

structure of this complex is probably similar to that of $(\text{py})_2\text{CuCl}_2$ since both have identical J values and similar far-infrared spectra. The spectrum of the 2,6-dimethylpyrazine complex has bands at 308 and 228 cm^{-1} , which are analogous to the bands observed¹⁸ for $(\text{Py})_2\text{CuCl}_2$ at 287 and 229 cm^{-1} . These bands have been assigned¹⁸ to Cu-Cl stretching frequencies and in both cases are indicative of a large amount of bridging character. On the basis of the above spectral and magnetic data, the structure shown in Figure 8 is proposed for this complex wherein each $(2,6\text{-DiMe(pz)})_2\text{CuCl}_2$ unit is linked together solely by chloride bridges.

(2,6-DiMe(pz))CuBr₂.—The magnetic properties of the complex are consistent with an Ising model from which $g = 1.89$ and $J = -33 \text{ cm}^{-1}$ may be calculated. A plot of experimental susceptibility *vs.* temperature is given in Figure 5 along with the best-fit curve. The fit which is obtained when the dimer equation is applied yields a $g = 1.61$, a value too small to be realistic. The halide-sensitive band in the far-infrared spectrum appears at 262 cm^{-1} , a position associated with a weakly bridging Cu-Br bond. The calculated J of -33 cm^{-1} is close to the $J = -29 \text{ cm}^{-1}$ for the complex $(\text{py})_2\text{CuBr}_2$,¹⁵ which is known¹⁷ to possess a bromide-bridged chain structure. The principal pathway for exchange is also probably a bromide bridge in $(2,6\text{-DiMe(pz)})_2\text{CuBr}_2$; however, the stoichiometry of this complex will not allow the same structure. A probable configuration would be one in which the nitrogen donor atom in the four position is weakly bonded to a neighboring copper atom forming links between the halide bridged chains (see Figure 9).

Conclusions

The results of this study support past proposals¹⁻⁴ that these complexes are generally polymeric with considerable interaction between chains. The magnetic interactions in all of these complexes are antiferromag-

(18) M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, **21**, 105 (1965).

netic in nature and the magnitude of the exchange energy, J , generally reflects the nature of the chain linkages. These chain linkages are highly dependent on the type and number of substituents on the pyrazine ring. Pyrazines such as 2,5-dimethylpyrazine, symmetrically substituted with respect to the nitrogen donor atoms, tend to form copper(II) halide complexes in which pyrazine forms the bridging unit in the primary chain. Steric hindrance from the methyl groups reduces the amount of halide bridging in the secondary chain. Similar behavior is observed with the stoichiometrically similar copper(II) halide complexes of 2,3-dimethylquinoxaline. Both chloride¹⁹ and bromide²⁰ complexes exhibit exchange coupling which appears to be too large to be transmitted through weakly bridging terminal Cu-X bonds. The nature of the polymeric linkages in complexes of 2-methylpyrazine is not clear, but probably both halides and pyrazines participate in the bridging with halide bridges transmitting much of the spin-spin interaction. The complexes of asymmetrically substituted 2,6-dimethylpyrazine probably consist primarily of halide bridged chains. The magnitudes of their J values are consistent with those of similar complexes for which structural data are available. Final conclusions regarding the relationship between type of chain linkage and exchange energy await precise structural data.

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(19) G. W. Inman, Jr., J. A. Barnes, and W. E. Hatfield, *Inorg. Chem.*, **11**, 764 (1972).

(20) M. J. M. Campbell, R. Grzeskowiak, and F. B. Taylor, *J. Chem. Soc. A*, 19 (1970).

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Bonding Studies from Charge-Transfer Absorption and Magnetic Circular Dichroism Spectra. I. D_{4h} Complexes of Iridium(IV)

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We have measured the absorption and MCD spectra of a series of complexes IrCl_4L_2 where $\text{L} = \text{PR}_3$, AsR_3 , SEt_2 , and pyridine and have identified transitions arising from charge-transfer transitions from chlorine and L to the metal. We find AsR_3 and $\text{PR}_3 \rightarrow \text{metal}$ to be at exceptionally low energy, $\text{SEt}_2 \rightarrow \text{metal}$ somewhat higher, and $\text{py} \rightarrow \text{metal}$ at still higher energy. These transition energies give a good approximation to the energies of the bonding orbitals of L with respect to the metal and these energies are used to draw correlations between the energy of the ligand σ orbital and the stability of the metal-ligand bond.

Introduction

There is considerable interest in determining the sequence of the filled bonding orbitals in metal complexes since this gives insight into the nature of the bonding processes and the distribution of the electrons

in bonds. This information may be obtained in two ways, first from photoelectron spectroscopy and second from a study of electronic transitions. Using this latter method researchers in inorganic chemistry have mainly concentrated on the intra-d-shell transitions

since the theory of these is well developed. However, the electron-transfer bands intrinsically contain more chemical information since in principle we can obtain the energies of the filled bonding molecular orbitals relative to the metal orbitals provided we can identify the transitions.

This latter problem can be a major obstacle in interpreting charge-transfer spectra in even the most symmetrical molecules since a large number of states generally arise if there are two or more open shells on excitation and the identification of these states can provide a major restriction on the method. However, there is a particularly simple situation in which only one state arises from each electron transfer and as a result some of the absorption bands can be unambiguously identified. This is the low-spin d^5 case found in $\text{Fe}(\text{CN})_6^{3-}$ and IrCl_6^{2-} for example and in these cases we are able to find the energies and symmetries of the filled bonding orbitals by a study of the absorption and MCD spectra.^{1,2} In the t_{2g}^5 case, the lowest energy charge-transfer transitions consist of successive electron jumps from the filled molecular orbitals into the vacancy in the t_{2g} shell. The simplicity of this case arises by virtue of the fact that there is only one open shell since electron transfer closes the metal shell as it opens the bonding orbital. Since there is only one hole at any time, only one state is formed and it has the symmetry of the open shell. Furthermore the differences between the electronic repulsion energies of terms from different excited configurations are minimized and hence, to a good approximation, we can infer the energies of the bonding MO's from the energies of the electronic transitions.

This has been done for the cases of IrCl_6^{2-} ,^{2,3} and IrBr_6^{2-} .⁴ Absorption and MCD studies have established that the orders of the bonding orbitals are $\pi t_{1u} > \pi t_{2u} > \sigma t_{1u}$ and the energies of the electron transfers from these orbitals to t_{2g} have been obtained. This identification has made it possible to assign the photoelectron bands of WF_6 ⁵ with more certainty and the energies of all the filled orbitals are available from this technique.

