at −20° (23% yield). *Anal.* Calcd for $H_4Ru_4(CO)_{11}P(C_4H_9)_3$: C, 30.06; H, 3.40; mol wt 918.7. Found: C, 30.4; H, 3.40; mol wt 985 (benzene solution).

$H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$ and $H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$.—(a) A suspension of 0.50 g (0.67 mmol) of $H_4Ru_4(CO)_{12}$ in 50 ml of tetrahydrofuran and 0.80 g (3.06 mmol) of $P(C_6H_5)_3$ was refluxed for 10 hr under nitrogen. The red solution obtained was evaporated and the solid residue, dissolved in the minimum amount of CH_2Cl_2, was separated into its components by thin layer chromatography. The solid phase was silica gel. A 2.3:1 mixture of pentane and benzene was initially used to get rid of the excess of phosphine while with a 1:1 mixture of the same solvents the solid could be split into two red bands. The two components could be recovered by elution with CH_2Cl_2 and were then both recrystallized from a CH_2Cl_2 solution by addition of pentane. We thus recovered 0.285 g (0.235 mmol) of $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$ as brown-red plates (35% yield) and 0.389 g (0.269 mmol) of $H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$ as deep red crystals (40% yield).

(b) A solution of 0.100 g (0.074 mmol) of $[Ru(CO)_3P(C_6H_5)_3]_3$ in 10 ml of tetrahydrofuran was heated in a 125-ml autoclave at 100° for 4 hr under a hydrogen pressure of 130 atm. The red solution obtained was worked up as described in procedure (a) giving 0.039 g (0.032 mmol) of $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$ (60% yield) and 0.026 g (0.018 mmol) of $H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$ (34% yield).

$H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$.—A tetrahydrofuran (7 ml) solution of $H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$ (0.10 g, 0.069 mmol) was heated at 130° for 2 hr in a 125-ml autoclave under pressure of carbon monoxide (100 atm) and hydrogen (40 atm). From the solution obtained, 0.081 g (0.067 mmol) of $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$ was recovered by addition of *n*-pentane (96.8% yield). *Anal.* Calcd for $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$: C, 45.5; H, 2.82; mol wt 1213. Found: C, 45.46; H, 2.85; mol wt 1202 (methyl ethyl ketone solution).

$H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$.—A tetrahydrofuran (8 ml) solution of 0.100 g (0.0595 mmol) of $H_4Ru_4(CO)_8[P(C_6H_5)_3]_4$ was heated in a 125-ml autoclave at 130° for 2 hr under pressure of carbon monoxide (110 atm) and hydrogen (40 atm). By addition of pentane to the solution obtained 0.0835 g (0.0577 mmol) of $H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$ was recovered (97% yield). *Anal.* Calcd for $H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$: C, 52.28; H, 3.41; mol wt 1447.2. Found: C, 52.28; H, 3.95; mol wt 1514 (methyl ethyl ketone solution).

$H_4Ru_4(CO)_8[P(C_6H_5)_3]_4$.—In a 125-ml autoclave were placed 0.100 g (0.134 mmol) of $H_4Ru_4(CO)_{12}$, 0.300 g (1.14 mmol) of $P(C_6H_5)_3$, 20 ml of cyclohexane, and then hydrogen up to the pressure of 100 atm. The autoclave was heated at 130° for 2 hr. After cooling, the gases were vented and the pressure was restored with new hydrogen. The heating of the autoclave was continued for 14 hr. After cooling, a pale red solution and a red microcrystalline solid (0.220 g; 97%) were recovered. After crystallization of the solid from CH_2Cl_2 and pentane 0.177 g (0.105 mmol) of $H_4Ru_4(CO)_8[P(C_6H_5)_3]_4$ was recovered (78% yield). This product has a low solubility in aliphatic solvents and a better one in the aromatic ones. *Anal.* Calcd for $H_4Ru_4(CO)_8[P(C_6H_5)_3]_4$: C, 57.14; H, 3.89. Found: C, 57.60; H, 3.65.

$H_4Ru_4(CO)_{11}P(C_6H_5)_3$.—In a 125-ml autoclave were placed 0.124 g (0.167 mmol) of $H_4Ru_4(CO)_{12}$, 0.200 g (0.165 mmol) of $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$, 20 ml of tetrahydrofuran, and finally hydrogen up to 90 atm. The autoclave was heated at 100° for 8 hr. After cooling, the gas was vented and a red solution was recovered which was evaporated to dryness. The residue was purified by thin layer chromatography on silica gel using pentane as the eluent. A 0.060-g (0.061-mmol) amount of $H_4Ru_4(CO)_{11}P(C_6H_5)_3$ was recovered as yellow-brown crystals after crystallization from a cyclohexane–pentane mixture (yield 18.5%). *Anal.* Calcd for $H_4Ru_4(CO)_{11}P(C_6H_5)_3$: C, 35.59; H, 1.96; mol wt 978.7. Found: C, 35.99; H, 2.00; mol wt 943 (benzene solution).

$Ru(CO)_4P(C_6H_5)_3$.—In a 125-ml autoclave a solution of 0.12 g (0.1 mmol) of $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$ in 7 ml of tetrahydrofuran was treated with CO under pressure (100 atm) in the presence of hydrogen (40 atm) at 150° for 3 hr. After cooling, the gas was vented and a yellow solution was recovered which was evaporated to dryness. The residue was purified by chromatography on an alumina column using a benzene–pentane mixture as the eluent and gave 0.08 g of $Ru(CO)_4P(C_6H_5)_3$[16] (84% yield).

Acknowledgment.—We wish to thank Dr. Tito Salvadori, Snam Progetti, Laboratori Studi Ricerche, San Donato Milanese, for determination and interpretation of mass spectra.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Electronic Spectra of Some Pentacarbonyl Compounds of Manganese and Rhenium

BY G. B. BLAKNEY AND W. F. ALLEN*

Received May 15, 1970

The electronic spectra of some $LM(CO)_5$ compounds of C_{4v} or related symmetry are reported in the range 5000–1900 Å in the vapor and solution phases. L may be CF_3, CH_3, H, Cl, Br, or I and M may be Mn or Re. The compounds have been classified according to the σ and π properties of the ligand. Band assignments are made and qualitative molecular orbital energy diagrams are given to account for charge-transfer bands. The low-energy spectra of the tetracarbonyl dimers of Mn are reported and related to those of C_{4v} compounds.

Introduction

In recent years a large number of metal carbonyl compounds have been prepared and examined. For most of these, structural interpretations based on the ir spectra and assignments have been published.[1-5] Only a limited amount of uv and visible spectral data has appeared and a small number of assignments and interpretations have been made.[6-8] Photoelectron (pe) spectra have appeared for a number of these compounds[9] and recent MO calculations have been published for $HMn(CO)_5$ and the pentacarbonyl halides.[10]

---

[1] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).

