Electronic Structure and Bonding in Four-Coordinate Organometallic Complexes of Aluminum. Valence Photoelectron Spectra of $(CH_3)_3Al$(pyridine) and $(CH_3)_2$(BHT)Al(pyridine) (BHT = 2,6-Di-*tert*-butyl-4-methylphenoxide)

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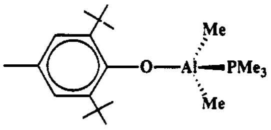
The He I valence photoelectron spectra of the Lewis acid–base adducts, Me_3Al(py) and Me_2(BHT)Al(py) (BHT = 2,6-di-*tert*-butyl-4-methylphenoxide, py = pyridine, Me = methyl) have been obtained in order to characterize the electronic structure and bonding in four-coordinate organometallic complexes of aluminum. In the photoelectron spectrum of the BHT ligand coordinated to aluminum in Me_2(BHT)Al(py), the phenyl π a_2 ionization of the phenoxide ligand (Phπ a_2) retains the vibrational structure observed in the free alcohol (BHT–H), but the individual vibrational components are lost in the ionization, which corresponds most closely with the Phπ b_1. The loss of vibrational fine structure associated with ionization from the Phπ b_1 orbital in the coordinated phenoxide is one evidence that the phenoxide is involved in a π interaction with the Me_2Al(py) portion of the molecule. The similarity of the splits of the Phπ a_2 and b_1 ionizations in $Me_2(BHT)Al(PMe_3)$ and Me_2(BHT)Al(py) shows that the extent of the π interaction of the BHT ligand with the $Me_2Al(PMe_3)$ and Me_2Al(py) portions of the molecules is about the same. The Phπ a_2 and b_1 ionizations of the BHT ligand experience a destabilizing shift on proceeding from Me_2(BHT)Al(py) to $Me_2(BHT)Al(PMe_3)$. This increase in negative charge potential at the metal center when the trialkylphosphine replaces the pyridine follows from the expected better σ-donor ability of the trialkylphosphine and the potentially better π-acceptor ability of the pyridine ligand. The pyridine ionizations show several interesting trends. First, the pyridine π ionizations in Me_3Al(py) are destabilized in comparison to the same ionizations of free pyridine, showing that the pyridine experiences a net negative charge potential when it is coordinated to Me_3Al. Since the aluminum is in its highest formal oxidation state, the net negative charge potential must involve the Al–Me σ bonds and/or π donation from the methyl C–H σ bonds. Second, on proceeding from Me_3Al(py) to Me_2(BHT)Al(py), the pyridine π ionizations show the expected stabilization from the more positive potential at the aluminum center that results from replacing a methyl group with the more electronegative alkoxide. However, the coordinated nitrogen lone-pair ionization shows no significant shift. This again traces to overlap interaction with the π-donor orbital of the alkoxide. These results suggest that π-symmetry interactions with ligands from the first row of the periodic table may be a prevalent aspect of the chemistry of four-coordinate aluminum complexes.

Introduction

We have recently reported the synthesis and structural characterization of four-coordinate Lewis acid–base adducts of aluminum containing the sterically hindered aryloxide derived from 2,6-di-*tert*-butyl-4-methoxyphenol (BHT–H, from the trivial name butylated hydroxytoluene).[1,2] These complexes typically display tetrahedral-like geometry and may conveniently be described as Lewis acid–base adducts in which the Lewis acid is a three-coordinate aluminum fragment, such as Me_2(BHT)Al (Me = methyl), and the base is a neutral 2-electron donor ligand, such as a phosphine or pyridine ligand. These adducts show a number of interesting structural features.



The Al–O–C angle [164.5 (4)°] in one of the compounds, $Me_2(BHT)Al(PMe_3)$, is much larger than that previously observed in main-group alkoxides. In addition, the Al–O distance [1.736 (5) Å] is short compared to the normal range 1.8–2.0 Å. The shortening of the Al–O bond length, along with the increase in the Al–O–C angle, suggests the presence of an additional bonding interaction, possibly of the π type between the oxygen and four-coordinate aluminum center. In an earlier study[3] we demonstrated the usefulness of photoelectron spectroscopic data[4–6] in providing an experimental probe of this interaction in four-coordinate organoaluminum complexes. The ionization information obtained from the photoelectron spectra of $Me_2(BHT)Al(PMe_3)$ and $Me_3Al(PMe_3)$ provided a wealth of chemical information on the relative strength of the Al–P bonds and the nature of the interaction between the BHT ligand and the aluminum center in these complexes.