A logical extension to the study of the hexahalides is to substitute one or more of the halogens with another ligand L and see how this modifies the spectrum. This should represent a small perturbation on the basic hexahalide spectrum, and provided we can make reliable identifications, we can obtain the energy of the new filled MO which is introduced by the ligand L. This gives us an idea of the energies of the bonds of ligand L compared to the halogen. If a series of ligands is studied, some trends might be expected to emerge which can be related to chemical properties and to the stability of the M-L bond. In a study of this kind it is clearly important that the choice of compounds should satisfy two requirements: (i) that the symmetry of the molecule should be such that σ - π mixing of the ligand orbitals is minimized and (ii) that the

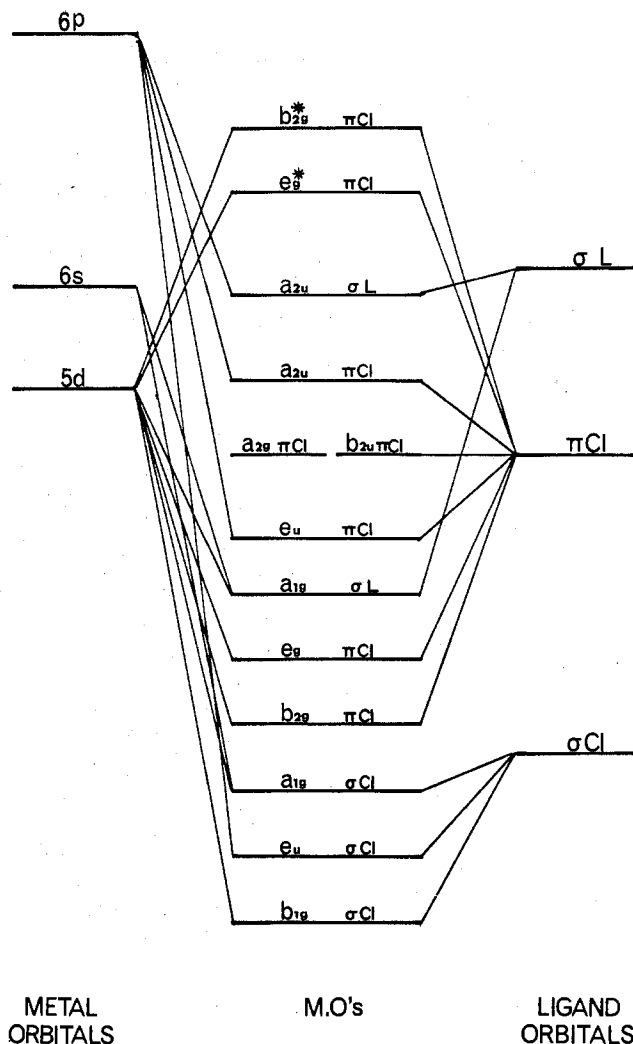


Figure 1.—Molecular orbital diagram for $\text{IrCl}_4(\text{PR}_3)_2$ or $\text{IrCl}_4(\text{AsR}_3)_2$

orbitals of ligand(s) should not mix strongly with those of the halogen. In this way we should see electron transfer from the σ orbitals of the M-L σ bond separated from those of the σ and π orbitals of the M-halogen bond.

In this work we have examined the series of compounds $\text{trans-IrCl}_4\text{L}_2$ where $\text{L} = \text{PR}_3, \text{AsR}_3, \text{SEt}_2,$ and pyridine. These have the low-spin d^5 configuration and trans geometry, giving D_{4h} symmetry, ensures that, to first order, the L σ orbitals are not appreciably mixed with Cl σ and π orbitals. We have measured the absorption and MCD spectra of these complexes in solution at room temperature and also in films at low temperatures. The results are discussed in terms of the energetics of bonding of the ligands to the metal.

Experimental Section

The samples used in this work were very kindly donated by Drs. G. J. Leigh and D. M. P. Mingos of the Unit of Nitrogen Fixation. Absorption spectra were measured on a Cary 14, and MCD spectra were run on a JASCO ORD/UV5 fitted with an Oxford Instruments superconducting magnet and also on a CD spectrometer built partly at the NPL and modified in these laboratories. With this latter instrument, which has considerably higher sensitivity than the JASCO, we have used the superconducting magnet and a 3000-G permanent magnet to obtain spectra. Spectra were run at room temperature in dichloromethane solution. For the low-temperature measure-

(1) P. N. Schatz, A. J. McCaffery, W. Suetaka, G. N. Henning, A. B. Ritchie, and P. J. Stephens, *J. Chem. Phys.*, **45**, 722 (1966).

(2) G. N. Henning, A. J. McCaffery, P. N. Schatz, and P. J. Stephens, *ibid.*, **48**, 5656 (1968).

(3) A. J. McCaffery, P. N. Schatz, and T. E. Lester, *ibid.*, **50**, 379 (1969).

(4) S. B. Piepho, T. E. Lester, A. J. McCaffery, J. R. Dickinson, and P. N. Schatz, *Mol. Phys.*, **19**, 781 (1970).

(5) D. R. Lloyd quoted in C. K. Jorgensen, *Progr. Inorg. Chem.*, **12**, 101 (1970).

TABLE I
CALCULATED FARADAY PARAMETERS^a

Excited state	C	D	C/D	C/D for IrCl ₄ (AsPr ₃) ₂ ^b	B
² A _{2u} E _u '	$\frac{-\beta A^2}{2}[2A^2(k+1) - C^2]$	A ²	$\frac{-\beta}{2}[2A^2(k+1) - C^2] =$ $-\frac{\beta}{4}g_x$	-0.20	$\frac{-\beta(k+2)}{9\Delta E}$
² B _{2u} E _u ''	$\frac{+\beta A^2}{2}[2A^2(k+1) - C^2]$	A ²	$\frac{+\beta}{2}[2A^2(k+1) - C^2] =$ $+\frac{\beta}{4}g_x$	+0.20	$\frac{+\beta(k+2)}{9\Delta E}$
² E _u E _u ''	$\frac{+\beta C^2}{4}[2A^2(k+1) - C^2] -$ $\frac{\beta AC[2ACk + C^2]}{4}$	$\frac{1}{2}[2A^2 + C^2]$	$\frac{-\beta AC[2ACk + C^2]}{A^2 + C^2} =$ $\frac{-\beta ACg_y}{2(A^2 + C^2)}$	-0.56	$\frac{-\beta(k+2)}{9\Delta E}$
² E _u E _u '	$\frac{-\beta C^2}{4}[2A^2(k+1) - C^2]$	C ² /2			$\frac{+\beta(k+2)}{9\Delta E}$

^a C, D, and B are expressed in terms of the reduced matrix elements $|\langle {}^2E_g || m || {}^2A_{2u} \rangle|^2$, $|\langle {}^2E_g || m || {}^2B_{2u} \rangle|^2$, $|\langle {}^2E_{2g} || m || {}^2E_u \rangle|^2$, and $|\langle {}^2E_g || m || {}^2E_u \rangle|^2$ where *m* is the electric dipole moment operator. We have calculated B terms arising from the two E_g' states resulting from spin-orbit coupling in the ground state. ΔE is the separation of these two states. ^b A = 0.485, C = 0.727, k = 0.97.

TABLE II
EXPERIMENTAL C, D, AND C/D VALUES

Transition	IrCl ₄ (PMe ₂ Ph) ₂			IrCl ₄ (PBt ₂ Ph) ₂			IrCl ₄ (PPr ₃) ₂		
	C	D	C/D	C	D	C/D	C	D	C/D
E _g '' → ² A _{2u} σ _L									
E _g '' → ² A _{2u} π _{Cl}	-0.28	1.6	-0.17	-0.42	2.2	-0.19	-0.21	1.3	-0.16
Band at 28 kK	+0.16	1.3	+0.12	+0.23	1.9	+0.12	+0.26	0.87	+0.30
Band at 35 kK	+0.94	15.5	+0.06	+1.34	25.1	+0.05			
Transition	IrCl ₄ (AsPr ₃) ₂			IrCl ₄ (PMe ₂ Ph) ₂ (20°K)			IrCl ₄ (Et ₂ S) ₂ (10°K)		
	C	D	C/D	C	D	C/D	C	D	C/D
E _g '' → ² A _{2u} σ _L									
E _g '' → ² A _{2u} π _{Cl}	-0.63	2.1	-0.30	-0.23	1.8	-0.13	-0.01	0.55	-0.02
Band at 28 kK	+1.56	1.88	+0.83	-0.08	2.0	-0.04	-0.95	4.9	-0.19
Band at 35 kK									

ments, the samples were prepared in rigid polymer matrices which were cut to the appropriate size and polished for optical examination. The preparation of these samples varies with the nature of the polymer. The simplest technique is to dissolve the polymer and sample in dichloromethane and to cast a film on a glass block. Excellent samples are obtained by dissolving the complex in the monomer which is then polymerized either by a thermal method or by a suitable, noninteracting initiator. The polymer matrices were found to be excellent hosts down to helium temperatures with the immense advantage of showing zero linear birefringence and hence no base line errors. We did find, however, that certain samples did not show 1/T behavior and we suspect this may be due to poor thermal conductivity of the polymer, though it may be caused by low-symmetry distortions. Spectra at 30°K were obtained by heating the sample in contact with the helium bore. The samples examined showed approximate 1/T behavior, and this is illustrated for the first band of Figure 5. In the analysis we have assumed C terms to dominate the spectra. This is justified by the temperature dependence work and also by the calculated B term magnitudes (Table I) which are very small when the experimental⁶ ΔE value is inserted.

