

The Intermetallic Bond in Some Carbonyl Compounds
with a Heterogeneous Metal-Metal Bond

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The intermetallic bond in compounds of formula $(CO)_5M-M'R_3$ ($M = Mn, Re; M' = C, Si, Ge, Sn, Pb$) and $\pi-C_5H_5(CO)_nMM'R_3$ ($M = Fe, Mo; n = 2, 3; M' = Ge, Sn, Pb$) was studied by using infrared ($C=O$ and $M-C$ stretchings) and n.m.r. (τ values of $\pi-C_5H_5$ ring) spectra and dipole moments in solution. It was found that only inductive effects of R groups were operative on the electronic density of the transition metal. The polarity of the metal-metal bonds was found low and with the following distribution of charge $M^{\delta+}-M'^{\delta-}$. However, the metal-metal bonds seem to be very polarisable in the following order $M-Si < M-Ge < M-Sn < M-Pb$.

In all these works a π interaction was proposed in order to explain the i.r. spectra of some carbonyl compounds⁸⁻¹¹ and the ¹⁹F chemical shift of some aryl platinum compounds having Pt to Sn bond.⁷

However, in our opinion a systematic investigation of related compounds of the type $(CO)_5M-M'R_3$ ($M = Mn, Re; M' = C, Si, Ge, Sn, Pb$) and $(\pi-C_5H_5)(CO)_nM-M'R_3$ ($M = Mo, Fe; n = 3, 2; M' = Ge, Sn, Pb$) (Table I) could give a more clear picture of the metal-metal interaction.

We report here an investigation by infrared and n.m.r. spectra and dipole moments in solution on these and related compounds.

Experimental Section

Infrared spectra in the region 200-400 cm^{-1} were recorded on Perkin-Elmer 621 (grating) spectrometer.

Infrared spectra at higher frequencies (combination bands) were determined using a Perkin-Elmer 125.

¹H n.m.r. spectra were recorded on a Perkin-Elmer R-10 instrument operating at 60 Mc./sec. with tetramethylsilane as internal standard.

Starting materials were prepared by standard methods. Reactions were carried out in a nitrogen atmosphere, according to a general method where $Na[Mn(CO)_5]$, $Na[Re(CO)_5]$ and $Na[\pi-C_5H_5Fe(CO)_2]$ were involved.

The compounds are listed in Table I, where analytical data are also given. Other properties are reported on the tables.

$Mn(CO)_5Sn(C_2H_5)_3$. A tetrahydrofuran (THF) solution of $Na[Mn(CO)_5]$ was prepared from 300 mg of $Mn_2(CO)_{10}$ and sodium amalgam (100 mg of Na and 1 ml of Hg) in 10 ml of dry THF. The reaction mixture was stirred at room temperature for 1 hr. and then the mercury was separated. Subsequently a solution of triethyltin chloride (0.26 ml) in dry THF (10 ml) was added in small portions and the reaction mixture was stirred at room temperature for 3 hr. The solvent was removed under vacuum and the residual oil was extracted with n-hexane. Distillation on small scale (130°C/0.3 mm) gave the pure compound.

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Introduction

The increasing interest on the preparation¹ and reactivity² of transition metal compounds with metal-metal bonds has stimulated many speculations on the nature of this type of bond. In a general survey^{3,4} of some physical properties such as magnetic interactions, bond distances and reactivity, the nature of this bond was correlated with oxidation states and configurations of the metals involved in the bond. The strength of the metal-metal bond was found to decrease from a multiple bond, such as in $[Re_2Cl_8]^{2-}$,⁵ to a weak interaction such as in some d^8 complexes compounds.^{4,6}

Between the many classes of compounds with metal-metal bond, compounds with an heterogeneous bond between a transition metal and a group IV B metal were the more extensively studied.

The nature of this type of bond has been investigated by Parshall,⁷ Stone,⁸ Graham,⁹ Bigorgne¹⁰ and by us.¹¹

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Table I.