[2] L. E. Orgel, *Inorg. Chem.*, **1**, 726 (1962).

[3] F. A. Cotton, *ibid.*, **3**, 707 (1964).

[4] W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *ibid.*, **5**, 2217 (1966).

[5] F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **6**, 1357 (1967).

[6] H. B. Gray, E. Billig, A. Wojcicki, and M. Farona, *Can. J. Chem.*, **41**, 1281 (1963).

[7] R. T. Lundquist and M. Cais, *J. Org. Chem.*, **27**, 1167 (1962).

[8] D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, **7**, 959 (1968).

[9] S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard, and D. W. Turner, *Discuss. Faraday Soc.*, **No. 47**, 112 (1969).

[10] R. Fenske and R. DeKock, *Inorg. Chem.*, **9**, 1053 (1970).

TABLE I
CLASS 1 COMPOUNDS
SUMMARY OF UV DATA AND ASSIGNMENTS

	Type of transition								
	1. M → L (CT),[a] $e\pi \rightarrow \pi^*(CO)$(NI)			2. M → L (CT), $e\pi \rightarrow e\pi^*(CO)$			3. M → L (CT), $e\pi \rightarrow b_2\pi^*(CO)$ [and $b_2\pi \rightarrow e\pi^*(CO)$ for $CH_3Mn(CO)_5$]		
Compd	λ_{max}, Å	$\tilde{\nu}_{max}$, cm^{-1}	ϵ[b]	λ_{max}, Å	$\tilde{\nu}_{max}$, cm^{-1}	ϵ[b]	λ_{max}, Å	$\tilde{\nu}_{max}$, cm^{-1}	ϵ[b]
$CF_3Mn(CO)_5$									
C_6H_{12}	~2700 sh	~37,000	~3000	2155	46,380	30,000	<1900 sh	>52,600	>12,000
Vapor	~2700 sh	~37,000	(0.09)	2120	47,170	(0.9)	<1900	>52,600	
$CH_3Mn(CO)_5$									
C_6H_{12}	~2800 sh	~35,500	~3000	2220	45,050	28,000	1960	51,020	36,000
Vapor	~2750 sh	~36,500	(0.07)	2190	45,660	(0.6)	~1925	52,000	(0.7)
$HMn(CO)_5$									
Vapor	~2850 sh	~34,500	(0.1)	2140	46,730	(0.75)	~1950 sh	51,300	(1.0)
$HRe(CO)_5$									
Vapor	2700 sh	37,000	(0.25)	2115	47,280	(1.46)	1975	50,630	(1.72)
C_6H_{12}	2725 sh	36,700	(1.30)	2150	46,510	. . .			

[a] See text. [b] Molar absorptivity (in the absence of known concentrations, relative intensity values are given in parentheses).

We have found it useful to classify $LM(CO)_5$ compounds according to the π-donating or π-accepting properties of the L group. We report here on class 1 compounds in which L has little or no π-bonding capability ($HMn(CO)_5$, $HRe(CO)_5$, $CH_3Mn(CO)_5$, and $CF_3Mn(CO)_5$) and class 2 compounds in which L is a π-donating atom or group ($ClMn(CO)_5$, $BrMn(CO)_5$, and $IMn(CO)_5$). (Class 3 compounds, not reported here, are those in which L is a π-accepting group. The frequencies reported by Gray[6] for $Cl-Mn(CO)_5$, $Br-Mn(CO)_5$, and $I-Mn(CO)_5$ do not agree with our results. Since the spectra themselves were not published, it is impossible to make precise comparisons, but the ready formation of the bromine and chlorine tetracarbonyl dimers may account for some of the earlier reported values. $CF_3-Mn(CO)_5$ and $CH_3-Mn(CO)_5$ are included in the spectra reported by Lundquist and Cais,[7] who assigned in a general way all bands for these compounds, including the end absorption for which no $\tilde{\nu}_{max}$ is reported, to the M–CO moiety.

The spectra reported here have generally been recorded for both solvent and vapor phases. Reasonable assignments of the bands are made; these are correlated with pe and ir results and comparisons are made with the MO calculations where possible. Qualitative MO energy level diagrams based on a simple bonding picture are presented.

The correlation of the uv spectra with available pe spectra affords an approximate placement of the antibonding levels which is not generally available from ionization work, pe spectra, or quantum mechanical calculations. The examination of the spectra and assignments for some of these more common pentacarbonyl compounds will also serve as a basis for study of $LM(CO)_5$ compounds involving metal–metal bonding.

Some low-temperature studies have been reported.[11] These give additional information but restrictions in choice of solvent and in frequency range limit their usefulness for the compounds examined here.

Experimental Procedure

The class 1 and 2 compounds examined, with the exception of $IMn(CO)_5$, were obtained in pure form from W. A. G. Graham and coworkers. Purity checks on the crystal compounds were carried out using ir and mass spectrometry. The compounds had been prepared as recommended by King.[12] Visible and uv spectra were obtained using a Cary 14 spectrometer covering the range 1900–5000 Å. High-energy absorption bands were rechecked on a Jasco uv 5 ORD–CD instrument with an N_2-flushed system. Spectral grade solvents were used in all cases.

$HMn(CO)_5$ was purified by trap-to-trap transfer and was collected *in vacuo* in a 1-mm cell. The spectrum was obtained at much less than the saturated vapor pressure of the compound. A satisfactory but unknown pressure for the compound was obtained by pumping off $HMn(CO)_5$ until this desired pressure was reached as shown by a reasonable absorbance value in the uv spectrum. When the cell was allowed to stand for a period of 3 hr, there were no observable changes in the spectrum. This was taken as an indication of the absence of decomposition.

$HRe(CO)_5$ was obtained in a similar manner to its Mn analog. However the vapor pressure at room conditions was low enough to yield a good spectrum covering the uv region. The spectrum of this compound was also obtained in C_6H_{12} by introducing the solvent into the evacuated cell in successive amounts until a suitable concentration was reached.

Spectra of CF_3- and $CH_3Mn(CO)_5$ were obtained in CH_3OH and C_6H_{12}. Vapor spectra were obtained in air at room temperature in 5-mm cells above pure crystals of the compounds.

