of the H–C ($H_{5,6}$) resonance and hence is assigned to $H_{2,7}$; the remaining area 2 H–B signal must then be due to the $H_{3,9}$ protons. Furthermore, the H–C and $H_{3,9}$ multiplets are clearly coupled to each other, as shown by homonuclear ^{1}H-decoupling experiments, in accord with their nearest-neighbor relationship in the molecule.

In the 1,7,5,6 isomer (Figure 9) the area 1 H–B resonance is again readily assigned to the unique (H_4) proton. The low-field H–C resonance is attributed to H_6 due to its proximity to the cobalt atoms, an assignment supported by the proton–proton coupling patterns in the molecule. From homonuclear decoupling it is shown that H_6 is split into a triplet by the low-field area 2 BH, which is consequently assigned to $H_{3,9}$ (the nearest pair of equivalent H–B protons); in turn, the $H_{3,9}$ resonance is split into a doublet by H_6. As expected, the $H_{3,9}$ protons are also coupled to the other H–C proton, H_5. The H_5 resonance is split into a triplet by the remaining pair of H–B protons $H_{2,8}$; the latter nuclei are also coupled to another proton that could not be identified but may be H_4.

Conclusions

The existence of proton–proton coupling in carboranes and metallocarboranes is not in itself surprising, but the extent to which it was found to occur in this study was not anticipated. These results lead us to suggest the following generalizations:

1. All three-bond couplings (H–C–B–H, H–B–B–H, H–C–C–H) can be expected to occur, with four-bond coupling rarely observed except for protons in trans locations.

2. The magnitudes of these interactions are strongly and characteristically influenced by the nature of the attached atoms (i.e., boron vs. carbon) and by the coordination number of the occupied vertex. The ranges of observed J values are 10–20 Hz for H–C–C–H, 1–10 Hz for H–C–B–H, and 0–4 Hz for H–B–B–H. In pentagonal-bipyramidal cages, equatorial protons are more strongly coupled to each other than to apical protons; apical–equatorial interactions are usually small ($J < 1$ Hz) and are frequently not directly observed.

3. H–B and H–C resonances are inherently sharp, with natural line widths of ~1–2 Hz (as determined from T_1 measurements[17]). The broad H–B and H–C peaks observed in undecoupled spectra are, as suggested by Onak,[8] due primarily to unresolved coupling which can be removed with ^{11}B and ^{1}H decoupling. From this work as well as from extensive T_1 measurements in this laboratory,[17] it is clear that although ^{11}B quadrupolar relaxation contributes broadness to ^{11}B NMR spectral lines, *it is not a significant factor in ^{1}H NMR line broadening.* This fact is important to recognize, since it means that with appropriate decoupling the ^{1}H spectra of many boron compounds can be analyzed in detail in much the same manner as those of organic compounds, with ^{1}H NMR thereby assuming the role of a major structural tool.

Acknowledgment. This work was supported by the Office of Naval Research. The NMR equipment and associated computer were purchased through a departmental instrument grant from the National Science Foundation.

Registry No. 2,4-$C_2B_5H_7$, 20693-69-0; 1,2,3-$(C_5H_5)CoC_2B_4H_6$, 50860-25-8; 1,2,4-$(C_5H_5)CoC_2B_4H_6$, 41660-23-5; 3-$C_{10}H_7$-1,2,4-$(C_5H_5)CoC_2B_4H_5$, 41660-25-7; 1,7,2,3-$(C_5H_5)_2Co_2C_2B_3H_5$, 39388-45-9; 1,7,2,4-$(C_5H_5)_2Co_2C_2B_3H_5$, 39388-44-8; 2-CH_3-1,7,-2,4-$(C_5H_5)_2Co_2C_2B_3H_4$, 56679-06-2; 1,2,4,5-$(C_5H_5)_2Co_2C_2B_3H_5$, 56669-15-9; 1,2,3,5-$(C_5H_5)_2Co_2C_2B_3H_5$, 53421-57-1; 1,8,5,6-$(C_5H_5)_2Co_2C_2B_5H_7$, 41636-82-2; 1,7,5,6-$(C_5H_5)_2Co_2C_2B_5H_7$, 53452-50-9; ^{11}B, 14798-13-1.