Compound	Colour	M.P. °C ^a		C		Analyses	
		obs.	lit.	calc.	found	calc.	H found
Mn(CO) ₅ SnCl ₃	white	167-68	168 ^b				
Mn(CO) ₅ SnCl ₂ C ₆ H ₅	white	84.5	83.5 ^b				
Mn(CO) ₅ SnCl(C ₆ H ₅) ₂	white	94.5	97.8 ^b				
Mn(CO) ₅ Sn(C ₆ H ₅) ₃	white	151	148-50				
Mn(CO) ₅ Sn(C ₂ H ₅) ₃	white	liquid	this work	32.9	33.2	3.7	3.9
Mn(CO) ₅ Pb(C ₆ H ₅) ₃	pale-yellow	146	146-48 ^b				
Mn(CO) ₅ Pb(C ₂ H ₅) ₃	yellow	liquid	liquid ^b	27.0	27.4	3.1	3.2
Mn(CO) ₅ Ge(C ₆ H ₅) ₃	white	162	162-64 ^c				
[Mn(CO) ₅] ₂ SnCl ₂	white	145	143-44 ^b				
[Mn(CO) ₅] ₂ Sn(C ₆ H ₅) ₂	white	137	137-39 ^b				
<i>trans</i> -Mn(CO) ₄ PPh ₃ SnCl ₃	white	157	159 ^b	40.4	40.6	2.3	2.3
<i>trans</i> -Mn(CO) ₄ PPh ₃ Sn(C ₆ H ₅) ₃	white	228	228-30 ^b				
Re(CO) ₅ SnCl ₃	white	220	220 ^d	10.8	11.3	0.0	0.0
Re(CO) ₅ Sn(C ₆ H ₅) ₃	pale-yellow	145-46	142-43 ^d	40.8	40.7	2.2	2.0
Re(CO) ₅ Ge(C ₆ H ₅) ₃	pale-yellow	156	157.5-158.5 ^e	43.8	43.5	2.4	2.8
Re(CO) ₅ C(C ₆ H ₅) ₃	pale-yellow	98-100	this work	49.5	48.4	2.6	2.9
π-C ₅ H ₅ Fe(CO) ₂ SnCl ₃	ocre-yellow	158	157 ^f				
π-C ₅ H ₅ Fe(CO) ₂ Sn(C ₆ H ₅) ₃	yellow	140	139-41 ^b				
π-C ₅ H ₅ Fe(CO) ₂ Sn(C ₂ H ₅) ₃	red-orange	liquid	this work	40.8	40.1	5.2	5.0
π-C ₅ H ₅ Fe(CO) ₂ Pb(C ₆ H ₅) ₃	brown	130	this work	48.8	48.1	3.2	3.4
π-C ₅ H ₅ Fe(CO) ₂ Pb(C ₂ H ₅) ₃	red-orange	liquid	this work	33.1	32.7	4.2	4.5
π-C ₅ H ₅ Fe(CO) ₂ Ge(C ₆ H ₅) ₃	yellow	160	160-61 ^c				

^a Melting points were determined on a Leitz Heitzschmikroskop and are uncorrected. ^b See ref. (1a). ^c See ref. (31). ^d See ref. (32). ^e See ref. (9). ^f See ref. (1b).

Re(CO)₅C(C₆H₅)₃. To a THF solution of Na-[Re(CO)₅], obtained from Re₂(CO)₁₀ (0.5 g) in dry THF (10 ml) and sodium amalgam (200 mg of Na and 1.8 ml of Hg), a solution of triphenylcarbonchloride (220 mg) in dry THF (10 ml) was added in small portions. After 3.5 hr. under stirring the solvent was removed under vacuum and the residue was extracted several times with n-hexane in a nitrogen atmosphere. On evaporating the filtered solution and on cooling, pale-yellow crystals of the compound were obtained.

π-C₅H₅Fe(CO)₂Sn(C₂H₅)₃. A THF solution of Na-[π-C₅H₅Fe(CO)₂] was prepared from [π-C₅H₅Fe(CO)₂]₂ (300 mg) in dry THF (15 ml) and sodium amalgam (100 mg of Na and 1 ml of Hg). The mixture was stirred at room temperature overnight and after the mercury was removed. Subsequently a solution of triethyltin chloride (0.3 ml) in dry THF (10 ml) was added in small portions, and the reaction mixture was stirred at room temperature for 3 hr. The solvent was removed under vacuum, and the residual red oil was extracted with n-hexane. Distillation on small scale (150-180°C/0.4 mm) gave the compound.