Spectra of Cl- and $BrMn(CO)_5$ were observed in CCl_4, C_6H_{12}, and CH_3OH. Molar absorptivity values in CH_3OH were calculated for the high-energy bands and in CCl_4 for the low-energy bands. CH_3OH was used in preference to C_6H_{12} because of a smaller tendency of the monomer to form the tetracarbonyl dimers in CH_3OH. The solubility of these compounds in CCl_4 made possible the dererminations of low-energy, low-ε bands but the formation of the tetracarbonyl dimers in some cases precluded accurate λ measurements. Gentle heating of solutions of the chlorine and bromine pentacarbonyl compounds resulted in the rapid formation of tetracarbonyl dimers. This, combined with the fact that solubilities of these compounds are very low, made the determination of the ε values difficult in nonpolar solvents.

$IMn(CO)_5$ was prepared from $Na^+Mn(CO)_5^-$ and I_2 in tetrahydrofuran solution. After the solvent was removed, the $IMn(CO)_5$ was purified by sublimation at room temperature and 1 mm pressure. A small amount of the tetracarbonyl dimer was isolated from the residue by sublimation at higher temperature than that used to separate and purify the $IMn(CO)_5$ compound. The ir spectra for these compounds agreed with those reported by Kaesz.[13] The uv spectra of $IMn(CO)_5$ were obtained in a variety of solvents, since solubility posed no problem.

The tetracarbonyl dimers [$Cl_2Mn_2(CO)_8$ and $Br_2Mn_2(CO)_8$] were formed in C_6H_{12} from the corresponding pentacarbonyl halide. A small amount of the crystalline Br dimer was isolated from C_6H_{12} and the uv spectrum was studied in nonpolar solvents. The ir spectrum corresponded to that reported by Kaesz.[13] A similar procedure was used to isolate and identify the Cl dimer. Figure 1 shows the changeover of the $ClMn(CO)_5$ compound to the chlorine tetracarbonyl dimer in C_6H_{12} in the visible region of the spectrum.

---

[11] N. A. Beach and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5713 (1968).

[12] R. B. King, "Organometallic Synthesis," Vol. I, Academic Press, New York, and London, 1965.

[13] M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, **2**, 158 (1963).

TABLE II

SUMMARY OF UV DATA AND ASSIGNMENTS FOR CLASS 2 COMPOUNDS

C_6H_{12} soln			CH_3OH soln			
λ_{max}, Å	$\bar{\nu}_{max}$, cm^{-1}	ϵ (rel intens)	λ_{max}, Å	$\bar{\nu}_{max}$, cm^{-1}	ϵ	Assignment[b]
			$ClMn(CO)_5$			
3750	26,670	(0.01)	3770	26,520	600 (570)[a]	A
c	*c*	*c*	~2700 sh	37,000	~1,500	B (D hidden)
2270	44,050	(0.5)	2220	45,050	13,000	C, G (weak)
1980	50,500	(0.6)	<1900	>52,600		E (F, H out of range
			$BrMn(CO)_5$			
3855	25,940	(0.02)	3835	26,070	420 (390)[a]	A
~2700 sh	~37,000	(0.07)	2700	37,000	1,700	B (D hidden)
2325	43,010	(0.45)	2275	43,950	15,000	C, G
~2000 sh	~50,000	(0.2)	1980	50,500	7,000	E
1880	53,000	(0.75)	*d*	*d*	*d*	H, F
			$IMn(CO)_5$			
4250	23,530	380	4000	25,000	360 (330)[a]	A
3050	32,800	2,310	2980	33,600	3,000	B
c	*c*	*c*	2750 sh	36,400	1,500	D
2380	42,000	15,300	2340	42,700	20,000	C, E
1970	50,800	79,000	1900	52,630	88,000	F, H

[a] Values in parentheses for CCl_4 solution. [b] Letters refer to transition assigned as shown in Figure 7. [c] Not observable. [d] Beyond spectral range.

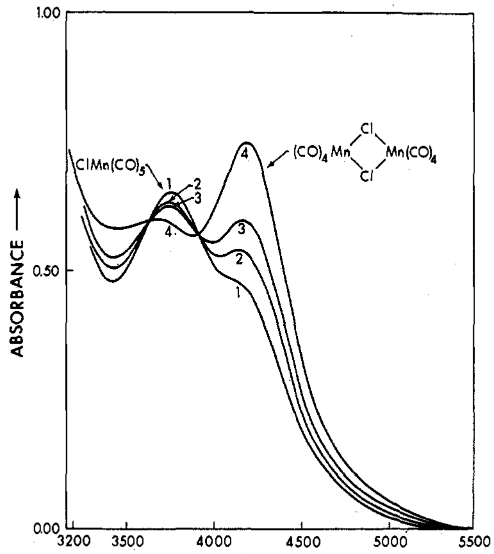

Figure 1.—Tetracarbonyl dimer formation from $ClMn(CO)_5$ in cyclohexane solution at room temperature; cell path length 10 cm. Curve 1 obtained 10 min after solution made up; curve 2, after 30 min; curve 3, after 50 min; curve 4, after 120 min.

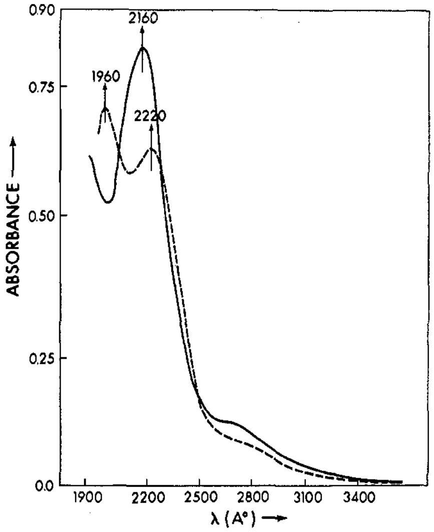

Figure 2.—Electronic spectra: – – – –, $CH_3Mn(CO)_5$, 1.7 × 10^{-4} *M*; ———, $CF_3Mn(CO)_5$, 2.4 × 10^{-4} *M*. Solvent and reference is cyclohexane; path length 1 mm.

Results

Tables I and II give the results of the uv and visible spectra of class 1 and 2 compounds. Figures 2–4 show the uv and visible spectra of these compounds.

Discussion

A generalized model used to describe the σ and π bonding in $LM(CO)_5$ compounds assumes that metal–CO σ bonding is accomplished by interaction of the lone pair on the carbon atom with some combination of metal s, p, and d orbitals. In σ bonding with the L atom or group s, p_z, and d_{z^2} metal orbitals are used in combination with appropriate L (σ) orbitals. π bonding involves the interaction of the filled d_{xy}, d_{xz}, and d_{yz} orbitals on the metal atom with the empty π^* orbitals on the carbonyl groups to give d–π^* back-bonding.

π interactions between filled metal d orbitals of suitable symmetry and p or d orbitals of the L atom or group may take place, *e.g.*, π repulsion between Cl 3p and Mn $3d_{xz,yz}$. In the absence of orbitals of suitable symmetry, size, and energy no π interactions are possible, as when L is H or CH_3.