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Contribution from the Department of Chemistry,
University of Delaware, Newark, Delaware 19711

Ultraviolet Spectroscopy Study of Intramolecular Charge Transfer in $(C_6H_5)_3M$ Compounds (M = B, Ga, In) and Effects of Ring Substitution in Triarylgallium Systems

J. H. SMITH and T. B. BRILL*

Received May 5, 1976 AIC60323D

The near-ultraviolet spectra of $(C_6H_5)_3B$, $(C_6H_5)_3Ga$, and $(C_6H_5)_3In$ are recorded in methylcyclohexane to locate the charge-transfer bands and to determine their periodic trend. The charge-transfer excited states fall in the energy series of B ≪ Ga < In. The charge-transfer energy trend compares favorably to the ^{13}C chemical shift of the carbon atom para to the central atom in the pseudoisoelectronic series $(C_6H_5)_3M$, M = C^+, B, Ga, In. Ring substitution by CH_3, CH_3CH_2, $(CH_3)_3C$, CH_3O, F, Cl, and Br in the para position of triphenylgallium causes E_{CT} to vary according to the ionization potential of the monosubstituted benzene. Meta and ortho substitution causes E_{CT} to behave as though the gallium atom, perhaps through steric effects, has been removed from any active participation in the electronic changes occurring in the phenyl ring.

Introduction

The group 3A elements react in a variety of ways in an effort to obtain a coordinately saturated valence shell. The dramatic behavior of boron and aluminum are, of course, well known.[1] For the heavier elements, gallium and indium, less unusual bonding patterns occur but the desire of these elements to continue to accept electron density after forming three covalent bonds is still considerable. For example, in the solid state, $(C_6H_5)_3Ga$[2] and $(C_6H_5)_3In$[2] associate at the axial position with the phenyl rings of neighboring molecules. The interaction strength is far weaker than that found for dimeric $[(C_6H_5)_3Al]_2$. Similar intermolecular interactions routinely occur between group 3A compounds and Lewis bases to give four-, five-, and six-coordinate complexes.[3]

When the opportunity does not exist for intermolecular interactions, it is of interest to know the extent to which compounds such as $(C_6H_5)_3Ga$ and $(C_6H_5)_3In$ will undergo intramolecular electron density shifts in an attempt to increase the valence-shell electron density of the metal. A ring-to-metal electron density flow can be thought of as an intramolecular donor–acceptor or charge-transfer interaction. Recently we examined this possible effect in the ground state by measuring the ^{13}C NMR and ^{69}Ga, ^{71}Ga, and ^{115}In NQR parameters in a series of substituted triarylgallium and -indium compounds.[4] On the basis of a number of criteria and comparisons it was determined that ring-to-metal electron delocalization (pp_π or pd_π) does not occur in the ground state. That is, the Ga–C and In–C bonds should be thought of as single σ bonds. A complete picture, however, requires an examination of the tendency for charge transfer to occur in the higher energy states as well. In this paper we have investigated this problem using near-ultraviolet spectroscopy.

The ultraviolet spectra of triarylboron compounds have been discussed in some detail before,[5–7] but uv data for the heavier group 3A element organometallics are virtually nonexistent.[8] This is in spite of the fact that an effectively empty orbital may exist in the valence shell of the metal and thus the results directly relate to the bonding tendencies of that shell. Regrettably it was not feasible to include $(C_6H_5)_3Al$ and $(C_6H_5)_3Tl$ in this study. Triphenylaluminum is dimeric and triphenylthallium is too insoluble. However, the periodic trend in the charge-transfer bands of triphenylboron, -gallium, and -indium was determined. The results obtained help to explain their observed ^{13}C chemical shifts. As a probe of the nature of steric and electronic contributions to ring–metal charge transfer, the excited states were modulated by ortho, meta, and para substitution of the ring. Steric effects appear to be important in ortho and meta substitution while direct electronic effects are observable in para substitution. The ^{69}Ga and ^{71}Ga NQR frequencies are valuable in establishing what factors are operative. The analysis presented here is necessarily qualitative because even in the more readily parameterized triarylboron compounds, only modest success has been achieved using a Pariser–Parr–Pople SCMO treatment for explaining the uv spectra of triarylboron compounds.[6]

