater ν_s displacement than does allene-HF. The σ bonds of the methyl substituents can be expected to interact with the unsubstituted π bond and donate some electron density to that π bond, especially when an electrophilic ligand such as HF binds.

Conclusion

The HF complexes of a series of conjugated dienes, 1,3,5hexatriene, two nonconjugated dienes, and two cumulenes have been produced in solid argon matrices. The nonconjugated dienes, 1,4-pentadiene and 1,5-hexadiene, give complexes strongly analogous to propylene-HF, and no evidence is found for complexes in which HF interacts with both π bonds. The conjugated dienes, on the other hand, form complexes with 1/1 stoichiometry such that HF interacts with the entire π system, rather than with an individual π bond, with the HF proton oscillating between the π electron density maxima. An analogous structure is expected for trans-1,3,5-hexatriene; however, the possibility that HF interacts with only two of the three π bonds cannot be excluded entirely. Allene and HF produce a complex in which the degeneracy of the CH_2 groups is split, indicating a complex to one localized π bond with HF. While the possibility of matrix site splitting cannot be absolutely ruled out, 3-methyl-1,2-butadiene apparently produces two different complexes with HF ligation at one of the two different π bonds.

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Interaction of Frontier Orbitals of Group 15 and Group 16 Methides with the Frontier Orbitals of Benzene[†]

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Abstract: Electron transmission spectroscopy has been employed to determine the energies of low-lying negative ion states of group 15 (M = N, P, and As) and group 16 (M = O and S) methides, $M(CH_3)_n$, as well as p-benzenes containing the related substituents, $M(CH_3)_{n-1}$. Spectral peaks are observed corresponding to electron capture into benzene π^* orbitals perturbed by interactions with the substituents and into substituent σ^* orbitals. Nitrogen substituents give a substantial splitting and destabilization of the benzene LUMO ($\pi_{4,5}^*$) while P and As substituents cause little splitting and a slight stabilization of this orbital. Virtual orbital eigenvalues from minimum basis set SCF-MO calculations on the monosubstitued benzenes show the same trends. Reduction in the p character of the substituent lone pair, reduction in the magnitude of interactions, and increased stabilization of the benzene LUMO's by mixing with the substituent σ^* orbitals along the N \rightarrow As series may all contribute to this trend. Similarly, O substituents give a substantial $\pi_4^*-\pi_5^*$ splitting while S substituents give primarily an inductive stabilization of the $\pi_{4,5}^*$ orbitals.

Main group hydrides, MH_n , and their alkyl derivatives, such as $M(CH_3)_n$, have an important role as ligands in coordination and organometallic chemistry. Transition-metal complexes with the group 15 and 16 hydrides and methides are especially wellknown. In these complexes, the metal-ligand bond is described as resulting from the donation of a lone pair of electrons from the ligand to form a coordinate covalent bond. A problem with this description of metal-ligand bonding is the buildup of formal negative charge on the metal. However, in many cases, including those considered here, the ligand is more electronegative than the metal and can thus exercise an electron-withdrawing or *inductive* effect which will permit a delocalization of electron density to stabilize the system. A second means of stabilizing a metal-ligand coordinate covalent bond involves the donation of charge density from the metal to metal-ligand orbitals of π symmetry arising from *resonance* interaction¹ of metal d orbitals and unfilled ligand orbitals of π symmetry with respect to the metal-ligand bond axis $(d\pi-p\pi$ back-donation).² In either case, the frontier molecular orbitals of the ligand are paramount in determining the donoracceptor properties of the ligand.