Models based on this bonding picture have accounted reasonably for changes in the CO stretching force constants as L is varied.[1,14]

Electronic structures and MO diagrams for group VIb metal hexacarbonyls (O_h symmetry) have been reported with varying degrees of sophistication and some controversy.[11,15–17]

The corresponding diagrams for $LM(CO)_5$ compounds are based on C_{4v} symmetry, and the O_h energy levels are split accordingly. Changes in the levels for the C_{4v} compounds are dictated by the following. (i) The metal core has now a charge of 1+ compared to zero in the hexacarbonyl species. This results in a lowering of all the energy levels. (ii) One :CO group has been replaced by :L^-. This will raise energy

---

(14) W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).

(15) H. B. Gray and N. A. Beach, *J. Amer. Chem. Soc.*, **85**, 2922 (1963).

(16) A. F. Schreiner and T. L. Brown, *ibid.*, **90**, 3366 (1968).

(17) (a) D. S. Carroll and S. P. McGlynn, *Inorg. Chem.*, **7**, 1285 (1968); (b) K. S. Caulton and R. F. Fenske, *ibid.*, **7**, 1273 (1968).

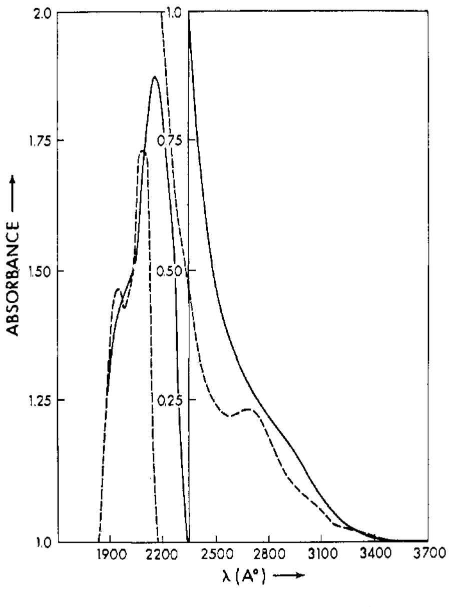

Figure 3.—Electronic spectra of (——) $HMn(CO)_5$ and (- - - -) $HRe(CO)_5$ in the vapor phase in 1-mm cells with air as the reference. Absorbance values for the higher λ region of the spectra extend from 0.0 to 1.0 and in the lower λ region from 1.0 to 2.0.

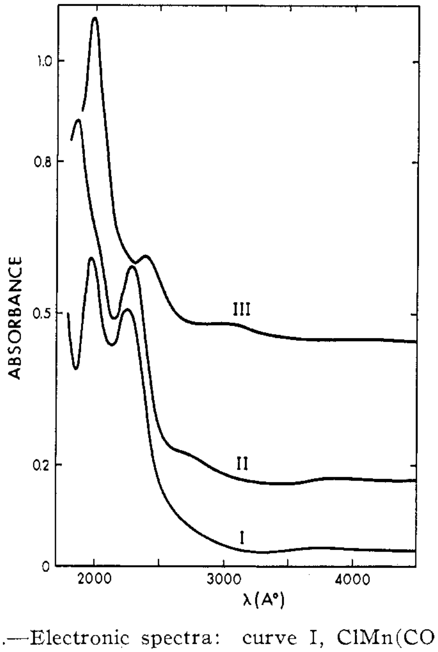

Figure 4.—Electronic spectra: curve I, $ClMn(CO)_5$, 3.5 × 10^{-4} *M;* curve II, $BrMn(CO)_5$, 2.0 × 10^{-4} *M;* curve III, $IMn(CO)_5$, 0.8 × 10^{-4} *M.* Path length 1 mm. Solvent and reference is cyclohexane. The base line has been successsively displaced in going from curves I to III. Concentrations for the chlorine and bromine pentacarbonyl halides have been estimated from more precise ε values determined in methanol.

levels, especially those associated with the $+z$ axis, by amounts which depend upon the size and electronegativity of the L group or atom. (iii) The ligand will differ from CO in its π characteristics: it may be a better or a poorer π acceptor, or it may have π-donating ability.

The net effect of (i) and (ii) will be a general lowering of all levels, since (i) will predominate. Other specific interactions as cited by (ii) and (iii) may raise or lower particular levels.

Class 1 Compounds

If we now consider class 1 Mn compounds, we propose an energy level diagram as in Figure 5. A number of the levels are essential to the bonding in the molecule but are not expected to play a significant part in the observation of the electronic spectra. For this reason little more will be said of the strongly σ-bonding orbitals (grouped at one level for convenience), the filled π orbitals on the CO's, and the strongly antibonding σ* orbitals.

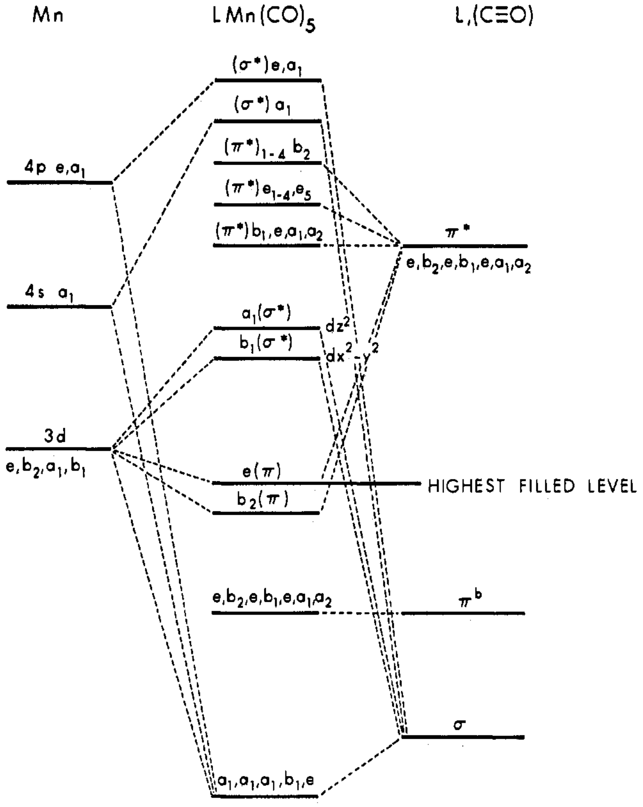

Figure 5.—Qualitative energy level diagram for class 1 $LM(CO)_5$ compounds.