π-C₅H₅Fe(CO)₂Pb(C₆H₅)₃. To a THF solution of Na-[π-C₅H₅Fe(CO)₂], obtained from [π-C₅H₅Fe(CO)₂]₂

(300 mg) in dry THF (15 ml) and sodium amalgam (100 mg of Na and 1 ml of Hg), a solution of triphenyllead chloride (780 mg) in dry THF (15 ml) was added in small portions. After 2 hr. under stirring the solution was filtered and evaporated to dryness. The residue was extracted several times with n-hexane. On evaporating the filtered solution and on subsequent cooling, brown crystals of the compound were obtained.

π-C₅H₅Fe(CO)₂Pb(C₂H₅)₃. This compound was prepared in a similar manner as the analogous tin derivative, but distillation on small scale or column chromatography always gave decomposition products. The red oil obtained evaporating the extraction solutions was sufficiently pure (see Table I) for our purposes.

Dipole moments. Dielectric constants were measured on a WTW dipolmeter DMO1. Dipole moments (Table II) were calculated by the Halverstand-Kumler formula¹²

$$P_{200} = \frac{3V_1\alpha_0}{(\epsilon_1 + 2)^2} + (V_1 + \beta) \frac{\epsilon_1 - 1}{\epsilon_1 + 2}$$

Table II. Dipole moments of some Manganese compounds

Compound	Solvent	W ₂ 10 ²	α ₀	-β	P ₂₀₀	P _E ^a	μ
Mn(CO) ₅ SnCl ₃	dioxane	0.962	15.2	0.4994	1114.2	50.5	7.21
Mn(CO) ₅ Ge(C ₆ H ₅) ₃	benzene	1.323	0.605	0.5063	151.8	109.1	1.45
Mn(CO) ₅ Sn(C ₆ H ₅) ₃	benzene	1.099	0.564	0.5063	161.7	109.1	1.60
Mn(CO) ₅ Pb(C ₆ H ₅) ₃	benzene	1.001	0.419	0.5063	170.7	109.1	1.87
<i>trans</i> -Mn(CO) ₄ PPh ₃ Sn(C ₆ H ₅) ₃	benzene	1.068	6.367	0.5063	1081.8	189.5	6.60
<i>trans</i> -Mn(CO) ₄ PPh ₃ SnCl ₃	dioxane	1.100	31.4	0.5433	3478.5	127.0	12.81

^a Calculated with the atomic refractivities, ref. (48).

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Results and Discussion

Infrared spectra: carbonyl stretching region. We have first examined the carbonyl stretchings of compounds of the series $(\pi\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe-X}$ and $(\pi\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo-X}$ (Tables III and IV). The iron compounds showed two strong absorptions which, on the ground of a probable local C_s symmetry, can be assigned to A' and A'' modes of vibration.

between the A'' vibration and Taft's polar constants σ^* of X groups¹⁴ (Figure 1).

No such correlation was obtained using Hammett's σ_H or resonance σ_R constants.

The frequencies of the A_1 or A'' absorptions in molybdenum compounds (which were assigned to the bands at higher frequency on the basis of their intensities)¹⁵ showed to be in linear correlation with Taft's polar constants σ^* (Figure 2).

Table III. C-O stretching frequencies and cyclopentadienyl hydrogen chemical shifts in $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$ molecules

X	Solvent	A''	A'	Solvent	$\tau\text{-C}_5\text{H}_5$ ^a
SnCl ₃	CH ₂ Cl ₂	2047 (vs)	2007 (vs)	CDCl ₃	4.80
SnBr ₃	^b	2045	1996	CDCl ₃	4.81
SnI ₃	^b	2032	1990	CDCl ₃	4.98
Sn(C ₆ H ₅)Cl ₂	^b	2033	1970	CDCl ₃	5.01
Ge(C ₆ H ₅) ₃	CH ₂ Cl ₂	1996 (vs)	1943 (vs)	CDCl ₃	5.26
Sn(C ₆ H ₅) ₃	CH ₂ Cl ₂	1993 (vs)	1941 (vs)	CDCl ₃	5.25
Pb(C ₆ H ₅) ₃	CH ₂ Cl ₂	1994 (vs)	1947 (vs)	CDCl ₃	5.20 - 5.27
Sn(C ₂ H ₅) ₃	CH ₂ Cl ₂	1978 (vs)	1924 (vs)	CDCl ₃	5.30
Pb(C ₂ H ₅) ₃	CH ₂ Cl ₂	1973 (vs)	1922 (vs)	CDCl ₃	5.23
Sn(CH ₃) ₃	— ⁱ	—	—	CHCl ₃	5.11
Cl	CCl ₄ ^c	2050 (vs)	2010 (vs)	CDCl ₃	4.98
I	CHCl ₃	2044 (vs)	2000 (vs)	CDCl ₃	4.99
CF ₃	nujol ^e	2053 (s)	2003 (s)	CHCl ₃ or CS ₂ ^e	5.01
CH ₃	CCl ₄ ^f	2010 (vs)	1955 (vs)	toluene ^f	5.70
C ₂ H ₅	CCl ₄ ^f	2010 (vs)	1950 (vs)	as pure liquid ^g	5.40
n-C ₃ H ₇	film ^g	2013 (vs)	1953 (vs)	as pure liquid ^g	5.41
iso-C ₃ H ₇	film ^g	2012 (vs)	1953 (vs)	as pure liquid ^g	5.42
C ₆ H ₅	nujol ^e	2021 (vs)	1969 (vs)	—	—
COCH ₃	cyclohex. ^h	2035 (s)	1969 (s)	CS ₂ ^h	5.13
COOCH ₃	cyclohex. ^h	2046 (s)	1995 (s)	CS ₂ ^h	5.14
CH ₂ COCH ₃	CS ₂ ⁱ	2028 (vs)	1976 (vs)	CCl ₄ ^f	5.10