The highest occupied molecular orbitals of nearly all the main group hydrides and their methyl derivatives have been characterized by photoelectron spectroscopy (PES). Recently, we have undertaken analogous studies of properties associated with the lowest unoccupied orbitals of these compounds using the technique of electron transmission spectroscopy (ETS).³

The extent of participation of a formally unoccupied ligand orbital in a coordinate covalent bond depends upon both energetics

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[†]In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)

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and spatial distribution. In general, the lower the energy of an unfilled ligand orbital, the greater the possibility of its mixing with metal orbitals and hence the greater its effect upon the bond stability of the complex. The energy associated with a particular orbital is not observable. However, the trends in orbital energies through an homologous series, such as $M(CH_3)_3$ [M = N, P, and As], can be determined by using ETS since electron affinities measured in this experiment have been shown to track the energies of the corresponding unfilled orbital energies just as the ionization potentials measured in PES track the energies of occupied orbitals.⁴

In the following, we identify the measured electron affinities with various types of orbitals, e.g., benzene π^* or nitrogen lone pair orbitals. We realize that it is not correct to thus imply that the added electrons are entirely localized in this manner, however, we assume the reader is familiar with this terminology and is aware of its lack of precision.

The spatial extent and orientation of electron density associated with a ligand orbital determines the nature of both resonance and inductive interactions of the ligand with a metal to which it is bonded. To assess these interactions, we have found it useful to study substituted benzenes which contain a model of the ligand of interest:



Although the occupied σ -electron system is of course different for $M(CH_3)_n$ and $C_6H_5M(CH_3)_{n-1}$, we are interested in those unoccupied orbitals of the $M(CH_3)_n$ species which can interact in a π fashion with the benzene ring. We shall show that both orbitals of predominantly $M(CH_3)_{n-1}$ type, with energies like those for M(CH₃)_n, and benzene π orbitals perturbed by the M(CH₃)_{n-1} orbitals, are observed in the ETS system. The spectra of these compounds yield electron affinities associated with ligand orbitals as well as the well-known π^* orbitals of benzene. The perturbation of the energies measured for the substituted benzenes relative to the corresponding energies in the isolated ligands or unsubstituted benzene provides insight into the types of interaction which might occur in metal-ligand bonds. For example, in the group 14 compounds, $M(CH_3)_4$ [M = C, Si, Ge, and Sn], we observe⁵ an electron affinity associated with electron capture into a M-C σ^* orbital. In the M(CH₃)₃-substituted benzenes, the π^* -orbital energy perturbations reflect a pseudo- π -resonance interaction between the ligand σ^* and benzene π^* orbitals with no significant inductive effect. By contrast, in the group 17 substituted benzenes (the 1,4-dihalobenzenes), the interaction is mostly inductive.⁶ In the present work on permethylated group 15 (M = N, P, and As) and group 16 (M = O and S) atoms, we identify low-lying negative ion states arising from electron capture into a M-C σ^* orbital. In the corresponding substituted benzenes, we see evidence for inductive interactions as well as resonance interactions of benzene π^* orbitals with both unoccupied ligand σ^* orbitals and occupied ligand np lone pairs.

Experimental Section

Electron transmission spectroscopy is a technique for measuring the energy of a temporary negative ion formed by electron capture into an unoccupied orbital of a molecule. The experiment involves the measurement of the transparency of a gas to an electron beam as a function of energy. The transparency depends in an inverse fashion upon the electron-scattering cross section. Temporary negative ion formation occurs with large cross section only over a narrow energy range. Since the negative ion promptly decays by giving up the trapped electron, the



Figure 1. Derivative electron transmission spectra of (a) trimethylamine, trimethylphosphine and trimethylarsine, and (b) dimethyl ether and dimethyl sulfide.

formation and decay process appears as a sharp fluctuation in the electron-scattering cross section. The process, as well as the corresponding feature in the transmission vs. electron energy spectrum, is referred to as a "resonance".