Theory

The symmetry of the molecules in this study is approximately *D*_{4h}. In some of the phosphine complexes, esr results⁶ suggest that there are three principal *g* values and therefore there are lower symmetry perturbations. These distortions do not appear to affect the optical spectra, however, and we will assume *D*_{4h} to be the effective symmetry.

We have constructed a qualitative MO diagram for these systems based on the ordering of energy levels in the general octahedral case subjected to a tetragonal distortion. It has been assumed that the phosphine, arsine, and sulfide ligands bond to the metal *via* the σ orbitals only. This point will be pursued further in

discussing the results. Clearly the π orbitals will affect the spectra of the pyridine complex. We also discuss later the role of the phosphorus, arsenic, and sulfur d orbitals in the bonding process. The molecular orbitals are shown in Figure 1, and we here utilize the ordering of the chlorine π orbitals determined experimentally for IrCl₆²⁻.² Figure 2 shows the ground state and allowed charge-transfer states together with the functions. The ground and excited states are classified under the *D*_{4h} point group. This is particularly suitable for the chlorine π excited states since the Cl atoms can be formally considered to be in a square-planar system.

The ground state is located predominantly on the central metal atom which experiences an octahedral environment perturbed by spin-orbit coupling and the lower symmetry tetragonal distortion. The spin-orbit coupling is the larger of these latter two perturbations in the ground state since ξ_d for Ir⁴⁺ is ≈2000 cm⁻¹. To obtain a good ground-state function the octahedral basis must be diagonalized with respect to both these perturbations as outlined by Hudson and Kennedy⁶ and discussed by Griffith.⁷ For calculating the ground-state energy levels it is convenient to use *O_h** functions and in general form the lowest Kramers doublet can be written as

$$\begin{aligned} |E''\alpha\rangle &= iA|T_{2x}^{-1/2}\rangle - A|T_{2y}^{-1/2}\rangle + iC|T_{2z}^{1/2}\rangle \\ |E''\beta\rangle &= iA|T_{2x}^{1/2}\rangle + A|T_{2y}^{1/2}\rangle - iC|T_{2z}^{-1/2}\rangle \end{aligned} \quad (1)$$

The matrix of spin-orbit coupling and tetragonal distortion then becomes

(7) J. S. Griffith, "The Theory of the Transition Metal Ions," Cambridge University Press, London, 1964.

$$\begin{array}{ccc|ccc}
 & |i\langle T_{2x} -1/2 \rangle & -|T_{2y} -1/2 \rangle & i\langle T_{2z} 1/2 \rangle & & & \\
 \hline
 -i\langle T_{2x} -1/2 & \nabla/2 - \epsilon & -\xi_d/2 & -\xi_d/2 & & & \\
 -\langle T_{2y} -1/2 & -\xi_d/2 & \nabla/2 - \epsilon & -\xi_d/2 & & & \\
 -i\langle T_{2z} 1/2 & -\xi_d/2 & -\xi_d/2 & -\nabla - \epsilon & & & \\
 \hline
 & & & & & & (2)
 \end{array}$$

where $\nabla = 1/3\langle T_2 || V || T_2 \rangle$ and ξ_d is the spin-orbit coupling constant for the metal.

Solving the secular determinant of this matrix in terms of A and C gives us ∇ and ϵ as a function of ξ_d

$$\begin{aligned}
 \nabla &= \frac{(C^2 + AC - 2A^2)\xi_d}{3AC} \\
 \epsilon &= \frac{-(A^2 + C^2 + AC)\xi_d}{3AC}
 \end{aligned}
 \quad (3)$$

values of A and C can be obtained from esr data⁶ in the case of $\text{IrCl}_4(\text{AsPr}_3)_2$.

The ground-state g values calculated using the functions (1) are

$$\begin{aligned}
 g_x &= 2\beta[2A^2(k+1) - C^2] \\
 g_y &= 2\beta[2ACk + C^2] \\
 g_z &= 2\beta[2ACk + C^2]
 \end{aligned}$$

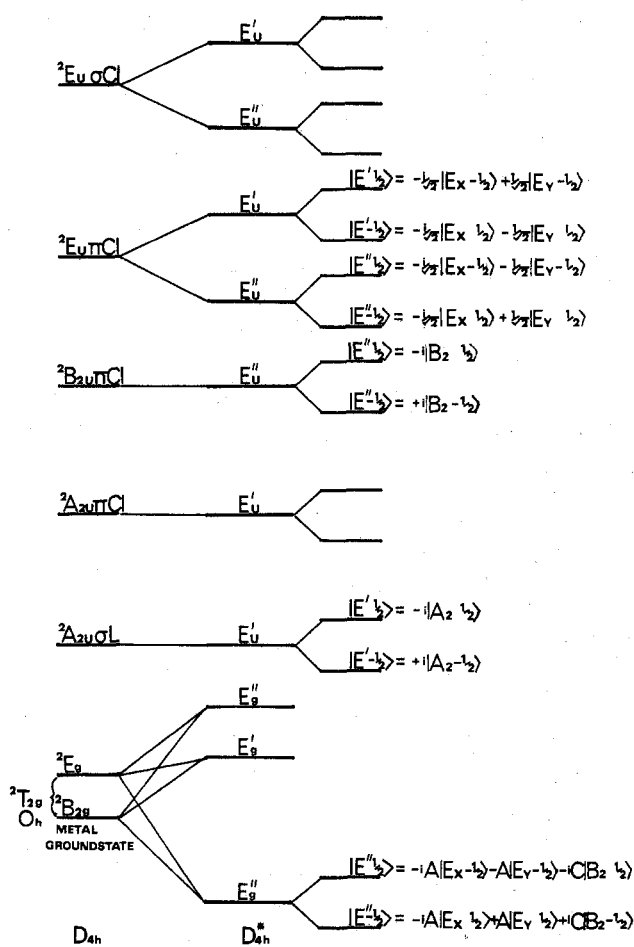


Figure 2.—Allowed charge-transfer states arising from transitions from filled ligand orbitals to the vacant metal (t_{2g}) orbital.