Experimental Section

Compounds. The triarylgallium compounds used in this work were prepared by the transmetalation reaction of the diarylmercurial with gallium metal according to procedures discussed elsewhere by Miller.[9] At no time were any of the compounds exposed to air. All manipulations were carried out in Schlenk tubes and a nitrogen-filled Vacuum Atmospheres drybox. The triarylgallium compounds were multiply recrystallized from carefully purified solvents to obtain the highest purity samples possible. The melting points were determined to be equal to or slightly greater than those reported earlier.[9] The melting points were found to be as follows: $(C_6H_5)_3Ga$, 170 °C; $(p\text{-}CH_3C_6H_4)_3Ga$, 177 °C; $(p\text{-}(CH_3)_3CC_6H_4)_3Ga$, 266 °C; $(p\text{-}CH_3OC_6H_4)_3Ga$, 162 °C; $(p\text{-}CH_3CH_2C_6H_4)_3Ga$, 94 °C; $(p\text{-}FC_6H_4)_3Ga$, 202 °C; $(p\text{-}ClC_6H_4)_3Ga$, 217 °C; $(p\text{-}BrC_6H_4)_3Ga$, 200 °C dec; $(m\text{-}CH_3C_6H_4)_3Ga$, 117 °C; $(m\text{-}BrC_6H_4)_3Ga$, 150 °C; $(m\text{-}ClC_6H_4)_3Ga$, 139 °C; $(m\text{-}FC_6H_4)_3Ga$, 161 °C; $(o\text{-}ClC_6H_4)_3Ga$, 133 °C. Trimesitylgallium, $(2,4,6\text{-}(CH_3)_3C_6H_2)_3Ga$, has not been reported before. It was prepared by the above method using benzene as a solvent. The yield was very low (8%). The compound was identified by mass spectrometry and found to contain no mercurial impurity. The melting point after several recrystallizations from petroleum ether was 186–187 °C. Triphenylboron (Aldrich) was partially oxidized when received but four careful recrystallizations from benzene raised the melting point to 149 °C (lit.[5] mp 150 °C). Triphenylindium was prepared in the same way as the gallium compounds and was recrystallized several times from benzene to give a melting point of 212 °C.

The extremely great reactivity of these compounds is vividly illustrated by the fact that if the uv cells are merely opened while recording a spectrum, the charge-transfer bands rapidly disappear. The air sensitivity of the ortho-substituted compounds is less than that of the others, probably because the reactive site of the gallium atom is more protected by the substituents.

Methylcyclohexane (Aldrich) was distilled twice over P_2O_5 and only the fraction boiling at 100.5–101.5 °C was taken. This fraction was then distilled from $LiAlH_4$ while dry N_2 gas bubbled through the solvent and flushed the system. All distillations and solvent manipulations were carried out in such a way that the solvent was never exposed to air. Very tedious precautions are necessary in order to obtain reproducible spectra for these compounds.

Uv Spectra. Spectra were recorded on a Cary 14 recording spectrophotometer in sealed 1-mm quartz cells. The samples were weighed on a Cahn electrobalance in the drybox and dilutions were performed in volumetric flasks. The concentration range of samples in this work was $(1.9\text{–}6.0) \times 10^{-4}$ M with most concentrations being in the $(4.0\text{–}6.0) \times 10^{-4}$ M range. Using triphenylgallium in the concentration range of $(2.0\text{–}9.6) \times 10^{-4}$ M we examined the Beer's law dependence of the charge-transfer spectra. The intensities as measured by ϵ_{max} varied somewhat but the band positions did not. The lack of a linear relation between concentration and molar absorptivity causes some uncertainty in the comparative values of ϵ_{max}. This concentration range is a trade-off between the higher concentrations where the spectra become too intense and Beer's law is expected to be even further violated and the lower range where uncertainty in the weight of the samples and the extreme reactivity of the compounds can cause errors in the real concentration values. The ϵ_{max} error resulting from the lack of strict Beer's law dependence is ±6% of the given values but may be slightly larger for bands that are shoulders. These errors are not important to arguments made in this paper in that cases are not made based on small intensity differences. There is no ambiguity in identifying the most intense band in any of the spectra. The error in the absorption wavelength is ±1 nm.