In this study we extend the photoelectron investigations into the electronic structure and bonding in four-coordi-

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nate organoaluminum complexes by observing the electronic effects which result from replacing a PMe_3 ligand with a pyridine ligand. This paper describes the valence ionizations of $Me_3Al(py)$ and $Me_2(BHT)Al(py)$ in comparison to the ionizations of the analogous phosphine complexes reported earlier.[3] The valence photoelectron spectrum of the free alcohol BHT–H is included as an aid in the assignment of the ionizations. Particular emphasis is placed on the observation of vibrational fine structure in the valence ionization bands and the shifts in ionization energies between related compounds, in order to evaluate the σ and π contributions to the Al–O and Al–N bonds. A special feature of this study is the pyridine ring π ionizations, which provide an additional probe of the charge distribution in the complexes that was not available in the study of the analogous phosphine complexes. These shifts provide significant new insights into the electronic description of these complexes, particularly in terms of a substantial negative charge potential at the aluminum center in Me_3Al.

Experimental Section

$Me_3Al(py)$ and $Me_2(BHT)Al(py)$ were prepared by previously reported methods.[1,2] Photoelectron spectra were recorded on an instrument which features a 36 cm radius hemispherical analyzer (10-cm gap) and customized sample cells, excitation sources, detection and control electronics, and data collection methods that have been described previously.[7-10] He I data were collected at sample cell temperatures of 12 and 93 °C for $Me_3Al(py)$ and $Me_2(BHT)Al(py)$, respectively. All samples sublimed cleanly. The data are represented analytically with the best fit of asymmetric Gaussian peaks (program GFIT).[11,12] The asymmetric Gaussian peaks are defined by the peak position, the amplitude, the half-width indicated by the high binding energy side of the peak (W_h), and the half-width indicated by the low binding energy of the peak (W_l). The confidence limits of the peak positions and widths are generally ±0.02 eV. The individual parameters used to define peaks that overlap appreciably are not independent, even though the sum of the peaks accurately represents the overall band contour. These cases are discussed where necessary in the Results. The observed fine structure in a band is modeled with an evenly spaced progression of component peaks that are constrained to be equally spaced and have the same shapes. These constraints held to a minimum the number of independently varying parameters required to model the vibrational progression. The number of peaks and the spacing between them are optimized to model the band contour.[12]

Results

Valence Ionization Bands and Assignments. The He I valence photoelectron spectra of $Me_3Al(py)$ and $Me_2(BHT)Al(py)$ are shown in Figure 1. The assignment of the spectrum of $Me_2(BHT)Al(py)$ is aided by comparison to the spectra of the BHT–H molecule,[3] pyridine, and the analogous phosphine complexes. The spectrum of BHT–H is included in Figure 1 for comparison.

The spectra of BHT–H and the corresponding aluminum molecule show a broad band of overlapping ionizations from about 10.5 to 15.5 eV. This forest of ionizations is due to C–H, C–C σ, C–C π, and oxygen lone pairs (for BHT–H and $Me_2(BHT)Al(py)$) and also includes the C–N σ and Al–ligand bonding orbitals for the aluminum molecule. Individual assignments in this region will not be attempted.