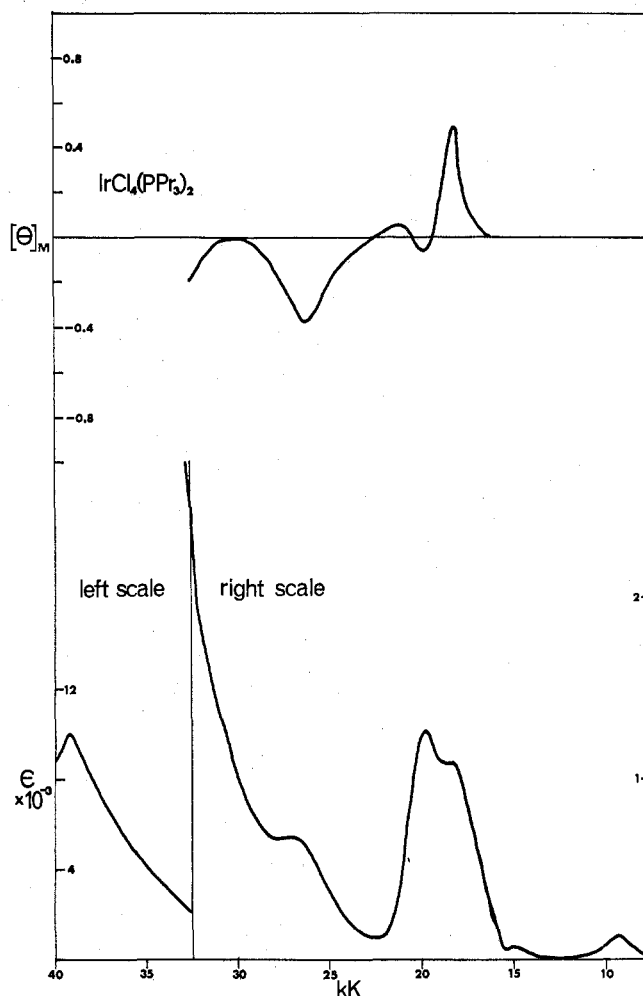


Figure 3.—MCD and absorption spectra of $\text{IrCl}_4(\text{PPr}_3)_2$ in dichloromethane at room temperature. $[\theta]_m$ is the molar ellipticity defined as in natural optical activity in $\text{deg dl dm}^{-1} \text{mol}^{-1} \text{G}^{-1}$. ϵ is the molar extinction coefficient.

where k is the orbital reduction factor. The matrix (2) can then be diagonalized using these values of A and C to calculate ∇ , and the three values of ϵ obtained together with the form of the other two Kramers doublets are not of importance in this work.

The allowed charge-transfer excited states shown in Figure 2 can be considered to be predominantly localized on the ligand atoms. Thus the excited state spin-orbit splittings will depend on the nature of the ligand MO and on the nature of the ligands. The one-dimensional states show no spin-orbit splitting so we are concerned only with the ${}^2E_u(\pi\text{Cl})$ and ${}^2E_u(\sigma\text{Cl})$ states. We can show this to be very small in the following way⁸

$$\begin{aligned}
 \langle {}^2E E_{\alpha''} | H_{so} | {}^2E E_{\alpha''} \rangle &= \frac{i}{\sqrt{2}} \left\langle E_x - \frac{1}{2} \right| - \\
 &\frac{1}{\sqrt{2}} \left\langle E_y - \frac{1}{2} \right| H_{so} \left| \frac{-i}{\sqrt{2}} E_x - \frac{1}{2} \right\rangle - \frac{1}{\sqrt{2}} \left| E_y - \frac{1}{2} \right\rangle = \\
 &-\frac{i}{2} \left\langle E_x - \frac{1}{2} \right| - iL_z S_0 \left| E_y - \frac{1}{2} \right\rangle + \\
 &\frac{i}{2} \left\langle E_y - \frac{1}{2} \right| - iL_z S_0 \left| E_x - \frac{1}{2} \right\rangle
 \end{aligned}$$

(8) J. S. Griffith "The Irreducible Tensor Method for Molecular Symmetry Groups," Prentice-Hall, Englewood Cliffs, N. J., 1962. Note that our E_x and E_y functions are Griffith's E_c and E_s , respectively.

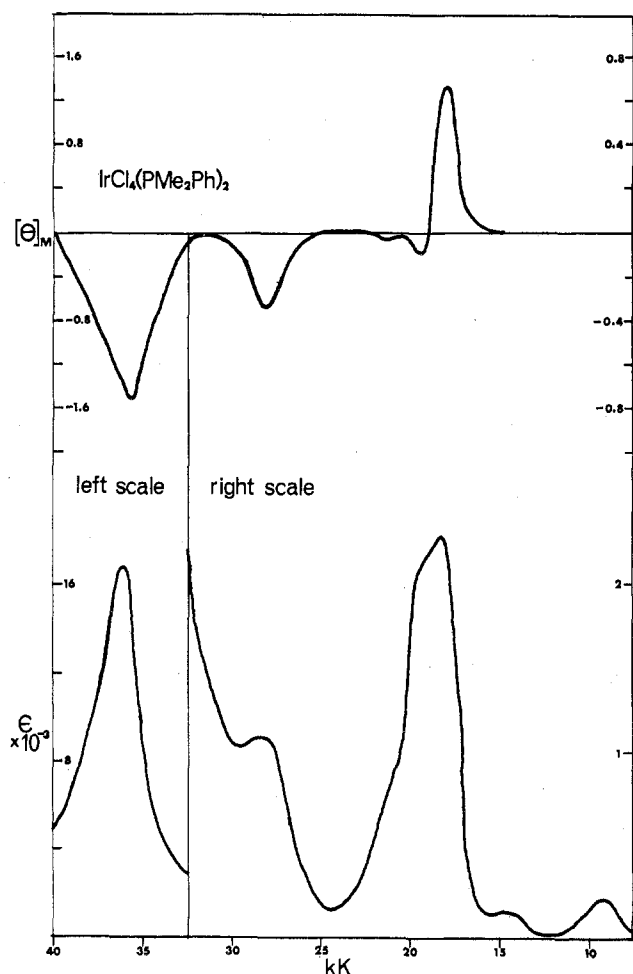


Figure 4.—MCD and absorption spectra of $\text{IrCl}_4(\text{PMe}_2\text{Ph})_2$ in dichloromethane at room temperature. $[\theta]_m$ and ϵ are as defined in Figure 3.

$$\left\langle E_x - \frac{1}{2} - iL_z S_0 E_y - \frac{1}{2} \right\rangle = -i \langle e^3 {}^2E || \sum s \cdot l || e^3 {}^2E \rangle \times$$

$$(-1)^{1/2+1/2} \begin{pmatrix} 1/2 & 1/2 & 1 \\ 1/2 & -1/2 & 0 \end{pmatrix} V \begin{pmatrix} E & E & A_2 \\ x & y & i \end{pmatrix} =$$

$$\frac{i}{2\sqrt{3}} \langle e^3 {}^2E || \sum s \cdot l || e^3 {}^2E \rangle$$

$$\langle e^3 {}^2E || \sum s \cdot l || e^3 {}^2E \rangle = - \left\langle \frac{1}{2} e || s \cdot l || \frac{1}{2} e \right\rangle =$$

$$-\frac{1}{2} i \sqrt{6} \langle e || l || e \rangle \xi_{Cl}$$

Now the π_{Cl} MO's are⁹

$$|e_x^\pi\rangle = \frac{1}{\sqrt{2}} (y_2 - x_4)$$

$$|e_y^\pi\rangle = \frac{1}{\sqrt{2}} (x_1 - y_3)$$

The only nonzero matrix element

$$\langle e_x | l_z | e_y \rangle = \frac{1}{2} (y_2 - x_4 | l_z | x_1 - y_3)$$

This must be very small since when the ligand coordinates are lined up with the metal, we get a matrix element which does not involve terms on the same atom

(9) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1965.