Results and Discussion

Identification of Charge-Transfer Bands. Cryoscopic measurements show triphenylgallium to be monomeric in benzene solution.[10] Additional details of the structures of $(C_6H_5)_3Ga$ and $(C_6H_5)_3In$ in solution are not known on the time scale of electronic transitions. On the NMR time scale they are found to contain equivalent phenyl rings.[4] The phenyl rings must be "pitched" relative to one another because of steric hindrance. In the solid state triphenylgallium and -indium contain phenyl rings that are tipped about 30–40° out of the plane formed by the C_3M framework.[2] If the molecule could be entirely planar with respect to the phenyl rings, the charge-transfer transitions involving phenyl rings and the p_π orbital on the central atom would be degenerate or not allowed. Steric restrictions preclude this geometry and the required twisting of the phenyl rings removes the charge-transfer state degeneracy. Hence a splitting into more than one charge-transfer band must occur. Concomitant with the twisting of the phenyl rings is reduction of metal–ring π-orbital overlap and thus an increase in the energy of the electronic states generated by this overlap.

Triphenylboron indeed shows several bands in the energy range below that expected for transitions localized on the phenyl rings.[5–7] It is believed that these are charge-transfer bands arising from $^1A_1 \rightarrow {}^1A_2, {}^1E, {}^1A_1$ transitions made up from orbitals on the three phenyl rings and the boron atom p_π orbital in D_3 symmetry.[5,6] However, a PPP–SCMO calculation predicts 36 excited states in a 2.5-eV range which makes a definite assignment very difficult.[6] Fitting the computed model of the electronic structure to the observed

Table I. Ultraviolet Spectra of Group 3A Triaryls (in nm)[a,b]

Compd	λ_1	λ_2	λ_3
$(C_6H_5)_3B$[c]	287 (39)	276 (35)	238 (19)
$(C_6H_5)_3Ga$	275 (3)	267 (5.5)	243 (21)
$(C_6H_5)_3In$	270 (3)	259 (5.5)	236 (18)

[a] Parenthetical numbers are ϵ_{max} values $\times 10^{-3}$. [b] Solvent was methylcyclohexane. [c] Reference 5.

Table II. Ultraviolet Spectra of Triarylgallium Compounds, $(XC_6H_4)_3Ga$[a,b]

Substituent, X	λ_1	λ_2	λ_3
H	275 (3)	267 (5.5)	243 (21)
p-CH_3	258 (22)[c]	250 (22)[c]	
p-CH_3CH_2	274 (18)	258 (19)	252 (18)
p-$(CH_3)_3C$	264 (17)	255 (17)	
p-CH_3O	282 (30)	274 (26)	242 (9)
p-F	254 (14)	244 (13)	
p-Cl	263 (19.5)	250 (17)	240 (15)
p-Br	276 (22)	239 (19)	
m-CH_3	284 (4)	274 (6)	246 (21)
m-F	274 (6.5)	265 (6)	242 (18)
m-Cl	278 (3.5)		242 (16)
m-Br	278 (3)		243 (15)
o-Cl	270 (2)		236 (10)
2,4,6-$(CH_3)_3$	277 (7)		232 (27.5)

[a] Parenthetical numbers are ϵ_{max} values $\times 10^{-3}$. [b] Solvent was methylcyclohexane in all cases. [c] Peak is very broad so the center of the peak at 254 nm was used.

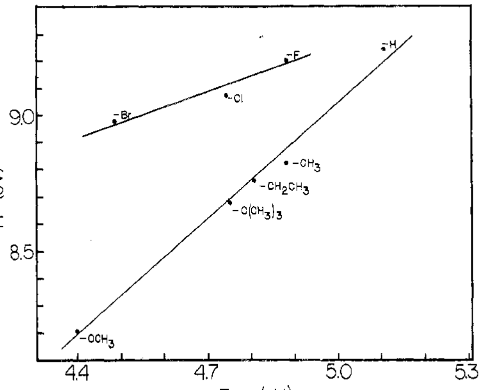

Figure 1. Relationship of the most intense charge-transfer band in $(p\text{-}XC_6H_4)_3Ga$ to the ionization potential of C_6H_5X.