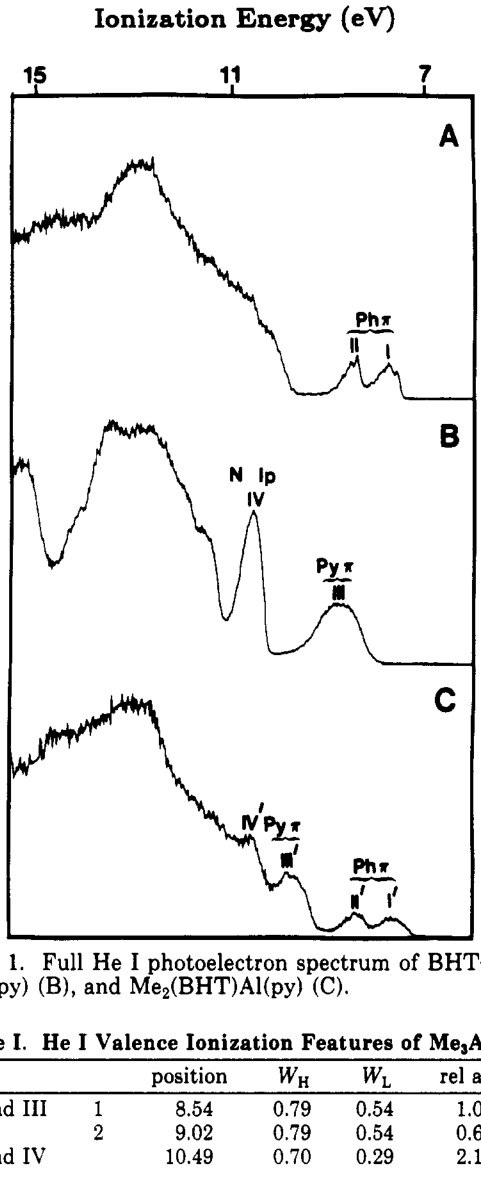

Figure 1. Full He I photoelectron spectrum of BHT–H (A), $Me_3Al(py)$ (B), and $Me_2(BHT)Al(py)$ (C).

Table I. He I Valence Ionization Features of $Me_3Al(py)$

		position	W_H	W_L	rel area
band III	1	8.54	0.79	0.54	1.00
	2	9.02	0.79	0.54	0.61
band IV		10.49	0.70	0.29	2.18

The first two ionization bands of BHT–H, labeled I and II for purposes of comparison later, have been discussed in detail in an earlier publication.[3] The first corresponds to the b_1 symmetry combination of the phenyl π orbitals, and the second corresponds to the a_2 symmetry combination. Both show vibrational fine structure in the ionization band due to C–C stretching in the ring with ionization.

The photoelectron spectrum of $Me_3Al(py)$ (see Figure 1) displays two broad features in the low valence ionization region. One is at about 8.5 eV (band III), and the other is at about 10.5 eV (band IV). The overall width of band III and the flattening on top indicate that the ionization band is composed of more than one ionization. Attempts to model the band with a single asymmetric Gaussian resulted in deviations that were well outside the signal-to-noise ratio of the spectrum. The band is accurately described in terms of two similarly shaped, overlapping peaks (1 and 2) with IP's at approximately 8.5 and 9.0 eV, respectively. The approximate half-widths and positions associated with peaks 1 and 2 are summarized in Table I. The appearance of the overall band is similar to that observed in the photoelectron spectrum of free pyridine,

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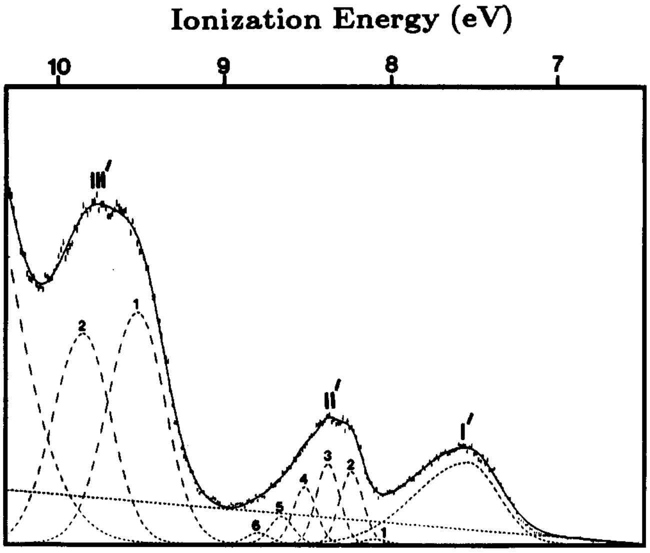

Figure 2. Close-up He I spectrum of $Me_2(BHT)Al(py)$.

where the two overlapping ionizations are assigned to the a_2 and b_1 pyridine π orbitals.[13,14] The energies of the a_2 and b_1 vertical ionizations of free pyridine are reported at 9.60 and 9.75 eV, respectively. Thus the positions of peaks 1 and 2 correspond to a destabilization of about 1 eV for the pyridine π orbitals upon coordination to aluminum in $Me_3Al(py)$. The increased splitting and broadening of these π ionizations of pyridine with coordination to the aluminum also indicate some additional interaction with the Me_3Al portion of the molecule which will be discussed later.