The electron spectrometer^{3,6} consists of an electron source followed by an electron monochromator, a gas cell, and an electron collector. In practice, the first derivative of the transmitted current as a function of energy is recorded since the derivative is sensitive to the abrupt change in transmitted current associated with a resonance.⁷ The energy associated with a resonance is known as an "attachment energy" (AE) and, with respect to the derivative spectrum, is defined as the point vertically midway between the minimum and maximum which characterize the resonance. For the present purposes, an attachment energy may be identified with the negative of the corresponding electron affinity (EA).³

Results

The derivative electron transmission spectra of $M(CH_3)_3$ [M = N, P, and As] and $(CH_3)_2M$ [M = O and S] are presented in Figure 1. The spectra are dominated by a single broad feature which decreases in energy with increasing atomic number within each series. Our previous work indicates that this resonance is associated with electron capture into a σ^* orbital which is M-C antibonding in character.⁸ In the P and As compounds, there is a suggestion of a second, very broad resonance at higher energy. The spectra of the corresponding $M(CH_3)_{n-1}$ substituted benzenes are given in Figure 2 along with the spectrum of benzene. There are two features in the benzene spectrum, the first corresponding to electron capture into the degenerate pair of orbitals (π_4^*, π_5^*) of e_{2u} symmetry, and a second feature at higher energy corresponding to electron capture into $\pi_6^* (b_{2g})$.⁹ The first negative

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Figure 2. Derivative electron transmission spectra of (a) benzene; (b) p-bis(dimethylamino)benzene, and p-bis(dimethylarsino)benzene; and (c) p-dimethoxybenzene and p-dimethylthiobenzene.

ion resonant state is sufficiently long-lived for vibrational structure associated with the symmetric ring-breathing mode to appear. Substitution on benzene lifts the (π_4^*, π_5^*) degeneracy. This is most evident in the first member of each series where two lowenergy resonances appear, one at the energy of the benzene (π_4^*, π_5^*) resonance and another about 0.7 eV higher. In the higher molecular weight members of the group 15 series, the low-energy region consists of a broad feature extending upward from 0 eV with a shoulder at an energy slightly lower than that of the (π_4^*, π_5^*) resonance in benzene. In the group 16 analogue, p-dimethylthiobenzene, a low-energy resonance appears at about 0.4 eV. A resonance, intermediate in energy between the (π_4^*, π_5^*) and the π_6^* features, is quite apparent in the P, As, and S compounds. In the N and O compounds, there is a broad feature in the region of the resonance which corresponds to electron capture into π_6^* . Finally, it should be noted that in the P and As compounds, there is no feature readily identifiable with π_6^* . In these two compounds, there is only a very broad resonance near 6 eV.

The attachment energies measured by ETS along with vertical ionization potentials from photoelectron spectroscopy are assem-



Figure 3. Diagram showing correlation of electron attachment energies and ionization potentials of group 15 methides, $M(CH_3)_3$ [M = N, P, and As] and the corresponding $M(CH_3)_2$ para-disubstituted benzenes.



Figure 4. Diagram showing correlation of electron attachment energies and ionization potentials of group 16 methides, $(CH_3)_2M$ [M = O and S] and the corresponding MCH₃ para-disubstituted benzenes.

bled in Figures 3 and 4 as a correlation diagram. The PES data for all the compounds except *p*-bis(dimethylarsino)benzene are taken from the literature.¹⁰ The data on this latter compound are presented here for the first time. The correlation diagrams place the experimental data in a useful perspective. Lines of correlation and orbital designations indicate some obvious conclusions about state assignments. For example, the assignment of the resonance associated with electron capture into the substituent-based σ^* orbital in the substituted benzenes is obvious. Other conclusions as well as some interesting questions arise upn examination of the correlation diagrams.

In the benzene derivatives containing substituents based upon the first-row elements O and N, the π_4^*, π_5^* splitting is quite large with one component remaining at the energy of the (π_4^*, π_5^*) resonance of benzene and the other moving up in energy. This