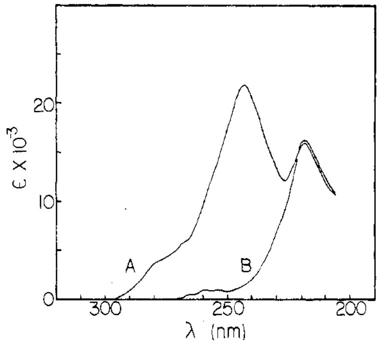

Figure 2. Uv spectrum of $(C_6H_5)_3Ga$ in noncomplexing methylcyclohexane before (A) and after (B) exposure to the air.

results requires an extensive amount of configuration interaction in the excited state and even then is only partially successful.[6] Any chance of a decisive quantitative picture of triarylgallium and -indium compounds seems to be beyond reach for some time to come. Instead we wish to demonstrate that the bands observed in $(C_6H_5)_3Ga$ and $(C_6H_5)_3In$ are of the same origin as those seen in $(C_6H_5)_3B$ and to extract the systematic features of the electronic spectrum that are of chemical interest.

Table I contains the ultraviolet wavelength absorption bands found in $(C_6H_5)_3M$ compounds (M = B, Ga, In) and Table II summarizes the uv spectra of para-, meta-, and ortho-substituted triphenylgallium compounds as measured in methylcyclohexane solvent. Painstaking effort is necessary to obtain reproducible and reliable spectra in all of these systems. This has been noted before for triarylboron compounds[11] and the same definitely holds true for the gallium and indium homologues. Two or more bands of moderate to great intensity are found in the charge-transfer energy region for all triarylgallium compounds and for triphenylindium. From the evidence that follows these bands can be confidently assigned as being of charge-transfer origin.

In a very simple sense the energy of the charge-transfer bands, E_{CT}, can be related to the ionization potential of the phenyl rings, E_{IP}, the electron affinity of the central atom, E_{EA}, and a Coulombic interaction term between the electron and the positive hole it has left behind, e^2/r, by eq 1.[12] This

$$E_{CT} = E_{IP} - E_{EA} - e^2/r \qquad (1)$$

equation suggests two things of importance to this work—that it should be possible to calculate an approximate value for the energy of the charge-transfer band and, providing a series of closely related triarylgallium compounds is used, the charge-transfer band energy should correlate linearly with the ionization potential of the phenyl rings. Both of the expectations seem to be followed well considering the crudeness of the model used in eq 1. In the first case Ramsey[5] has calculated that the charge-transfer band in $(C_6H_5)_3B$ should be at 280 nm using E_{IP} = 9.2 eV for benzene and 0.0 eV for E_{EA} of boron. Employing these same values and computing *r* from the M–C bond lengths in $(C_6H_5)_3Ga$[2] and $(C_6H_5)_3In$[2] and adding 1.4 Å to *r* to reach the center of the ring, we find that the main charge-transfer band in $(C_6H_5)_3Ga$ should lie at 250 nm and in $(C_6H_5)_3In$ at 240 nm. Comparison of these values with those in Table I shows good agreement. In the second case, Figure 1 is a plot of E_{CT} in the para-substituted triarylgallium compounds vs. the E_{IP} for the corresponding phenyl compounds.[13] The correlation requires two lines, one for halophenyl groups (coefficient of correlation R = 0.965) and one for organophenyl groups (R = 0.994), but is good. Moreover, the slopes are those anticipated, i.e., the better the electron-donating power of the substituent the lower the ionization potential of the ring and hence the lower the ring-to-metal charge-transfer energy. In making this plot the most intense charge-transfer band was used. It seems reasonable that the most intense band is the one that is mainly important in the electron delocalization in the excited state.

A third criterion used to verify the charge-transfer character of the uv bands comes from their disappearance upon decomposition of the sample. Figure 2 shows the triphenylgallium spectrum recorded in methylcyclohexane before and after exposure of the sample to the air. After exposure the lowest energy transitions disappear leaving only the weak $^1A \rightarrow {}^1L_b$ transition (250–260 nm) localized on the phenyl rings. The intense absorptions in the 210–220-nm range are phenyl ring localized transitions ($^1A \rightarrow {}^1L_a$) and are observed in all compounds. They are not eliminated by decomposition. The complete extinction of the intense bands in 230–290-nm range upon decomposition is immediately observed in all compounds except $[2,4,6\text{-}(CH_3)_3C_6H_2]_3Ga$ where the bands remain for some time. The ortho substitution in the latter compound appears to block sterically the axial position on gallium from attack by oxygen. These results further suggest that the 230–290-nm absorptions involve the gallium atom acceptor orbital and thus are charge-transfer bands.