Band IV appears as a single, somewhat asymmetric Gaussian peak with an ionization potential of 10.49 eV. This ionization is accurately represented by a single asymmetric Gaussian peak. The position of this band is essentially identical with the position of the ionization of the predominantly nitrogen lone pair of free pyridine (10.51 eV[13,14]). We have generally found about a 1-eV stabilization from the ionization of the lone pair of a good σ-donor ligand to the ionization of the resulting dative σ bond between the ligand and the metal. For example, in the previous case of PMe_3 coordinated to Me_3Al, the stabilization was 1.3 eV. Although an absolute stabilization is not observed, a relative stabilization is reflected in the approximately 1-eV-increased separation between the ionizations of the pyridine π levels (a_2 and b_1) and the coordinated nitrogen lone pair. The significance of this observation will be discussed later. One feature of band IV that is not easily explained is the cross section relative to band III, which increases dramatically in comparison to the relative cross sections observed in the spectrum of free pyridine. This might indicate that another ionization is coincident with the ionization of the nitrogen donor orbital to the metal. However, examination of the spectra of pyridine and $Me_3Al(PMe_3)$ shows that any other ionization would have to be selectively destabilized by 1.5–2 eV. This is unlikely. The detailed contour of ionization band IV gives no hint of an additional ionization process at this energy. There is no statistical justification of the need for more than one ionization to accurately represent the band.[12] A change in cross section could be due to a change in the atomic composition of the lone pair, a tighter spatial distribution, or possible resonance phenomena. Whether it is overlapping ionizations or some other phenomena is not important to this particular study.

Table II. He I Valence Ionization Features of $Me_2(BHT)Al(py)$

		position	W_H	W_L	rel area
band I'		7.54	0.75	0.43	1.00
band II'	1	8.10	0.16	0.17	0.02
	2	8.24	0.16	0.17	0.25
	3	8.38	0.16	0.17	0.27
	4	8.52	0.16	0.17	0.19
	5	8.66	0.16	0.17	0.09
	6	8.80	0.16	0.17	0.04
band III'	1	9.52	0.42	0.39	1.94
	2	9.84	0.42	0.39	1.77

A close-up photoelectron spectrum of the low-valence region of $Me_2(BHT)Al(py)$ is shown in Figure 2. The first two ionizations correlate with ionizations from the b_1 and a_2 phenyl π orbitals of the phenoxide ligand and are labeled bands I' and II', respectively. Band I' lacks resolvable fine structure and is best represented by a single broad asymmetric Gaussian peak. The profile of this ionization is important to the interpretation of the electronic interactions in this molecule. Band II' gives weak evidence of a vibrational progression that is quite similar to that observed in the previous study of $Me_2(BHT)Al(PMe_3)$. The signal-to-noise ratio is not quite as good in this case. However, there is a clear double hump across the top of the peak. Similar to that of the previous study, band II' is approximated by six symmetric Gaussian peaks. The half-widths and positions are given in Table II. The spacing between Gaussian components in band II' indicates that the vibrational frequency responsible for these components falls in the range 950–1300 cm^{-1}. Vibrational fine structure has occasionally been observed in the b_1 and a_2 ionizations of monosubstituted benzene molecules.[15] In molecules with simple substitutions, two vibrational modes may be observed, one in the range 1540–1690 cm^{-1}, assigned to the symmetric C–C stretching mode, and one in the range 520-560 cm^{-1} depending on the heteroatom bound to the benzene ring. The possible presence of two progressions complicates the frequency analysis. In the a_2 ionization of $Me_2(BHT)Al(PMe_3)$, an intermediate frequency in the range 1350–1550 cm^{-1} is observed from this fitting analysis.[3] An even lower frequency is obtained in the case of $Me_2(BHT)Al(py)$, but little significance should be placed on this point because of the lower signal-to-noise ratio of the data and the possibility of overlapping progressions.

Band III' is best described in terms of two closely overlapping peaks (1 and 2) with IP's of about 9.5 and 9.8 eV, respectively. These correlate with ionizations from the a_2 and b_1 π orbitals of the pyridine ring. These ionizations are stabilized by about 1 eV from the corresponding ionizations in the spectrum of $Me_3Al(py)$, as one might expect when one replaces a methyl group with the more electronegative alkoxide ligand. As a result, these ionizations are in nearly the same position as the corresponding ionizations of free pyridine.