Orbitals of the $:L^-$ group (not all shown in Figure 5) may have either σ or π symmetry with respect to the L–Mn bond axis. In the ionic approach taken here the corresponding energy levels will be high for the $:L^-$ anion but will drop sharply as charge is transferred to the $Mn(CO)_5^+$ group through σ bonding. For the class 1 and class 2 compounds considered here the resultant energy levels will be low-lying σ or high-energy σ* levels and will not participate directly in uv transitions at less than 50,000 cm^{-1}.

We shall discuss the levels that are primarily involved in the transitions we observe beginning first with the filled d_π orbitals, then the empty d_{σ^*} levels, and finally the π* CO levels. We place the $e(d_{xz}, d_{yz})$ level above the $b_2(d_{xy})$ level because of the lack of any π accepting properties of class 1 ligands. This lack results in a decrease in *total* π back-bonding with the $e(d_{xz}, d_{yz})$ orbitals, although there may well be a greater π back-bonding *per CO* for the remaining carbonyl groups, since there are now only five such groups as compared to six in the hexacarbonyl. This distinction between total π interaction and π interaction per CO is a major difference in ir and uv interpretations.

The placement of the Mn d_{σ^*} levels (a_1 and b_1) is dependent on the nucleophilic properties of L; they are generally expected to be just below the π^* (CO) levels.

Among the π^* levels of the CO groups, we distinguish three types: (i) those whose symmetry or geometry forbids interaction with the Mn orbitals [*i.e.*, π^* CO_{1-4} (a_1, a_2, b_1, and e)] and which we label π^* noninteracting or π^* NI; (ii) those which interact with $b_2(d_{xy})$ of Mn [*i.e.*, π^* CO_{1-4} (b_2)]; (iii) those which interact with e(d_{xz}, d_{yz}) of Mn [*i.e.*, π^* CO_{1-4} (e) and π^* CO_5 (e)].[18]

The final energy level diagram thus has as its highest filled levels the e and b_2 (Mn $3d_{xz}$, $3d_{yz}$, $3d_{xy}$) and as its lowest empty levels the a_1 and b_1 (Mn $3d_{z^2}$, $3d_{x^2-y^2}$) and the various π^*(CO) levels. The lowest energy transitions possible are d–d, followed by the Mn to CO charge-transfer transitions.

Recent pe spectral results[9] allow placement of the filled metal d orbitals on an absolute scale and, combined with the uv spectral results, can yield qualitative placement of the π^*(CO) levels. Because of its greater interaction, the $\pi^*(CO)b_2$ level is placed above that of the π^*(CO)e levels. The π^*(CO)NI levels will appear as the lowest of the antibonding π levels. The placement of the levels in this way indicates six possible CT transitions from the M(π) to the CO(π^*) levels. The placement of the energy levels corresponding to the bonding σ and π electrons of the CO ligands indicates that transitions from these levels to the empty levels in class 1 compounds should not appear within the range of our observations. Transitions from filled M(π) orbitals to metal σ^* orbitals (d–d transitions) are expected to be very weak and will often be masked by the M→L CT transitions. Figure 6 shows the placement of the M(π) and CO(π^*) levels on an energy scale which places the filled metal orbitals (e and b_2) at values calculated from pe spectra.[9] The π^* CO levels are placed at appropriate energies based on the observed uv transitions and the expected ordering of these levels.

The largest splitting in the antibonding levels is shown to be between the π^*(CO)NI levels and the π^*(CO)e levels. It is expected that the splitting between π^* levels that interact with the metal π orbitals and levels which do not interact will be larger than splittings between two levels whose interactions differ only slightly (π^*(CO)e and $\pi^*(CO)b_2$). Quantum mechanical calculations show that for $Cr(CO)_6$ there is little involvement of the metal p orbitals in π bonding[16] and any splitting brought about by the interaction of the metal p orbitals with π^* levels of appropriate symmetry is expected to be small. For this reason the π^*(NI) levels are grouped at one level in the energy diagram.

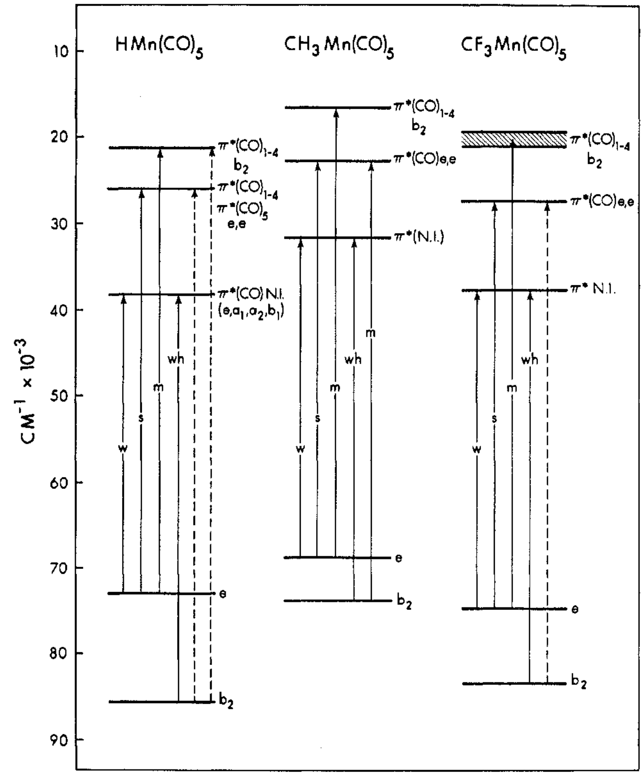

Figure 6.—Placement of the M(π) and CO(π^*) levels on an absolute energy axis for class 1 compounds. Legend: w, weak; s, strong; m, medium; wh, weak hidden; transitions denoted by dotted lines are beyond the range of the instrument.

Consistent with assignments in the hexacarbonyl compounds, transitions occurring from the metal π orbitals to the group of lowest lying π^*(CO) levels, in our case π^*(NI), are expected to be much weaker than transitions from the metal π orbitals to the π^*(CO) (e and b_2) levels. The summary of the assignments for the observed transitions for class 1 compounds is given in Table I. The assignment of the bands is internally consistent in terms of expected intensities and λ_{max} values of similar bands appearing in compounds of varying L. Where comparisons can be made, splittings in the filled metal π levels as calculated from the observed uv bands are consistent with those obtained from pe spectra.

Pe spectral results[9] indicate a reversal of the e and b_2 levels associated with the Mn d orbitals in $CH_3Mn(CO)_5$ as compared to other class 1 compounds examined. This is contrary to our expectations: there is no corresponding change in intensities of uv bands based on these two levels in our assignments (see Table I).