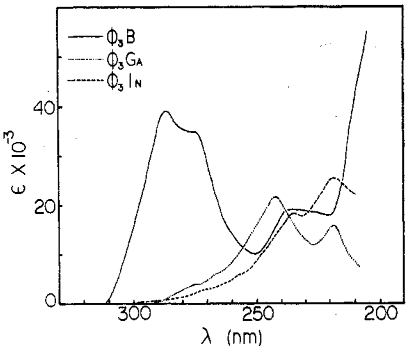

Figure 3. Uv spectra of $(C_6H_5)_3B$, $(C_6H_5)_3Ga$, and $(C_6H_5)_3In$.

Table III. Chemical Shift of Para Carbon and Charge-Transfer Energy in $(C_6H_5)_3M$ Compounds of D_3 Symmetry

M	E_{CT}, eV	δ, ppm	M	E_{CT}, eV	δ, ppm
C^+	2.87[a]	143.6[b]	Ga	5.10	129.8[c]
B	4.32	131.3[c]	In	5.26	129.2[c]

[a] W. B. Smith and P. S. Rao, *J. Org. Chem.*, **26**, 254 (1961). [b] G. J. Ray, R. J. Kurland, and A. J. Colter, *Tetrahedron Lett.*, 27, 735 (1971). [c] Reference 4.

Comparison of $(C_6H_5)_3M$, M = B, Ga, In. The elucidation of the periodic trends in group 3A elements was an important stimulus for this study. Figure 3 gives a comparison of the charge-transfer bands in these three compounds. Moving down in the group, the energy of the charge-transfer band increases and the intensity of the band as measured by ϵ_{max} decreases. This trend follows directly from the increasing mismatch in energy of the 2p orbitals on carbon and the *n*p orbitals on the central atom as *n* increases.

These low-energy electronic excitations should offer a rationale for trends in other molecular parameters. Specifically we have noted earlier[4] the trend in the ^{13}C chemical shift of the carbon atom para to the central atom in the compounds $(C_6H_5)_3M$, M = C^+, B, Ga, In. This position on the ring is sensitive to the various chemical shift contributions but is not subject to the neighboring atom effect of M. In hydrocarbon fragments not in close proximity to a metal, the ^{13}C NMR chemical shifts are thought to originate mainly from the temperature-independent paramagnetic effect of mixing the ground and lowest lying excited states by the magnetic field.[14] From Pople,[15] we have

$$\sigma_P(AA) = -\frac{e^2\hbar^2}{2m^2c^2(\Delta E)}\left\langle 1/r^3 \right\rangle_{2p}\left[Q_{AA} + \sum_{A\neq B} Q_{AB}\right] \qquad (2)$$

The bond order matrix and the radial wave function of the para carbon are relatively constant in these compounds and hence an inverse relationship of σ_P and ΔE should be observed if σ_P dominates in the chemical shift. The data in Table III reveal this to be the case and also show that within the group 3A elements a reasonably linear correlation exists ($R = 0.998$). A fourth point for $(C_6H_5)_3C^+$ does not give a quantitative correlation but is in the correct direction. The discrepancy is no doubt in part due to the fact that data for the carbo cation were gathered in H_2SO_4 solution and may be subject to different solvent effects. It does appear, however, that the ^{13}C chemical shift values are understandable in terms of the energy gap between the ground and excited states in these compounds.

Substituent Effects on $(C_6H_5)_3Ga$. Information on the characteristics of ppπ charge transfer in organometallic compounds can be obtained from examining the effect of substituents placed on the phenyl rings. The low solubility of the triarylindium compounds in methylcyclohexane precludes them from very extensive study, but the triarylgallium compounds are suitable. Table II and Figure 1 show the effects of para substitution on $(C_6H_5)_3Ga$. Several features are noteworthy. Both the organo group substituents and the halogen group substituents produce the expected trend of increasing charge-transfer energy with increasing ring ionization potential. However, the slopes are somewhat different as is the energy position of the two sets of substituents. The presence of the gallium atom on the halophenyl ring lowers the charge-transfer energy below what is expected based on the set of organo-based substituents. It is plausible that a slight enhancement of a resonance type interaction between the ring and the halogen atom is caused by the presence of the gallium atom, although the methoxy group would be expected to participate in this way also. The fact that the halogen atoms are electrostatically somewhat different from the organo substituents may lead to polarization of the phenyl ring and a slight alteration of the excited-state description. The details of what occurs here are admittedly not clear.