The spectrum of $Me_2(BHT)Al(py)$ gives evidence (shoulder marked IV' in Figure 1) of the ionization assigned to the nitrogen lone-pair donor to the Al center. The position of this peak is 10.5 (1) eV. In contrast to the pyridine π ionizations, which were clearly stabilized when a methyl group was replaced by the phenoxide, this ion-

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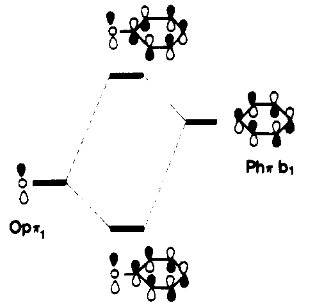
ization remains at the same energy within the certainty of the experiment. In the spectrum of the corresponding phosphine complex, the ionization of the phosphine lone pair coordinated to the metal was actually destabilized by about 0.5 eV when the alkoxide replaced the methyl group. In this case the very different shifts of the pyridine π and nitrogen lone-pair ionizations with alkoxide substitution provide additional evidence for the electron distribution and orbital overlap interactions in these systems.

Discussion

Four-coordinate organoaluminum complexes offer an interesting opportunity to carry out fundamental studies on the bonding characteristics of various ligands. The high local symmetry of these compounds combined with their low coordination number gives rise to few low-ionization energy bands, and the bands are sufficiently uncomplicated so that assignment of the ionizations is relatively straightforward. The shapes and structures of the individual ionizations of $Me_3Al(py)$ and $Me_2(BHT)Al(py)$, as well as the relative shifts, are particularly interesting. The discussion that follows shows that these ionizations provide new insight into the ligating characteristics of both the BHT and pyridine ligands.

Photoelectron Observations of π Donation from BHT to $Me_2Al(py)$. A previous study[3] established how changes in the vibrational fine structure of the phenyl π b_1 ionization between the free and coordinated phenoxide ligand provide evidence that the phenoxide ligand is acting as a π donor to the aluminum center in four-coordinate organometallic aluminum complexes. Only the pertinent points will be summarized here. The phenyl b_1 orbital is of the correct symmetry to interact with one of the oxygen lone-pair orbitals of the phenoxide ligand, as shown by



This lone pair also acts as a π donor in the complex, interacting with both the Al–P σ and σ^* orbitals in $Me_2(BHT)Al(PMe_3)$.[3] The phenyl b_1 orbital therefore gains some Al–P σ character. In the free ligand, ionization from this orbital gives rise to fine structure in the photoelectron spectrum owing to vibrational modes associated with the C–C stretching modes of the phenyl ring. In the complex, however, this ionization gives rise to a broad featureless asymmetric band owing to vibrational modes associated with the $Me_2Al(PMe_3)$ moiety as well as the C–C streching modes of the phenyl ring. As evidence that this is not just a consequence of σ coordination to the metal, the a_2 ionization, which has negligible orbital overlap interaction with the oxygen atom and the metal, retains some observable structure. Hence, the phenoxide ligand is acting as a π donor when the fine structure associated with the b_1 ionization in the free ligand is replaced in the spectrum of the coordinated phenoxide by a broad asymmetric Gaussian peak. In the phosphine complex, the donation is primarily into the Al–P σ^* orbital. The solid-state crystal structure of the phosphine adduct shows that the phenoxide is rotated so that the b_1 orbital has a nearly pure overlap interaction with the Al–P σ and σ^* orbitals.[1]

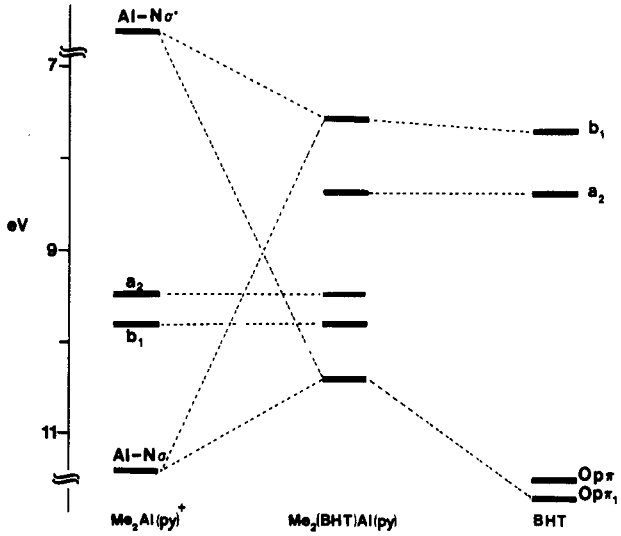


Figure 3. Ionization correlation diagram showing the interactions between the frontier orbitals of BHT and $[Me_2Al(py)]^+$.