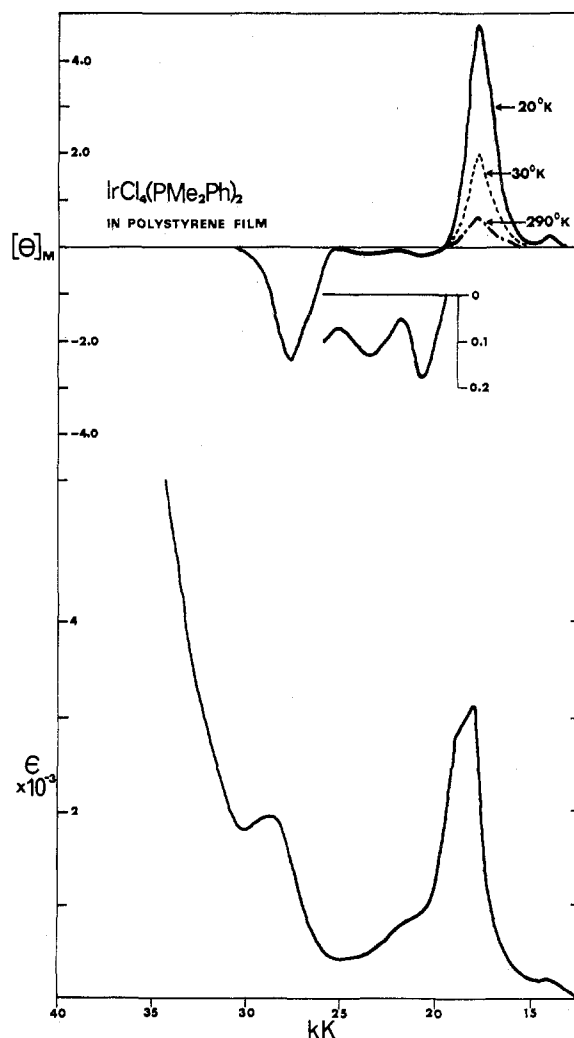


Figure 5.—MCD and absorption spectra of $\text{IrCl}_4(\text{PMe}_2\text{Ph})_2$ in polystyrene film at 290, 30, and 20°K. An inset is shown of the 20,000–25,000- cm^{-1} region on expanded scale.

and thus only overlap terms introduce spin-orbit coupling. A similar argument can be shown to apply to the ${}^2E_u \sigma_{Cl}$ state. Thus we expect the spin-orbit splitting of E' and E'' from 2E to be quite small particularly since ξ_{Cl} is only around 500 cm^{-1} .

C and B terms were calculated using the nonisotropic formulas given by Stephens¹⁰ in which for example

$$C = \frac{1}{d_a} \text{Im} \sum_{\alpha\alpha'} \langle A \alpha' | \vec{\mu} | A \alpha \rangle \cdot \langle \langle A \alpha | \vec{m} | J_\lambda \rangle \rangle \langle \langle J_\lambda | \vec{m} | A \alpha' \rangle \rangle$$

and dipole strengths via

$$D = \frac{1}{d_a} \sum_{\alpha\lambda} \langle A \alpha | \vec{m} | J_\lambda \rangle^2$$

The functions used are shown in Figure 2 and the calculated parameters are shown in Table I.

Results

The absorption and MCD spectra of IrCl_4L_2 ($L = \text{PR}_3, \text{AsR}_3, \text{SEt}_2, \text{pyridine}$) show very striking similarities in the region 18,000–22,000 cm^{-1} which suggests strongly that these bands are associated with the four chloride ligands in the xy plane. They are in the region of the chlorine π - t_{2g} transitions in IrCl_6^{2-} and these are

(10) P. J. Stephens, *J. Chem. Phys.*, **52**, 3489 (1970).

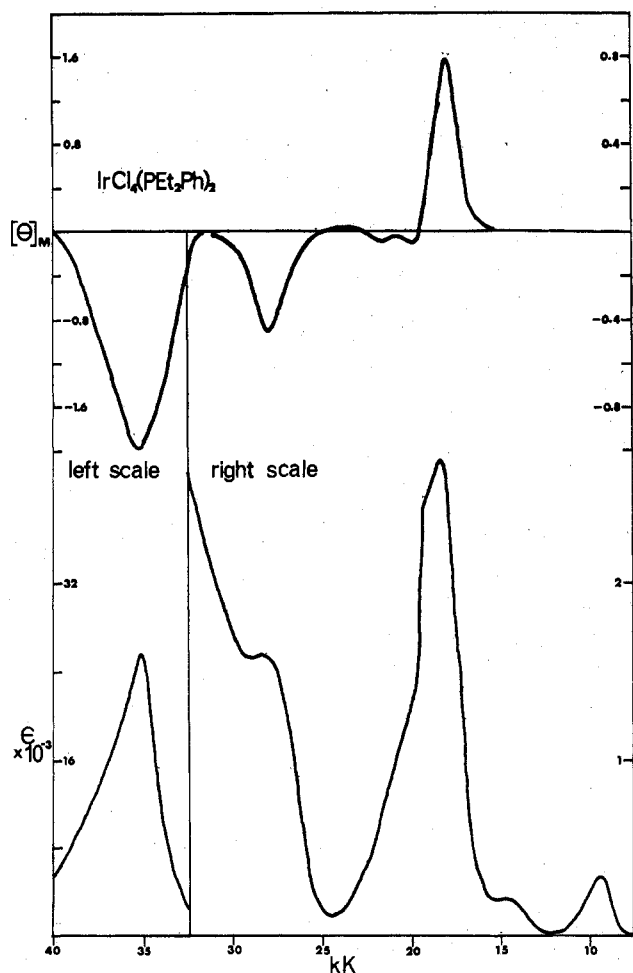


Figure 6.—MCD and absorption spectra of $\text{IrCl}_4(\text{PEt}_2\text{Ph})_2$ in dichloromethane at room temperature.

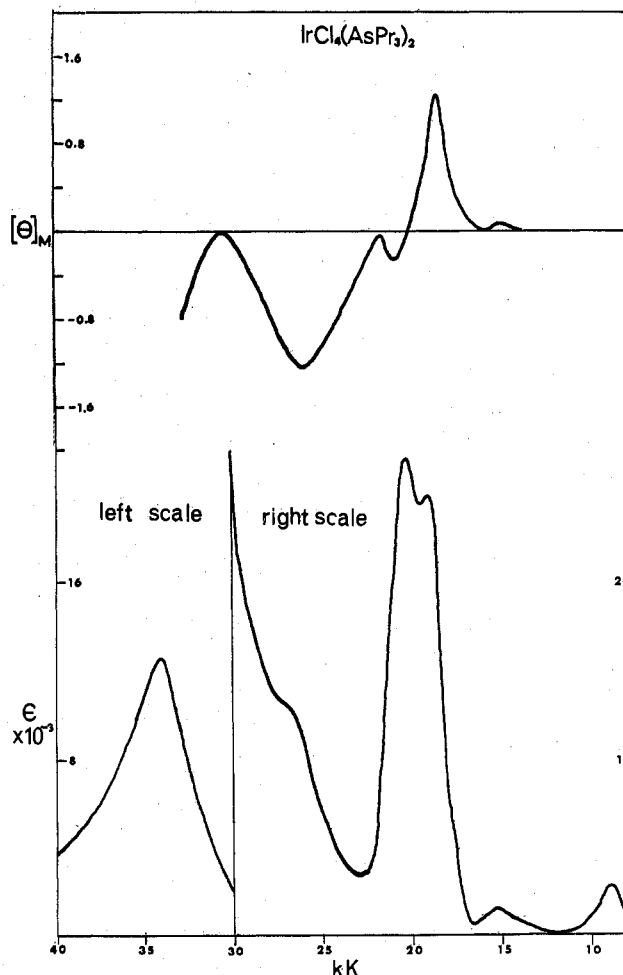


Figure 7.—MCD and absorption spectra of $\text{IrCl}_4(\text{AsPr}_3)_2$ in dichloromethane at room temperature.

assigned therefore as the a_{2u} , b_{2u} , $e_u \rightarrow$ metal (t_{2g}) charge-transfer transitions from the Cl π orbitals. In Table I are the calculated C/D values. Analogy to IrCl_6^{2-} would put $a_{2u} \rightarrow t_{2g}$ ($E_g'' \rightarrow E_u'$) lowest in energy and we find this gives good agreement with calculated C/D , thus we assign this lowest energy band in the "chlorine" region ($18,000 \text{ cm}^{-1}$) as $E_g'' \rightarrow E_u'$.