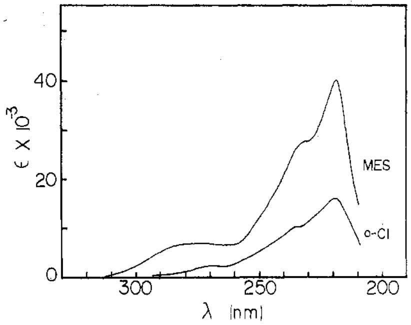

Figure 4. Similarity of ortho-substituted triarylgallium compounds in the ultraviolet region.

The meta-substituted compounds are interesting because they lead to practically no change in the charge-transfer band intensity or energy compared to triphenylgallium. That the charge-transfer bands occur at higher energy than those of the corresponding para compounds shows that a distinct difference in the electronic structure results from meta vs. para substitution. The halogen atoms cannot π donate to the metal at the meta position and if some small amount of π donation is involved as may be suggested in the para-substituted compounds, the lack of it should certainly produce an increase in the charge-transfer energy. However, with the meta-methyl compound included, the conclusion must be reached that as far as the excited state is concerned the meta position is comparatively uninvolved in direct electronic effects in triarylgallium compounds. Meta substitution could cause some change in the pitch of the rings compared to para substitution for steric reasons. This may have occurred to the point that the π-electronic states of the molecule are unaffected by variations in the electronic character of meta substituents.

The ortho-substituted compounds are only 2 in number, $(o\text{-}ClC_6H_4)_3Ga$ and $[2,4,6\text{-}(CH_3)_3C_6H_2]_3Ga$. The main charge-transfer bands have the highest energy of all of the compounds studied in this work. The mesityl compounds's sensitivity toward decomposition is low probably because of steric crowding of the gallium atom. By the same token, the phenyl rings should be pitched more than in the other compounds and the Ga–C bond lengths may be longer (as are the As–C bond lengths in tri-*p*-xylylarsine compared to tri-*p*-tolylarsine).[16] Both of these effects will lead to increased charge-transfer energy compared to the energy of the other compounds. The gross line shapes of these two compounds are in fact strikingly similar as shown in Figure 4 even though the substituents are electronically rather different. Since the ionization potential of mesitylene is different from that of chlorobenzene, the charge-transfer spectra could be expected to be similar only if the gallium atom were forced to play a

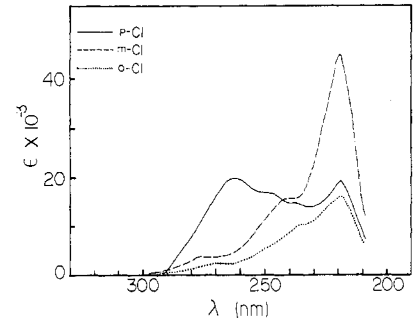

Figure 5. Effect on E_{CT} of chlorine atom substitution in the para, meta, and ortho positions of triphenylgallium.

relatively minor and constant role in the π excited state.

Comparison of the charge-transfer spectra of ortho, meta, and para chloro-substituted compounds in Figure 5 shows the effect caused by moving a common substituent to different positions on the ring. The main charge-transfer band increases in energy as the atom moves closer to the metal. Steric effects alone can account for this trend by causing a progressive increase in the pitch of the rings and hence increasing the gap between the ground and excited states. However attention should also be paid to possible changes in the Ga–C σ bond. It has been noted that ^{69}Ga and ^{71}Ga nuclear quadrupole rersonance frequencies in these same compounds decrease in this series (para, 49.14 MHz; meta, 47.11 MHz; ortho, 46.70 MHz).[4] In order to account for this change in the metal electric field gradient, a decrease in the Ga–C σ-bond covalency is indicated.[4] It is to be noted that decreased π bonding should increase the resonance frequency which is opposite the observed trend. An increase in steric hindrance is most likely the source of the suggested Ga–C bond length increase, but both the bond length increase and a ring pitch increase would lead to the increased charge-transfer energy.