In the spectrum of $Me_2(BHT)Al(py)$, the fine structure of the b_1 ionization in the free phenoxide ligand has indeed been replaced by a broad featureless asymmetric Gaussian peak. This indicates that the BHT ligand has a π interaction with the $Me_2Al(py)$ portion of the $Me_2(BHT)Al(py)$ molecule. In this case the interaction of the phenoxide b_1 orbital may not be cleanly with just the Al–N orbitals. The solid-state crystal structure shows that the phenoxide is rotated to include interaction with the Al–C σ^* orbitals.[2] It is not clear if this rotation is a result of molecular packing in the solid state. In any event, is should be remembered that any subsequent discussion of π donation from the phenoxide ligand may include donation into the Al–C σ^* orbitals as well as donation into the Al–N σ^* orbital.

The difference in energy between the Phπ a_2 and b_1 ionizations of the BHT ligand provides an experimental measure of the relative extent to which the BHT ligand is acting as a π donor in $Me_2(BHT)Al(PMe_3)$ and $Me_2(BHT)Al(py)$. This difference is 0.88 (3) and 0.84 (3) eV for $Me_2(BHT)Al(PMe_3)$ and $Me_2(BHT)Al(py)$, respectively. The similarity of the two values indicates that the extent of the π interaction of the BHT ligand with the $Me_2Al(PMe_3)$ and $Me_2Al(py)$ portions of the $Me_2(BHT)Al(PMe_3)$ and $Me_2(BHT)Al(py)$ molecules is therefore about the same. The similarity of the short Al–O bond lengths in $Me_2(BHT)Al(PMe_3)$ and $Me_2(BHT)Al(py)$ (1.736 (5) and 1.740 (4) Å, respectively) supports this view. It has been argued that the more acute Al–O–C angle in the pyridine complex (156.1°) compared to that in the phosphine adduct (164.5°) suggests a reduced π interaction from the phenoxide in the pyridine complex.[2] The observed trend of the smaller separation between the a_2 and b_1 ionizations of the pyridine complex supports this view, although the decrease in separation is on the edge of statistical significance.

Ionization Correlation Diagram. Additional evidence of the π interaction is provided by the shifts of the valence ionizations between the complexes. The interactions between the frontier orbitals of the BHT ligand and $Me_2Al(py)$ indicated by the photoelectron data are clarified by the ionization correlation diagram in Figure 3. The central column in Figure 3 shows the ionization energies of $Me_2(BHT)Al(py)$. The relative positions of the frontier orbitals of the BHT and $Me_2Al(py)$ fragments in the molecule are estimated from the ionization energies of the related molecules, BHT–H and $Me_3Al(py)$. This is accomplished for BHT by shifting the ionization energies of BHT–H so that the phenyl π a_2 ionization lines up with that in the aluminum complex. The a_2 ionization shifts primarily as a consequence of the change in charge potential at the ligand, because the phenyl π a_2 ionization has a node at the ring carbon atom bound to the oxygen and therefore has no significant overlap with the rest of the complex. Similarly, the ionizations of $Me_3Al(py)$ are shifted so that the predominantly pyridine a_2 ionization aligns with the corresponding ionization of the $Me_2(BHT)Al(py)$ complex. Again, the pyridine π a_2 ionization senses primarily the change in charge potential in the vicinity of the pyridine ligand.

The frontier orbitals of BHT on the right of Figure 3 are labeled according to their primary character, but it should be remembered that the predominantly phenyl π b_1 orbital includes mixing with an oxygen $p\pi$ orbital. The orbitals are the correct symmetry to form filled bonding and antibonding π combinations between the oxygen atom and the ring. The bonding combination is predominantly oxygen lone pair in character and is labeled $Op\pi_1$ in Figure 3, while the antibonding combination is largely the $Ph\pi$ b_1. The orbital labeled $Op\pi$ in Figure 3 is in the plane of the phenyl ring.