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can only be the result of a resonance interaction between a benzene π^* orbital and the occupied O2 p or N2 p lone pair of the substituent. Of the π_4^*, π_5^* pair, one has a nodal plane through the 1- and 4-positions, whereas the other has nonzero amplitude at these positions. Thus, one is symmetric (S) and the other antisymmetric (A) with respect to the 1.4-(para)-positions. By symmetry only, the symmetric π^* orbital can interact with the substituent p orbital. The same resonance interaction is apparent for the occupied π_2, π_3 pair which are similarly S or A with respect to para substituents. The PES data are consistent with the ETS data in implying that the interaction between substituent lone pairs and benzene π orbitals is much more significant for substituents derived from first-row elements than for substituents from the second and third rows. This effect can be attributed partly to the increasing s character of the hybridization at the main group atom of the substituent upon going down the periodic table from N to Sb or O to Te^{10a} and partly to reduced overlap between the C 2p of benzene and the np valence orbitals of atoms from later rows of the periodic table.¹¹

There is also the possibility of another type of resonance interaction in the group 15-substituted benzenes. In these compounds, unlike the group 16-substituted benzenes, the substituent M-C bond does not lie in the plane of the benzene ring. Thus a pseudo- π interaction between the substituent σ^* orbital and the benzene π^* orbitals is possible. The data for the P- and Assubstituted benzenes suggest this type of interaction since the (π_4^*, π_5^*) pair is apparently split in two with one component at about 0.9 eV (near the energy of the resonance associated with the unperturbed orbital) and the other stabilized relative to it.

By contrast to the benzenes containing first-row substituents, those with $P(CH_3)_2$, $As(CH_3)_2$, or SCH_3 substituents show the effect of a stabilizing inductive effect. This is most evident in *p*-dimethylthiobenzene where the π^* resonances are about 0.6 eV lower than in the unsubstituted benzene and there is no evident (π_4^*, π_5^*) splitting. Furthermore, the σ^* resonance is much lower in energy for the substituted benzene as compared to dimethyl sulfide. A similar stabilizing effect of sulfur substituents was observed by Modelli et al. for thiophenol, thioanisole ((methylthio)benzene), and (tert-butylthio)benzene.¹² It is interesting to note that the σ^* energy in thiophenol is only 0.1 eV lower than in hydrogen sulfide, while the analagous resonance is 0.6 eV lower in dimethyl sulfide and 0.9 eV lower in p-dimethylthiobenzene than in dimethyl sulfide, thus suggesting that the electron acceptor strength of the methylthio group greatly exceeds that of the thio group.

To aid in interpretation of the ETS results, we have performed SCF-MO calculations by using the program GAMESS¹³ and STO-3G minimum basis sets.¹⁴ We are primarily interested in the reproduction of trends in the experimental AE's rather than in calculating accurate values. Analysis of ETS² and valence photoionization cross-section data¹⁵ indicates that trends in virtual orbital eigenvalues from STO-3G calculations are in reasonable qualitative agreement with more accurate calculations and with experimental data. It is doubtful that more flexible s and p basis set calculations would be better since their diffuse components would simply represent the background continuum.¹⁶ Since the same effects are observed for both mono- and disubstituted benzenes, we present calculations only for the monosubstituted compounds. To aid in distinguishing between pseudo- π interaction of the M-C σ^* with the benzene π system and M lone pair interaction with the benzene π system, STO-3G vitual orbital eigenvalues were calculated for two different geometries of the

 Table I. STO-3G Orbital Eigenvalues (electronvolts) for Benzene and Group 15 Monosubstituted Benzenes

	C ₆ H ₆	$C_6H_5NH_2,$ exptl ^{<i>a</i>,<i>b</i>}	$C_6H_5N-H_2,$ planar ^c	C ₆ H ₅ PH ₂ , exptl	C ₆ H ₅ PH ₂ , planar
${\pi_6}^*$	13.6	13.9	14.0	13.7, 14.8	13.6
σ*		15.9	15.5	9.8, 11.2	9.1
$\pi_{5}^{*}(A)$	7.3	7.4	7.4	7.3	7.4
$\pi_4^{*}(S)$	7.3	7.8	8.0	7.1	7.6
$\pi_3(S)$	-7.6	-6.2	-6.0	-6.9	-7.5
$\pi_2(\mathbf{A})$	-7.6	-7.6	-7.5	-7.6	-8.2
n		-10.4	-10.3	-9.0	-4.4