The λ_{max} of the intense CT band in class 1 compounds varies with the σ property of L as shown by the transition: CF_3, 47,200 cm^{-1}; H, 46,700 cm^{-1}; CH_3, 45,700 cm^{-1}. It appears that the stronger the σ-accepting ability of L the lower the d orbitals (e and b_2) will be placed and the higher will be the energy of the transition.

The reversal of the e and b_2 bands would affect the assignments of the uv bands only in that bands assigned as originating from the e and b_2 levels would be reversed in origin.

The comparison of CF_3- and $CH_3Mn(CO)_5$ (Figure 2) shows marked similarities. The highest energy band in the CH_3 compound appears red shifted and more intense than in the CF_3 compound. Figure 6 shows that the $M(b_2)\pi$–$CO(e)\pi^*$ transition, which is out of the spectrometer range for the CF_3 compound, should appear at approximately the same energy as the

[18] The π^* CO_{1-4} orbitals combine to yield two e combinations, one of which is oriented parallel to the z axis and one perpendicular to the z axis. Thus there are orientation limitations upon the interactions of these e levels with the four levels of the Mn(d_{xz}, d_{yz}); one of the π^* CO(e) levels is noninteracting (NI).

assigned $M(e)\pi$–$CO(b_2)\pi^*$ transition in the CH_3 compound and enhance the intensity of this highest energy band.

The ability of CF_3 to accept π charge from Mn by means of d–σ^* back-bonding has been suggested by Cotton.[19] This should result in a lowering of the $M(\pi)e$ level for the CF_3 as compared to the CH_3 compound. The uv results are inconclusive since the recognized differences in σ inductive effects can easily explain the observed blue shift.

A comparison of the uv spectra of the pentacarbonyl hydrides of Mn and Re (Figure 3) shows blue shifts of the uv bands in going from $HMn(CO)_5$ to $HRe(CO)_5$. This suggests that the filled d levels of Re lie at a lower level than those of Mn. If so, there should be less d–π^* back-bonding for Re than for Mn. Reported force constants for these hydrides[20] are in agreement with this interpretation.

Although pe spectra are not currently available for the $HRe(CO)_5$ compound, uv spectra and assignments similar to those for $HMn(CO)_5$ are shown in Table I.

The spectrum of the rhenium pentacarbonyl hydride (Figure 3) indicates that there are two weak bands on the low-energy side of the band assigned as $M(\pi)e$–$CO(\pi^*)NI$. Although the origin of these bands is not certain, we suspect that they are either d–d transitions from the filled metal π orbitals to the σ^* metal orbitals or triplet components of higher intensity bands.

Class 2 Compounds

Class 2 compounds are represented by $ClMn(CO)_5$, $BrMn(CO)_5$, and $IMn(CO)_5$ whose uv spectra and corresponding assignments are illustrated in Figure 4 and Table II. A level diagram is presented in Figure 7. The bands are lettered in this diagram for quick reference. The placement of the filled metal and halide π levels in Figure 7 is based on pe spectra and their interpretation.[9]

The energies of the $\pi(X)e$ levels have a direct bearing on the amount of halide character expected in the uppermost filled e level. Quantitative measures of halide character are uncertain, but the iodine compound is expected to have the largest such character because its filled orbitals are closest in energy to the $Mn(\pi)d$ levels. The $CO(\pi^*)NI$ levels are grouped at one level as for class 1 compounds. The $CO(\pi^*)b_2$ level is placed above that of the $CO(\pi^*)e$ since the b_2 level has the greatest interaction with the filled metal orbitals. The $(CO)_{1-4}(\pi^*)e$ and the $(CO)_5(\pi^*)e$ are grouped at one level since, as later results show, bands with separations of 2500 cm^{-1} are not resolvable. It is assumed that the splitting in these levels is less than this. The π^*-antibonding levels are placed in accordance with arguments developed for class 1 compounds.

The assignments as outlined in Table II are based on the following general considerations. (i) Transitions to the lower antibonding $\pi^*(CO)$ levels ($\pi^*(NI)$) are generally much weaker than transitions to higher $\pi^*(CO)$ interacting levels. (ii) Transitions to $\pi^*(CO)$-NI levels from predominantly metal bonding orbitals show little solvent effect; transitions to higher π^* states show marked solvent shifts.[11,15] (iii) Transitions which originate from filled levels involving a large amount of halide character may be expected to exhibit a solvent effect, regardless of the π^*-antibonding level to which the transition takes place. (iv) The antibonding states are expected to exist over a range of energies. This accounts in part for the broadness of the observed bands and the fact that weak bands may be hidden by bands of greater intensity which occur at or near the same energy. (v) Triplet states are neglected although it is possible that they may play some role in the case of iodine compounds.

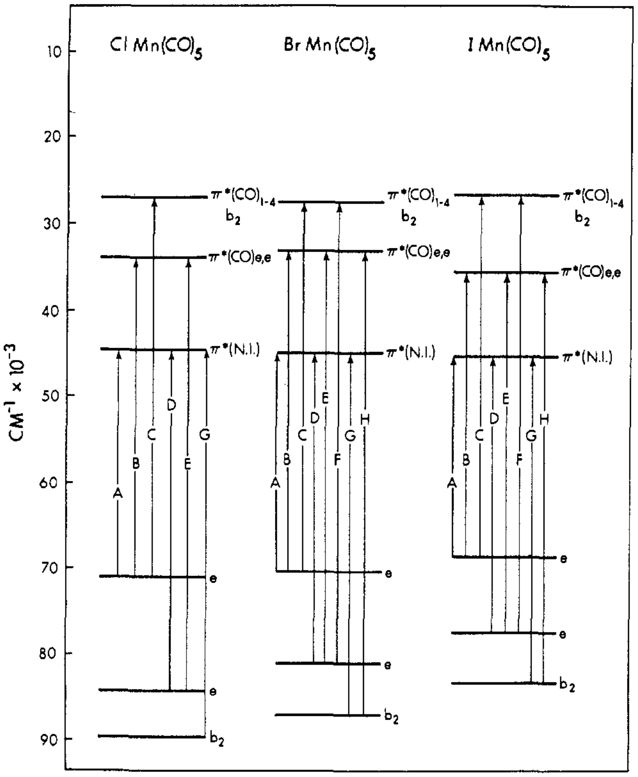

Figure 7.—Placement of the $M(\pi)$, $X(\pi)$, and $\pi^*(CO)$ levels for class 2 compounds.