The remainder of this region ($19,000$ – $25,000 \text{ cm}^{-1}$) contains the $E_u' + E_u''$ (from e_u) and E_u'' (from b_{2u}) π chlorine transitions. These can be discerned in the absorption spectra and more clearly in the MCD. They have opposite signed C/D values and these will tend to cancel. The two components can be seen clearly in the low-temperature spectrum of $\text{IrCl}_4(\text{PMe}_2\text{Ph})_2$ and in the room-temperature MCD of $\text{IrCl}_4(\text{AsPr}_3)_2$ and $\text{IrCl}_4(\text{PPr}_3)_2$. (Note that esr evidence⁶ indicates that these latter two complexes have full D_{4h} symmetry.) These two components appear to move around somewhat from compound to compound and the degree of cancelation changes. The experimental values of C/D for these two bands will clearly not be too meaningful. The negative ($[\theta]_M$) band is the $b_{2u} \rightarrow t_{2g}$ ($E_g'' \rightarrow E_u''$) transition and the positive, the $e_{2u} \rightarrow t_{2g}$ ($E_g'' \rightarrow E_u' + E_u''$) transition. These two absorption bands have quite different intensities and it appears that the positive band ($e_{2u} \rightarrow t_{2g}$) is the weaker of the two. We have attempted to calculate the transition moments for these two absorptions in order to con-

firm our assignments. This procedure is rather unsatisfactory since we must assume a relationship between the transition moment and an overlap integral between atomic orbitals on the ligand and metal. If we do this using Ballhausen and Gray⁹ functions for the ligand orbitals and their coefficients for TiF_6^{3-} , we find that the transition $b_{2u} \rightarrow t_{2g}$ is larger than $e_{2u} \rightarrow t_{2g}$ since they are multiplied by a different overlap factor which is smaller in the latter case. The approximations involved in this procedure make the results none too meaningful, though there is some justification for the relative magnitudes of the ${}^2B_2'$ and 2E chlorine π transitions.

These bands therefore comprise the chlorine $\pi \rightarrow t_{2g}$ transitions and therefore give us the energies of these π MO's relative to the metal orbitals and indicate the "balance" between the chlorine-bonding orbitals and the metal leading to a stable bond. These three bands do not change particularly over a wide range of axial substituents and therefore we must look for new bands in the spectra which might arise from the axial ligands. The spectra (Figures 3–9) show the presence of a moderately intense band which occurs at 9010 cm^{-1} in $L = \text{AsR}_3$, 9400 cm^{-1} in $L = \text{PR}_3$, $15,100 \text{ cm}^{-1}$ in $L = \text{SEt}_2$, and $22,000$ or $25,000 \text{ cm}^{-1}$ in $L = \text{pyridine}$. We assign this transition as charge transfer from the L σ or π bond to the metal shell (the rather unusual case of pyridine is discussed separately in the next section).

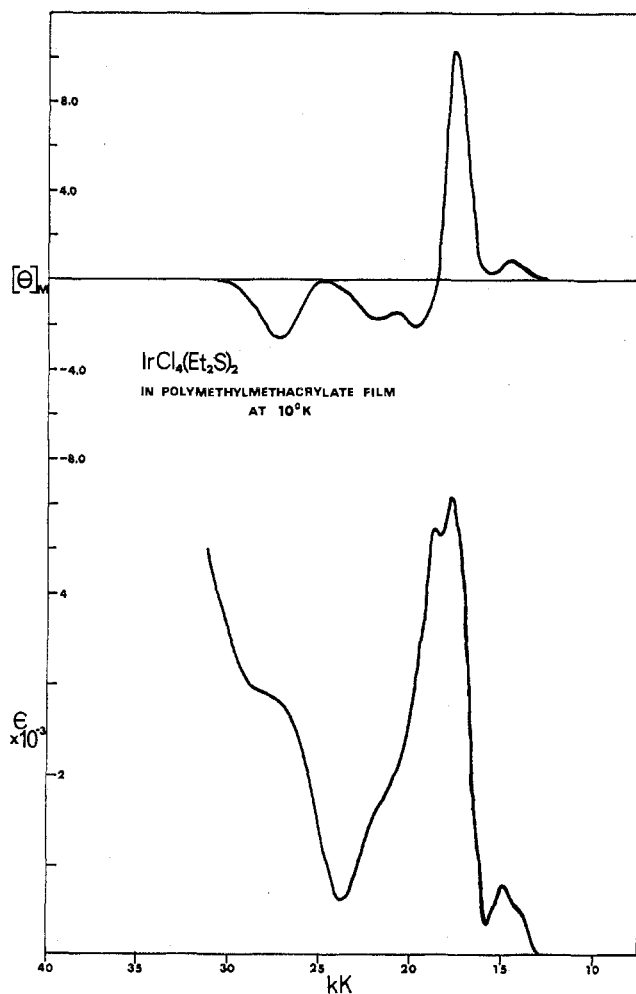


Figure 8.—MCD and absorption spectra of $\text{IrCl}_4(\text{Et}_2\text{S})_2$ in poly(methyl methacrylate) at 10°K .

Calculations suggest that this should have negative C/D , *i.e.*, positive $[\theta]_m$. The bands in the phosphine and arsine complexes are at too low an energy to be measurable on our MCD apparatus and we have been unable to measure the Faraday effect of these bands. In the sulfide and pyridine cases, the new bands are within reach and the sulfide has a positive $[\theta]_m$. The significance of these results is discussed in the next section. The identification of the band giving negative $[\theta]_m$ at $28,000\text{ cm}^{-1}$ is not so straightforward. It is virtually unchanged throughout the range of complexes studied here. It is in the region of the $t_{1u}(\sigma) \rightarrow t_{2g}$ transition in IrCl_6^{3-} though it is of opposite sign. The analogous transition in the D_{4h} complex has a calculated C/D negative which suggests that this is not the assignment we are looking for. We feel that this is most likely to be a parity-forbidden charge-transfer transition, probably from an even chlorine σ orbital judging by the intensity and breadth of the band. Any attempt to calculate the C values for this requires an assumption as to the nature of the intensity-giving perturbation. The very intense, broad transition at approximately $36,000\text{ cm}^{-1}$ is assumed to be due to transitions to the e_g level (as in IrCl_6^{2-}) and these probably mask the $\text{Cl } \sigma \rightarrow t_{2g}$ transition.