^a For 1,4-C₆H₄(NH₂)₂, the π_4^* and π_5^* orbital energies are 7.44 and 7.99 eV in the experimental geometry. ^b Exptl indicates experimental geometry (ref 18). ^c Planar indicates MH₂ group coplanar with benzene ring.

substituted benzenes. Initially, a hypothetical planar geometry was assumed so that only the lone pair interaction was possible. Then the calculation was carried out for the experimentally observed nonplanar geometry to permit the possibility of a pseudo- π interaction and to reduce the lone pair- π interaction to its proper value. The results are collected in Table I. Trends in $\pi_5^* - \pi_4^*$ and $\pi_3 - \pi_2$ energy differences are similar to the observed trends in IP's and AE's for the N- and P-disubstituted benzenes. In particular, the destabilization of the symmetric (S) π orbitals (π_3) and π_4^*) by interaction with the lone pair of the group 15 atoms is greater for the N compound than for the P. In fact, for the experimental geometry of C₆H₅PH₂, the $\pi_4^*(S)$ orbital is actually stabilized relative to benzene. It is not clear whether the $\pi_4^*(S)$ and $\pi_5^*(A)$ orbitals are significantly split in the experimental spectrum of $C_6H_4(PH_2)_2$. This stabilization is not found for the hypothetical planar $C_6H_5PH_2$ molecule where π_4^* is slightly destabilized (although less than in $C_6H_5NH_2$) due to interaction with the P 3p lone pair. For the experimental geometry of $C_6H_5PH_2$, with $\angle C-P-H$ near 90°, the empty σ^* orbital of the PH₂ group can interact with and stabilize $\pi_4^*(S)$, while for planar $C_6H_5PH_2$ the $\sigma^*-\pi_4^*$ interaction is zero by symmetry. For $C_6H_5NH_2$, by contrast, the results for the experimental and planar geometries are much more similar since the $\angle C-N-H = 116^\circ$, very near the planar value (120°), and the benzene π^* -NH₂ σ^* interaction is weak. For the experimental geometry of $C_6H_5PH_2$, we also find that π_6^* interacts strongly with σ^* , giving two orbitals (with eigenvalues of +13.7 and 14.8 eV) having significant π_6^* character. This mixing and splitting may explain the absence of a distinct π_6^* feature in the P compound.

It is noteworthy that calculations which do not include 3d orbitals on P reproduce the observed difference of attachment energies (and ionization potentials) between the N and P compounds. On the basis of PES and charge-transfer spectra of SCH₃-substituted aromatics, Bock et al.^{10d} have similarly concluded that S 3d orbitals are not important in the bonding to S in these compounds. In support of this conclusion, Cradock and Whiteford^{10b} point out that even in Te, the 5d lies well above the 6s in energy and hence it is unlikely that d orbitals will participate in bonding to group 16 atoms. By contrast, Modelli et al.¹² not recognizing the weak interaction of the benzene π system with the lone pair of a second-row substituent such as SCH₃, were lead to postulate a strong 3d involvement to account for the stability of the benzene π_4^*, π_5^* orbitals.

Conclusions

Attachment energies from ETS indicate that benzene-substitutent lone pair $p\pi$ - $p\pi$ interactions decrease sharply from firstto second-row substituents. Calculations indicate that this is primarily a result of decreased $p\pi$ - $p\pi$ overlap between elements from different rows of the periodic table, and, for the group 15 compounds, partly a result of changes in geometry and hybridization at the M(CH₃)₂ group. Substituents with heavier group

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15 and 16 elements exert a stabilizing inductive effect upon the benzene π^* orbitals. In the P and As compounds, the π_6^* and σ^* orbitals apparently mix to the extent that no distinct π_6^* resonance is observed.