In sum, these data suggest that the spatial requirements of ortho and meta substitution cause structural changes in these compounds that effectively insulate the gallium atom from an active role in the π excited states. Electronic effects involving participation of the gallium atom do seem important in understanding para substituent effects, however.

Acknowledgment. We are grateful to Mr. E. I. Band for his efforts in trying to obtain spectra of these compounds before their extraordinary air sensitivity was fully appreciated. We also thank Dr. S. B. Miller[9] for originally preparing several of the compounds used in this study.

Registry No. $(C_6H_5)_3B$, 960-71-4; $(C_6H_5)_3Ga$, 1088-02-4; $(C_6H_5)_3In$, 3958-47-2; (p-$CH_3C_6H_4)_3Ga$, 18797-37-0; (p-$CH_3CH_2C_6H_4)_3Ga$, 58448-01-4; (p-$(CH_3)_3CC_6H_4)_3Ga$, 58447-98-6; (p-$CH_3OC_6H_4)_3Ga$, 58448-03-6; (p-$FC_6H_4)_3Ga$, 58448-00-3; (p-$ClC_6H_4)_3Ga$, 58447-99-7; (p-$BrC_6H_4)_3Ga$, 18797-36-9; (m-$CH_3C_6H_4)_3Ga$, 18797-38-1; (m-$FC_6H_4)_3Ga$, 58448-13-8; (m-$ClC_6H_4)_3Ga$, 58448-02-5; (m-$BrC_6H_4)_3Ga$, 58448-14-9; (o-$ClC_6H_4)_3Ga$, 58448-04-7; (2,4,6-$(CH_3)_3C_6H_4)_3Ga$, 60607-12-7.

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Contribution from the Department of Chemistry,
The University of Alberta, Edmonton, Alberta T6G 2G2, Canada

Aminolysis of Trifluoromethylchlorophosphoranes. Preparation and Characterization of the Trifluoromethyltris(dimethylamino)phosphonium Ion, $CF_3P[N(CH_3)_2]_3^+$

D. D. POULIN, A. J. TOMLINSON, and R. G. CAVELL*

Received March 8, 1976 AIC60179W

The new trifluoromethyltris(dimethylamino)phosphonium ion has been prepared from CF_3PCl_4 or $(CF_3)_2PCl_3$ and dimethylamine. The latter case involves substitution of CF_3 by dimethylamine yielding CF_3H. $(CF_3)_2PCl_2[N(CH_3)_2]$ also reacts with dimethylamine yielding CF_3H and the $CF_3P[N(CH_3)_2]_3^+$ ion. The ion is stable in aqueous solution but hydrolyzes in alkaline solution to $OP[N(CH_3)_2]_3$ and CF_3H. Spectroscopic properties of the phosphonium ion are reported.

Introduction

Dimethylamine reacts with $(CF_3)_3PCl_2$ to form $(CF_3)_3PCl[N(CH_3)_2]$ and $(CF_3)_3P[N(CH_3)_2]_2$ according to the amount of amine used.[1] $(CF_3)_2PCl_3$ however reacts in a more complicated fashion giving, in addition to the analogous $(CF_3)_2PCl_2[N(CH_3)_2]$, the phosphonium salt $CF_3P[N(CH_3)_2]_3^+Cl^-$ by elimination of CF_3H.

Experimental Section

$(CF_3)_2PCl_3$ and CF_3PCl_4 were prepared as described[2-4] by adding chlorine to the chlorophosphines $(CF_3)_2PCl$ and CF_3PCl_2,[5] respectively, which were prepared by reaction of mercury(II) chloride[6] with iodophosphines prepared from CF_3I and red phosphorus.[5] Commercial dimethylamine was vacuum distilled before use. All other chemicals were reagent grade products and were used without purification.

Infrared spectra of solids were obtained on Nujol and Fluorolube mulls using Perkin-Elmer 457 or 421 instruments. Volatile compounds were contained in a 9-cm cell with KBr windows. NMR spectra were obtained with Varian A56/60 or HA 100 or Bruker HFX-90 instruments. Where necessary samples were prepared in a dry atmosphere using carefully dried solvents. Capillaries of 5% TMS in CCl_3F were added to provide external reference for ^{1}H or ^{19}F chemical shift measurements. ^{1}H spectra were measured at 60 or 100 MHz and ^{19}F at 56.4 or 94.1 MHz except in the case of the Bruker in-