The identification of these transitions also gives some information on the role of the phosphorus, arsenic, and sulfur d orbitals in bonding. An oxidation state IV

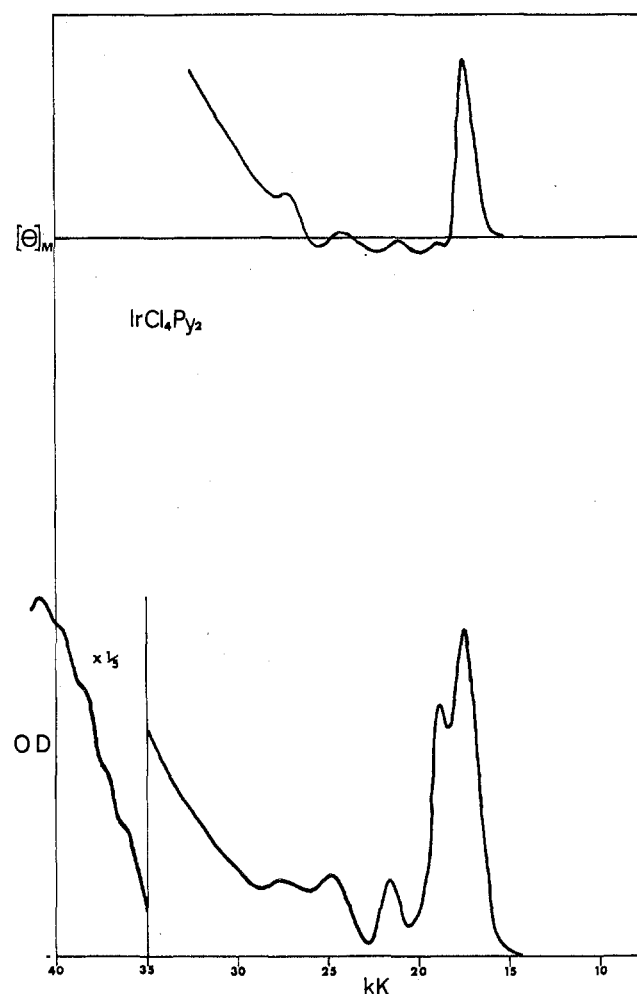


Figure 9.—MCD and absorption spectra of $\text{IrCl}_4(\text{py})_2$ in dichloromethane at room temperature. Both absorption and MCD scales are in arbitrary units because of the extremely low solubility of this compound.

complex would not be expected to be strongly π bonded through these orbitals but it is clear that they must be at least $38,000\text{ cm}^{-1}$ above the metal since no charge transfer to the L d orbitals is observed. The effect of appreciable d-orbital mixing into the ground state may be calculated through contributions to the g factor and we find that the experimental g factor⁶ does not indicate ligand d orbitals mixing into the ground state. We conclude that phosphorus, arsenic, and sulfur π bonding is unimportant in these complexes in agreement with the conclusions of Mason, *et al.*,¹¹ from a study of bond lengths in these and related complexes.

Discussion

In the stabilization of a complex of Ir(IV) the tendency of the metal to acquire an electron to form Ir(III) accommodates the tendency of the ligands to be oxidized by donating electrons to the metal. That is, the oxidizing power of the metal balances the reducing power of the ligand. This equilibrium manifests itself in the energetics of formation of the chemical bond which may be σ and π donating and π accepting by the ligand depending on its nature. The importance of the interplay of oxidizing and reducing power in a complex of well-defined oxidation state has been recognized

(11) L. Aslanov, R. Mason, A. G. Wheeler, and P. O. Whimp, *Chem. Commun.*, 30 (1970).

by Jorgensen,¹² who has devised the optical electronegativity scale to quantify this property. Optical electronegativity essentially measures the ease with which an electron is transferred to the metal from the ligand—*i.e.*, the energy of the ligand orbitals with respect to those of the metal. Clearly this balance is important chemically since the existence of a particular oxidation state implies that this process does not occur spontaneously.

The most direct measure of this important bonding property is, as Jorgensen has stated, the energy of the charge-transfer excitation from ligand to metal orbitals. If the ligand orbitals are low lying in energy, reduction of the metal will take place with difficulty but if they are close to the metal orbitals, a particular oxidation state may be rendered unstable with respect to the ligand.

In the compounds examined here, the halogen ligands are moderately reducing; for example, the chemical environment of six chloride ligands will stabilize the IV oxidation state in iridium. This is reflected in the energy of the $L \rightarrow M$ charge-transfer transitions which are well up in the visible region at 20,000 cm^{-1} and higher. In terms of optical electronegativities χ_{opt} defined as

$$\sigma = (30 \text{ kK}) [\chi_{\text{opt}}(\text{x}) - \chi_{\text{opt}}(\text{m})]$$

where σ is the transition frequency of the first $L \rightarrow M$ charge transfer, this gives an optical electronegativity of 2.3 for Ir(IV), utilizing Jorgensen's value of 3.0 for Cl^- . In the cases under discussion here where the metal and its oxidation state remain the same throughout the series of complexes there is no difference between discussions framed in terms of optical electronegativities and transition energies. Since the latter are the experimental observables, we shall use these. In the series of complexes IrCl_4L_2 we have examined, the energy of the $L \rightarrow M$ charge-transfer transition closely follows the chemical reducing nature of the ligand. Phosphines are more reducing than sulfides which are more reducing than amines. (The use of pyridine as a representative amine is of course not wholly justified though it seems unlikely that an aliphatic amine would have charge-transfer bands at significantly lower energies than pyridine.) The discovery that phosphines and arsines have an exceptionally low-energy charge-transfer band suggests that there is considerable chemical significance in this high-energy, exposed phosphorus or arsenic σ bond. For instance it is known that coordinated phosphine may be oxidized to phosphine oxide much more easily than the free ligand,¹⁸ coordinated sulfides are oxidized with more difficulty, and amines are not oxidized at all. The high-energy σ orbital may well be the key factor in this enhanced reactivity. The photochemical lability will also be dependent on the energy of the $L \rightarrow M$ σ -bond transitions and it has been observed that the phosphine and arsine complexes are decomposed on exposure to daylight whereas the sulfide and pyridine complexes are fairly stable. This process presumably is a direct photoreduction of the metal with consequent weakening of the M -P or M -As bond. Note that this is distinct from the reductions brought about by a second molecule or ion as discussed recently by Taube and coworkers¹⁴

though we should predict that the energy as well as the symmetry of the matching orbitals plays an important role in the "resonance" reduction process.

So far we have been rather vague about the differences in bonding between the sulfur and pyridine and the phosphorus and arsenic ligands. Both sulfur and pyridine act as σ donors but both have filled orbitals of π symmetry lying below the metal orbital. The transitions we have identified in these cases may be from these filled π orbitals to t_{2g} . If this is the case the $\sigma \rightarrow t_{2g}$ transitions are to higher energy, emphasizing more strongly the accessibility of the phosphorus and arsenic σ orbitals. In the case of pyridine, transitions from the metal to the ligand system and internal ligand transitions are possible in accessible spectral regions and we see structure on the spectrum of $\text{IrCl}_4(\text{py})_2$ which appears to be due to one of these processes.

One further question which is raised by the discovery of the exceptionally high-energy P and As σ bond is, to what extent is this related to the "softness" of the ligand? Clearly the complexes with high-energy bonds have electronic transitions which are low in energy and have a sizable transition moment. Thus the molecule has high polarizability. Note that this is in fact a consequence of the bond formation since the free ligand has no transitions below 40,000 cm^{-1} . The "softness" may therefore be much more to do with the energetics of the filled σ -bond orbitals than with overlap of the π orbitals of the ligand in line with suggestions by Venanzi and coworkers¹⁶ from a study of Pt-P nmr coupling constants. There is spectral evidence¹⁶ that the phosphorus σ bond lies even closer to the metal orbitals in the analogous Pt(IV) complexes (approximately 5000 cm^{-1}) and this suggests enhanced reactivity with the σ bond at a more accessible energy. We may obtain very rough estimates of this bond energy in Pt(II) and Pt(0) using Jorgensen's tabulations of χ_{opt} and these are 7000 and 12,000 cm^{-1} , respectively. Although these estimates are very crude, they give an idea of the accessibility of the σ orbitals in energy terms.