The most pertinent interactions for understanding the ionization shifts involve the predominantly Al–N σ and σ^* orbitals and therefore the virtual Al–N σ^* orbital is included in the diagram. There is no experimental evidence to guide exact placement of the Al–N σ^* energy, so it is simply indicated at some energy above the occupied levels. For clarity the Al–Me σ and σ^* orbitals are not included in the diagram, although they are also involved in overlap with the phenoxide $Ph\pi$ b_1 orbital depending on the rotation of the phenoxide, as mentioned earlier. The Al–Me σ ionizations would be off the bottom of the figure, and presumably the Al–Me σ^* would likewise be off the top of the figure.

The $Op\pi_1$ and $Ph\pi$ b_1 orbitals have the correct symmetry to interact with the filled Al–N σ bonding orbital (localized on nitrogen) and the unfilled Al–N σ^* orbital (which is largely $Alp\pi$ in character). The interactions of the Al–N σ bond with the filled orbitals on the phenoxide have a slightly destabilizing influence on the complex, since these are filled–filled interactions. As mentioned above, one consequence of these energy interactions is the observation of the additional destabilization of the phenyl b_1 ionization relative to the a_2. The separation between the vertical b_1 and a_2 ionizations of the free BHT–H molecule is 0.65 eV, and the separation of the corresponding ionizations of the coordinated phenoxide is 0.84 eV. Also as introduced above, the additional vibrational modes in the predominantly $Ph\pi$ b_1 ionization of the $Me_2(BHT)Al(py)$ molecule, which obscure the simple C–C ring stretching progression, follow from this mixing. The interaction of the filled $Op\pi_1$ and $Ph\pi$ b_1 orbitals with the unfilled Al–N σ^* results in additional stabilization of the complex and the transfer of electron density from the oxygen atom to the aluminum center. Another indication of the π interaction of the phenoxide ligand is revealed in the ionization associated with the Al–N bond when the phenoxide replaces a methyl group. The σ charge effect from changing methyl to phenoxide stabilizes the ionization, and the π interaction of the phenoxide destabilizes it. In the phosphine case, the π interaction dominated. In this case, the two effects cancel, and there is little net shift of the ionization. This π-overlap destabilization of the Al–N bond ionization is most clearly seen in the ionization correlation diagram, where the effects of charge potentials on the ionizations are largely accounted for by aligning the energies of the a_2 ionizations. The strengthening of the BHT bonding to the complex through π donation is therefore at the expense of the strength of the aluminum–pyridine bond.

Shifts in Electron Distribution with Ligand Substitution. The effects of the charge potentials on the ionizations also provide some interesting information and deserve further comment. First, the shifts in the ionizations that occur with substitution of phosphine for pyridine from $Me_2(BHT)Al(py)$ to $Me_2(BHT)Al(PMe_3)$ follow expectations. The $Ph\pi$ ionizations in $Me_2(BHT)Al(py)$ are stabilized relative to the same ionizations in $Me_2(BHT)Al(PMe_3)$. This is consistent with the poorer σ-donor and weak π-acid characteristics of pyridine relative to trimethylphosphine, which will tend to reduce the negative charge potential at the aluminum center in the pyridine complex.

The ionization trends of the pyridine π and nitrogen lone-pair ionizations with coordination to form $Me_3Al(py)$ and $Me_2(BHT)Al(py)$ are more surprising. In simple terms, the pyridine ligand acts as a 2-electron donor to the coordinatively unsaturated Lewis acids Me_3Al and $Me_2(BHT)Al$. The ionization corresponding to the pyridine σ donor should show stabilization with coordination as a result of overlap bonding with the metal as well as from transfer of electron density from the ligand to the metal center. The pyridine π ionizations should also sense the transfer of electron density to the metal and show stabilization. Even in the absence of bonding and electron transfer, the act of bringing the pyridine next to the aluminum, which is in its highest formal positive oxidation state, should stabilize the ionizations of the pyridine molecule. The stabilization of the pyridine-based ionizations with coordination is not observed. The ionization energy of the σ-donating nitrogen lone pair of the pyridine ligand in the two compounds remains largely unchanged from that of the free ligand. The pyridine ring π-ionization energies of $Me_2(BHT)Al(py)$ are about the same as those of free pyridine, while the corresponding pyridine π ionizations of $Me_3Al(py)$ are actually destabilized by a substantial 1 eV.