Band A is expected to be a weak band since it is a transition to the $\pi^*(CO)NI$ levels from the uppermost filled e level. Solvent shifts are an indication of the amount of halide character in this level. The negligible solvent shift for the Cl compound, the small blue shift for the Br compound, and the large blue shift for the I compound indicate that the largest degree of halide character occurs in the upper e level of the $IMn(CO)_5$. The pe spectrum indicates approximately 50% halide character in this e level for $IMn(CO)_5$,[9] although quantum mechanical calculations indicate that there is over 90% halide character in the uppermost filled e level,[10] for even the pentacarbonyl bromide and chloride. Our observed solvent shifts and changing intensities for the band originating from this e level suggest large decreases in the halide character from I to Br and Cl.

The width of band A for the I compound is double that for the Cl and Br compounds. This is in keeping with the spin–orbit coupling predicted by the pe spectrum[9] for $IMn(CO)_5$. In addition the behavior of this band in polar solvents (Figure 8) shows distinctly that two bands are present, although not completely

---

(19) F. A. Cotton and J. A. McCleverty, *J. Organometal. Chem.*, **4**, 490 (1965).

(20) P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **89**, 2851 (1967).

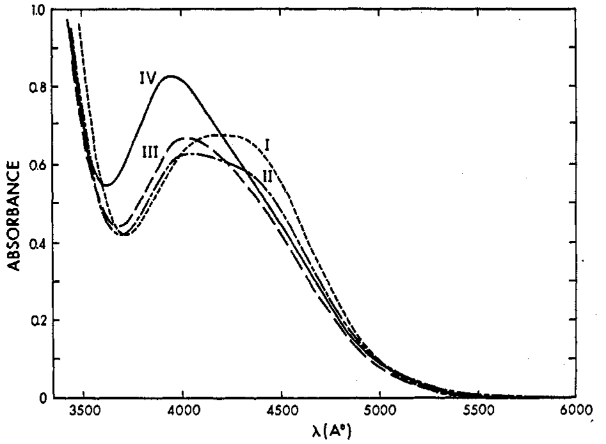

Figure 8.—Behavior of the e(π) → π^*(CO)NI band in polar and nonpolar solvents for IMn(CO)$_5$: curve I, 0.134 g/l., in CCl$_4$; curve II, 0.132 g/l., in CHCl$_3$; curve III, 0.120 g/l., in CH$_2$Cl$_2$; curve IV, 0.160 g/l., in CH$_3$OH.

resolvable. In nonpolar solvents the band width is large and the band is slightly asymmetric. The appearance of the spectra in polar solvents indicates not only an increased splitting of these two bands but also an apparent intensity enhancement of the higher energy component. The increased splitting is in keeping with expected increased spin–orbit coupling.

In the Cl compound no band appears in the region of 37,000 cm^{-1} in cyclohexane solution, but in CH$_3$OH solution a weak shoulder appears in this region. In BrMn(CO)$_5$ the shoulder appears in both polar and nonpolar solvents but with little observable solvent shift. For the I compound band B occurs in both solvents with a large solvent shift similar to that for band A (600 cm^{-1}). These observations and our assignment of this band as a transition from the upper filled e to the π^*(CO)e are consistent with the previous discussion of band A.

For all three pentacarbonyl halides a strong band appears in the region of 43,000 cm^{-1} which shows in all cases a blue shift from nonpolar to polar solvents. We assign this as a combination of two bands arising from the filled π levels: b$_2$–π^*(CO)NI in ClMn(CO)$_5$; e–π^*(CO)b$_2$ and b$_2$–π^*(CO)NI in BrMn(CO)$_5$; e–π^*(CO)b$_2$ and e–π^*(CO)e in IMn(CO)$_5$. The energy separation of these components is too small to allow resolution. In addition, one of these bands is expected to be weak since the transition is to the π^*(NI) levels. The intensity of this band increases slightly from the Cl to the Br to the I compound. The increase in band intensity for the I compound over those for the Br and Cl compounds may well be a result of the coincidence of the main band with the e$_{\text{lower}}$–π^*(CO)e, a band expected to be more intense than the b$_2$–π^*(CO)NI.

The e$_{\text{lower}}$–π^*(CO)NI band in the I compound is expected to be weak and also to occur at lower energies than for the Br and Cl compounds. No band is evident at the expected energy in cyclohexane solution, but in CH$_3$OH solution a weak shoulder appears at 37,000 cm^{-1} between the 42,000- and 32,800-cm^{-1} bands which could be this transition. The increasing metal character of the lower e level for the I compound could account for a smaller solvent shift than for the higher energy bands and the appearance of this weaker shoulder in IMn(CO)$_5$.

The end absorption region of the spectrum shifts to lower energy for the I and Br compounds from that of the Cl one. This is expected on the basis of the higher lying filled π levels and relatively unchanged antibonding levels for IMn(CO)$_5$. This would indicate a larger number of possible transitions of fairly high intensity. Although we suspect that the transitions in this region are mainly M–π^*(CO) and X–π^*(CO) or a mixture of these where M(π)–X(π) interaction is strong, we cannot rule out the possibility of L(σ) to M(σ^*) transitions contributing to the intensities. Pe spectral results do however suggest that the CO σ and π levels lie at such low energies that transitions from these levels to empty π^*(CO) levels occur at energies much larger than 50,000 cm^{-1}.

The placement of the energy levels for the various pentacarbonyl halides and the assignments of the bands are generally consistent internally for the series of compounds examined and indicate splittings in the ground-state levels consistent with those reported for pe spectra. However it must be borne in mind that the ground-state levels were calculated from compounds in the vapor state for pe spectra whereas the uv spectral results are taken from solutions in nonpolar solvents.

The ir spectra of the halide compounds and calculated C–O force constant values (k_1 and k_2) show a small but significant trend for which no entirely satisfactory explanation has been proposed. The values of the force constants listed below are taken from ref 14.

	k_1 (axial)	k_2 (equatorial)
ClMn(CO)$_5$	16.22	17.50
BrMn(CO)$_5$	16.26	17.41
IMn(CO)$_5$	16.30	17.28

Since the axial k's are more affected by π interaction than the equatorial ones, these values indicate that there is less π interaction for the I compound than for the Cl and Br compounds giving a higher axial force constant. The trend in equatorial k's, as expected from inductive effects, shows increasing π interaction from Cl to Br to I. The opposite trend in the axial force constants may well be the result of the increasing halide character in the M(π)e level from Cl through to the I compound, which should decrease the efficiency of the M(π)–CO(π^*) interaction by distortion of the M(π)e orbital. This is consistent with the relatively small changes in the antibonding levels we have shown in Figure 7.