We should also note that in the complexes examined here there is no mixing of the phosphorus (and arsenic, sulfur, pyridine) σ orbitals with the halogen σ or π system to first order, *i.e.*, due to the symmetry of the crystal field. In complexes of lower symmetry this may not be the case and mixing will occur. This will have the effect of changing the energy of all the filled ligand orbitals and may exert a "softening" effect on all the ligands of the complex.

A final point is made concerning Jorgensen's evaluation of χ_{opt} . We are primarily interested in bonding electronegativities, *i.e.*, the energetics of the M -L bond rather than those of the free ligand, and hence a more interesting scale may be that relating to transitions from σ -bonding orbitals rather than from nonbonding orbitals as in the original Jorgensen definition. As the spectra become more comprehensible, this refinement may become of some importance.

Conclusion

We find that in the series of complexes IrCl_4L_2 ($L = \text{PR}_3, \text{AsR}_3, \text{SR}_2, \text{pyridine}$) the energy of the L - M

(12) C. K. Jorgensen, "Orbitals in Atoms and Molecules," Academic Press, London, 1962.

(13) R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968).

(14) R. G. Gaunter and H. Taube, *Inorg. Chem.*, **9**, 2627 (1970).

(15) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966).

(16) G. J. Leigh and D. M. P. Mingos, *J. Chem. Soc. A*, 587 (1970).

charge-transfer transition moves from the infrared region (9000 cm^{-1}) for PR_3 and AsR_3 toward the uv region for Et_2S and pyridine. The halogen transitions remain unchanged throughout this process. The energy of the $\text{L} \rightarrow \text{M}$ transition parallels the reducing power of the ligand and we suggest that this may reflect the energy of the L σ -bond orbitals relative to the metal. Furthermore, we feel that the formation of high-energy orbitals with consequent low-lying excited states in the case of the phosphines and arsines may be

responsible for the "softness" of these ligands particularly since little evidence for π bonding from these can be found experimentally.

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Intramolecular Hydrogen Exchange in Tetraborane(10)¹

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Intramolecular hydrogen exchange in tetraborane(10) has been studied by utilizing isotopic labeling in conjunction with high-field nmr. Both qualitative and quantitative evidence, obtained by studying the scrambling reactions of $\mu\text{-B}_4\text{H}_9\text{D}$ and $\mu\text{-B}_4\text{D}_3\text{H}$, has established that intramolecular hydrogen exchange proceeds at two different rates. The faster exchange involves the bridge and four terminal positions while the slower exchange involves the bridge and the remaining two terminal positions. Further evidence established that the two unique terminal protons which were exchanging at the slower rate are attached to the 2,4 boron atoms. Rate data are presented for both exchanges and possible mechanisms of exchange are discussed. The gas-phase intermolecular exchange reaction of B_4H_{10} and B_2D_6 was reinvestigated, since it had previously been suggested that the 1,3 terminal positions exchange faster than the other positions in tetraborane(10). No evidence was found to support this suggestion.

Introduction

Slow intramolecular hydrogen exchange was first noted in tetraborane(10) by observing the ir spectrum *vs.* time of tetraborane(10) which had been partially deuterated in the terminal positions.^{2,3} A scrambling of the deuterium from the terminal to bridge positions was observed. Similar studies with the isotopically labeled compounds, μ ,1-dideuteriotetraborane(10)⁴ and μ -deuteriotetraborane(10)⁵ confirmed that slow intramolecular exchange involving the interconversion of bridge and terminal positions was taking place. In each study only qualitative information about exchange rates could be obtained and nonpreferential scrambling was assumed.

Further evidence for an intramolecular type of exchange in tetraborane(10) was found in the zero source contact mass spectral analysis⁶ of the specifically labeled compound, $\mu\text{-}^{10}\text{B}_4\text{H}_9\text{D}$. The spectrum of the scrambled material was found to be unchanged from that of the labeled material which is inconsistent with an intermolecular type of scrambling mechanism.

The introduction of new nmr spectrometers operating at higher field strengths than previously attainable now permits proton and deuterium nmr spectra to be a useful tool for the boron chemist. We have therefore applied these techniques to investigate intramolecular exchange in tetraborane(10).

Experimental Section

Preparation of Samples.—The standard high-vacuum techniques used in this investigation are described elsewhere.⁷

Lithium aluminum deuteride (isotopic purity >99.5%) was obtained from Metal Hydrides, Inc. Deuterium oxide was obtained from the Atomic Energy Commission and was used without further purification.

Isotopically enriched diborane, B_2D_6 , was prepared by the reduction of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ with LiAlD_4 . Normal diborane, $^2\text{B}_2\text{H}_6$, and tetraborane(10), $^{10}\text{B}_4\text{H}_{10}$, were obtained from laboratory supply. Pentaboranes(11) were prepared in a hot-cold circulating system described elsewhere.⁸

Isotopically labeled tetraboranes(10), $\mu\text{-B}_4\text{H}_9\text{D}$ and $\mu\text{-B}_4\text{D}_3\text{H}$, were prepared by cleavage of B_5H_{11} and B_5D_{11} with D_2O and H_2O , respectively.⁵ Tetraborane(10) labeled with an ^{11}B in the 4 position was prepared as reported.⁴

Spectroscopic Techniques.—Nuclear magnetic resonance spectra were obtained with a Varian Associates HR-220 spectrometer equipped with standard Varian variable temperature probe accessories. Multiple scans were obtained using the Varian Associates 1024 time averaging computer. Proton, deuterium, and boron spectra were obtained at 220 MHz, 33.1 MHz, and 70.6 MHz, respectively. In each case special care was taken to avoid saturation effects.

Procedure.—Scrambling reactions were carried out in the liquid phase in standard medium wall precision nmr tubes.

For each data point the nmr tube was placed into a slush bath and timing started 15 sec after immersion. After an appropriate time interval the nmr tube was removed and quenched at -196° to stop the reaction. To prevent further scrambling while the spectrum was taken, the nmr probe was cooled below -10° . Normally 16 sweeps were accumulated at each point with the aid of a time averaging computer. The time averaged spectrum was then printed and subsequently integrated by weighing. The nmr tube was then removed from the probe and the above procedure repeated. At various intervals a wider sweep width

(1) Studies of Boranes XXXIII; for paper XXXII of this series see L. G. Sneddon and R. Schaeffer, *Inorg. Chem.*, **11**, 3102 (1972).

(2) J. E. Todd and W. S. Koski, *J. Amer. Chem. Soc.*, **81**, 2319 (1959).

(3) W. S. Koski, *Advan. Chem. Ser.*, **32**, 78 (1961).

(4) A. D. Norman and R. Schaeffer, *J. Amer. Chem. Soc.*, **88**, 1143 (1966).

(5) A. D. Norman and R. Schaeffer, *Inorg. Chem.*, **4**, 1225 (1965).

(6) A. D. Norman, R. Schaeffer, A. B. Baylis, G. A. Pressley, Jr., and F. E. Stafford, *J. Amer. Chem. Soc.*, **88**, 2151 (1966).

(7) R. T. Sanderson, "Vacuum Manipulations of Volatile Compounds," Wiley, New York, N. Y., 1948.

(8) J. Dobson, R. Maruca, and R. Schaeffer, *Inorg. Chem.*, **9**, 2161 (1970).