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Electron Spin Resonance of the N-Methylpyrazine Radical: A New Spin-Labeled Ligand

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Abstract: The electron spin resonance spectrum of the N-methylpyrazine radical, obtained by dithionite reduction of Nmethylpyrazinium iodide, is reported. It is a long-lived, air-stable species which can be protonated in methanolic solution. It can also act as a ligand with metal ions and it is suggested that it may prove to be a useful probe for studying the details of metal-ligand bonding. To investigate this possibility the complex between the radical and the pentacyanoferrate(II) moiety has been prepared. The ESR spectrum of this molecule demonstrates that there has been a significant redistribution of spin density on complexation. Molecular orbital calculations show that both σ interaction with the complexing N atom and π interactions involving the metal d orbitals are required to interpret the ESR results. The use of spin-labeled ligands of this type allows a rather direct estimation of the molecular orbital parameters describing metal-ligand bonding. The structure of a second radical species produced during the reduction of the N-methylpyrazinium pentacyanoferrate(II) ion is discussed. It is concluded that it is probably the hydridotetracyano(N-methylpyrazine)ferrate(II) ion radical.

A variety of metal complexes containing free radical ligands have been reported.¹ Such compounds are of potential utility in elucidating the details of bonding in metal complexes by means of electron spin resonance (ESR) studies. The inverse experiment of bonding a suitable paramagnetic metal to a diamagnetic ligand and investigating the distribution of the small amount of spin delocalized to the ligand by measuring the NMR contact shifts has yielded valuable information on the electronic structures of the ligands involved.² Experiments of this type have, however, provided relatively little quantitative information on the details of metal-ligand bonding. The combination of a paramagnetic ligand with a diamagnetic metal ion is potentially more profitable. In this case the spin distribution in the ligand, measured by ESR, is perturbed by interaction with the metal ion and the details of this perturbation provide information regarding the symmetries and relative energies of the interacting metal orbitals. A free radical ligand which acts as a probe for metal-ligand interactions may be described as a "spin-labeled ligand" by analogy with the variety of spin labels developed as probes for biologically important systems.3.

A good spin-labeled ligand must satisfy a number of criteria. It should form stable complexes with a variety of metal ions in various ligand environments. These complexes should preferably be inert rather than labile, since rapid ligand exchange can complicate the ESR spectroscopy. The radical itself should be thermally stable at least over a period of several hours if direct synthesis of the paramagnetic complexes is envisaged. The ESR spectra should be of modest complexity. The more coupling parameters available for measurement the greater the potential information but ease of spectral analysis places a limit on the desirable complexity. The spin distribution in the ligand should

be sensitive to interaction with the metal ion but this interaction should not be so strong as to lead to complete, or almost complete, transfer of the odd electron to a metal orbital.

Of the various radical ligands reported in the literature none show all the desirable characteristics of a spin-labeled ligand. The earliest work involved o-semiquinone radicals.^{5,6} These do not complex well with the later group metals and tend to be chemically unstable. Semidiones have proved useful labels when attached to cyclopentadienyl ligands⁷ but not when attached to pyridine.⁸ Zelewsky and his collaborators9-11 have used diimine radicals but air sensitivity limits the variety of complexes. Most of the other ligands reported have used the nitroxide group as a spin label. Combination with pyridine was fairly successful⁸ but the complexes tend to be labile. Helbert et al.¹² have reported the ESR spectra of a series of metal complexes in which the nitroxide label is part of a five-membered heterocyclic ring. These are rather poor ligands and the hyperfine coupling constants (other than those involving the metal itself) do not change much from compound to compound. An attempt to obtain a wider range of more stable complexes by attaching the nitroxide label to an acetylacetonate ligand was not successful.¹³ With *tert*-butyl substituents steric restraints prevented complex formation and with trifluoromethylsubstituents the ESR spectra were not sensitive to metal complexation unless the nitroxide was directly coordinated. Basters¹⁴ has reported a very interesting series of aromatic pentacyanocobaltate(III) nitroxides but extension to other metal ions

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