The low-energy absorption bands for the tetracarbonyl dimers (TCD) of Cl, Br, and I are shown in Table III. Figure 1 shows the ready conversion of ClMn(CO)$_5$ to the Cl TCD in cyclohexane. The intensity of the lower energy band is obviously greater for the dimer than for the monomer. The Br monomer

TABLE III

Compd	λ, Å	$\tilde{\nu}_{\max}$, cm^{-1}	ϵ	Assignment
Cl$_2$Mn$_2$(CO)$_8$	λ_1 4200	23,800	~10^3	a$_g$,b$_{2u}$ → π^*(CO)NI
	λ_2 ~3400	29,400	10^2–10^3	b$_{2g}$,b$_{2u}$ → π^*(CO)NI
Br$_2$Mn$_2$(CO)$_8$	λ_1 4330	23,100	2300	a$_g$,b$_{2u}$ → π^*(CO)NI
	λ_2 ~3400	29,400	~700	b$_{2g}$,b$_{2u}$ → π^*(CO)NI
I$_2$Mn$_2$(CO)$_8$	λ_1 4380	22,800	10^2–10^3	a$_g$,b$_{2u}$ → π^*(CO)NI
	λ_2 ~3500	28,600	10^2–10^3	b$_{2g}$,b$_{2u}$ → π^*(CO)NI

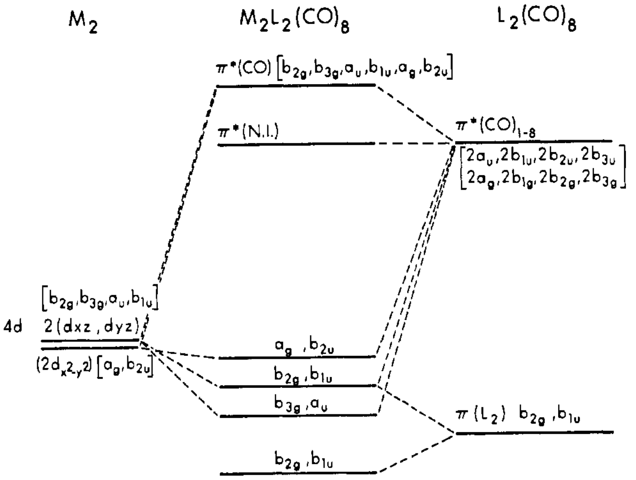

Figure 9.—Qualitative energy level diagram for the tetracarbonyl halide dimers of Mn. The symmetry labels are those for $L_2Mn_2(CO)_8$ (D_{2h}).

converts more slowly to the corresponding TCD in cyclohexane while the I monomer is stable. The decreasing *total* π interaction for the TCD compounds (since there are now only four carbonyls to accept π charge from each Mn) should result in a higher placement of the metal π levels. The a_g, b_{2u} level is placed highest since the $d_{x^2-y^2}$ orbitals interact with only two CO's each and the resulting orbital will have the least amount of *total* d–π^* interaction. This accounts for the red shift of the low-energy band from monomer to dimer. The highest lying filled orbitals in the tetracarbonyl dimer compound should not interact with the halide orbitals of π symmetry, which may account for the greater intensity of the first observed band in the TCD compound as compared to the monomer. Increasing halide character in the highest filled e level in the monomer compounds appears to have a similar effect on the intensity of a similar band. Figure 9 gives a qualitative energy level diagram for the tetracarbonyl dimers, showing only the filled π levels and the antibonding π^*(CO) levels. The assignments as proposed in Table III indicated a splitting of approximately 6000 cm^{-1} in the two uppermost filled π levels.

Acknowledgments.—We are grateful to W. A. G. Graham and his group for the compounds studied and for discussions and suggestions. We also thank the National Research Council of Canada for a scholarship to G. B. B.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CALIFORNIA STATE COLLEGE, LOS ANGELES, CALIFORNIA 90032

Carboranes from Alkylboron Hydrides

BY ELLIOTT GROSZEK, JOHN B. LEACH, GEORGE T. F. WONG,
CHARLES UNGERMANN, AND THOMAS ONAK*

Received April 13, 1971

Both one-carbon and two-carbon carboranes have been prepared from the flow pyrolysis of several alkylboron hydrides. Carbahexaborane(7) and 2-carbahexaborane(9) have been prepared from methylpentaborane(9) and the corresponding *C*-methyl derivatives of these carboranes are obtained from ethylpentaborane(9). Pyrolysis of 1,2-dimethylpentaborane gives a modestly high yield of 1,5-$C_2B_3H_5$ and, surprisingly, no detectable quantity of *B*-methyl derivatives of CB_5H_7. The four-carbon carborane $C_4B_2H_6$ is obtained in low yield from 1,2-tetramethylenediborane(6). Temperature-dependent nuclear magnetic resonance studies on CB_5H_7 and its *C*-methyl derivative reveal a bridge hydrogen tautomerism with a $\Delta G^{\ddagger}$ of *ca.* 14 and 12 kcal, respectively.

Introduction

Nearly all previously known synthetic routes to the parent carboranes involve either a reaction of acetylene with boron hydrides or a degradation of a larger carborane. As one example, preparation of the trigonal-bipyramidal $C_2B_3H_5$ has been accomplished, variously, by the electric discharge or pyrolysis of acetylene with either pentaborane or diborane or by the decomposition of $C_2B_4H_8$.[1] The latter carborane compound, itself, is prepared by the thermal interaction of pentaborane and acetylene.[1]

A preliminary experiment involving methylpentaborane as a starting material indicated that a low-pressure pyrolysis produces small amounts of the carborane CB_5H_7.[2] This paved the way for the present study into the conversion of alkyl carbons (as ligands on boron hydrides) to cage carborane carbons.

Experimental Section

Materials.—1-Methyl-, 2-methyl-, 1,2-dimethyl-, and 1-ethylpentaboranes were prepared using previously known synthetic methods.[3] 1,2-Tetramethylenediborane(6) was prepared by the ether-catalyzed reaction between diborane and 1,3-butadiene.[4] All chemical manipulations were carried out in a standard high-vacuum apparatus. All compounds were purified using either a special low-temperature, high-vacuum distillation column[5] or a 30% Kel-F on firebrick glpc column and identified by mass, ir, and nmr spectroscopic data.

---

[1] For references see R. E. Williams, "Progress in Boron Chemistry," Vol. 2, Pergamon Press, Oxford, 1969, Chapter 2, p 51; and R. N. Grimes "Carboranes," Academic Press, New York, N. Y., 1970.

[2] T. Onak, P. Mattschei, and E. Groszek, *J. Chem. Soc. A*, 1990 (1969).

[3] For appropriate references consult P. M. Tucker, T. Onak, and J. B. Leach, *Inorg. Chem.*, **9**, 1430 (1970).

[4] D. E. Young and S. G. Shore, *J. Amer. Chem. Soc.*, **91**, 3497 (1969).

[5] J. Dobson and R. Schaeffer, *Inorg. Chem.*, **9**, 2183 (1970).