These trends in ionization energies require reassessment of the basic concepts of the Al–pyridine bond and/or consideration of other electronic factors in the interaction of pyridine with a four-coordinate aluminum center. Changes in electron relaxation energies will influence the magnitudes of these shifts, but will not influence the qualitative evaluation of these shifts in comparison to the bonding of other donor ligands.[4] The trends are evaluated in terms of orbital overlap effects and one-center and two-center charge potential effects in the molecules.

Consider first the trends in ionization energies of the Al–N σ bonds in these complexes. One factor that has been emphasized to this point regarding the similarity of the Al–N σ ionization in $Me_2(BHT)Al(py)$ and $Me_3Al(py)$ is the overlap interaction of the Al–N σ bond with the π-donor orbital of BHT. The lack of stabilization of the nitrogen lone pair on coordination of the pyridine ligand to Me_3Al suggests the presence of a similar destabilizing electronic influence in this complex from filled–filled orbital overlap. One possible overlap interaction analogous to that discussed for BHT is a "π" symmetry combination of the C–H bonds of the methyl groups. Because the energies of these C–H bond ionizations are greater than the $Op\pi$ b_1 ionization of BHT, this interaction may be less important. Another possible factor is the "a" symmetry combination of the Al–Me bonds, which is of the correct symmetry to interact with the Al–N σ bond. This filled–filled interaction may contribute to destabilize the nitrogen lone-pair ionization of the coordinated pyridine ligand, countering the σ donation that stabilizes it, resulting in only small shifts of the ionization potentials of the nitrogen lone pairs in the complexes compared to the free ligand.

The pyridine ring π ionizations show that other considerations are also involved. Most significant is the destabilization of these ionizations when pyridine coordinates to Me_3Al. One simple explanation would be that the pyridine ring is not donating as much charge through the σ bond as it is accepting in π back-bonding. Because the Al center is in its highest oxidation state, the only direct orbitals of Al available for π back-donation to the pyridine ring are the appropriate symmetry combinations of the Al–Me σ bonds and the C–H σ bonds. The change in splitting of the pyridine π a_2 and b_1 ionizations in the different coordination environments may suggest some overlap interactions. However, pyridine is considered a weak π acid, and it seems that this π back-bonding is not likely to exceed the σ donation sufficiently to account for the total 1 eV destabilization in $Me_3Al(py)$.

This leaves two-center charge effects as the source of the destabilization of the pyridine π ionizations with coordination to Me_3Al. The Al center in Me_3Al apparently presents a more negative charge potential than indicated by the positive formal oxidation state. It may be that the electron density in the Al–Me σ bonds retains appreciable Al character. It is also possible that the π-symmetry combinations of the methyl C–H σ bonds act as π donors to help alleviate the electron deficiency at the metal center. Thus the shifts of the Al–N σ ionizations and the pyridine π ionizations both suggest the presence of π donation from the methyl C–H bonds and/or involvement of the Al–Me σ bonds. Additional studies are planned to further investigate these interactions.

Conclusions

A variety of electronic features associated with four-coordinate organoaluminum complexes have been revealed by the photoelectron ionizations. The loss of observable vibrational fine structure in the Phπ b_1 ionization between the free and coordinated BHT ligand, the split of this b_1 ionization from the Phπ a_2 ionization, and the similarity of the Al–N ionization when BHT replaces Me on the aluminum center provide evidence of phenoxide π donation. The extent of π interaction of the BHT ligand with $Me_2Al(PMe_3)$ and $Me_2Al(py)$ is very similar, as shown by the similarity of the splits of the Phπ ionizations in $Me_2(BHT)Al(PMe_3)$ and $Me_2(BHT)Al(py)$. The destabilization of the pyridine π ionizations with coordination to Me_3Al indicates appreciable π donation from the methyl groups to aluminum and/or involvement of the Al–Me σ bonds. These studies indicate that π interactions of ligands that contain first-row atoms coordinated to the metal may be a generally important feature of the four-coordinate chemistry of aluminum.

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