^a TMS as internal standard. ^b See ref. (33). ^c See ref. (34). ^d See ref. (35). ^e See ref. (36). ^f See ref. (13). ^g See ref. (37). ^h See ref. (38). ⁱ See ref. (39). ^j See ref. (40).

Table IV. C-O stretching frequencies and cyclopentadienyl hydrogen chemical shifts in $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{X}$ molecules

X	Solvent	ν_{C-O}	ν_{C-O}	ν_{C-O}	Solvent	$\tau\text{-C}_5\text{H}_5$ ^a
SnCl ₃	CH ₂ Cl ₂ ^b	2049 (s)	1988 (s)	1964 (s)	CDCl ₃ ^c	4.34
Sn(CH ₃) ₂ Cl	CCl ₄ ^d	2013	1947	1913	CCl ₄ ^d	4.63
Sn(C ₆ H ₅) ₃	CCl ₄ ^d	2004	1934	1909	CDCl ₃	4.74
Sn(CH ₃) ₃	CCl ₄ ^d	1997	1922	1895	CHCl ₃ ^d	4.59
Cl	CCl ₄ ^e	2055 (vs)	1980 (vs)	1960 (vs)	CDCl ₃	4.71
Br	CCl ₄ ^e	2049 (vs)	1977 (vs)	1958 (vs)	—	—
I	CCl ₄ ^e	2040 (vs)	1968 (vs)	1955 (sh)	—	—
CF ₃	nujol ^f	2054 (s)	1976 (vs)	—	CS ₂ or CHCl ₃ ^f	4.41
H	CS ₂ ^e	2030 (vs)	1949 (vs)	—	toluene ^e	5.4
CH ₃	CCl ₄ ^e	2020 (vs)	1937 (vs)	—	toluene ^e	5.3
C ₂ H ₅	CCl ₄ ^e	2016 (vs)	1932 (vs)	—	CHCl ₃ ^d	4.68
iso-C ₃ H ₇	CCl ₄ ^e	2010 (vs)	1930 (vs)	—	CDCl ₃	4.75
					toluene ^e	5.2

^a TMS as internal standard. ^b See ref. (20). ^c See ref. (41). ^d See ref. (1f). ^e See ref. (13). ^f See ref. (36).

The molybdenum compounds showed two or three strong absorptions: the different number of bands could be attributed to an accidental degeneration or to a different coordination stereochemistry. In fact, as previously pointed out,¹³ a local C_{3v} symmetry (2 bands $A_1 + E$) or a local C_s symmetry (3 bands $2A' + A''$) could be present in such molecules.

The frequencies of the A'' vibration in the series $(\pi\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe-X}$ (when X is different from $M'R_3$) were found strictly dependent from the inductive power of the X group. In fact a linear correlation was found

A discontinuity was found in the correlation by passing from compounds with C_{3v} symmetry to compounds with C_s symmetry with the exception of the trifluoromethyl derivative for whom, however, a spectrum in nujol mull was reported.

No correlation was obtained using Hammett's σ_H or resonance σ_R constants. On the ground of these linear correlations it is reasonable to suppose that only inductive effects are operative on the frequencies of

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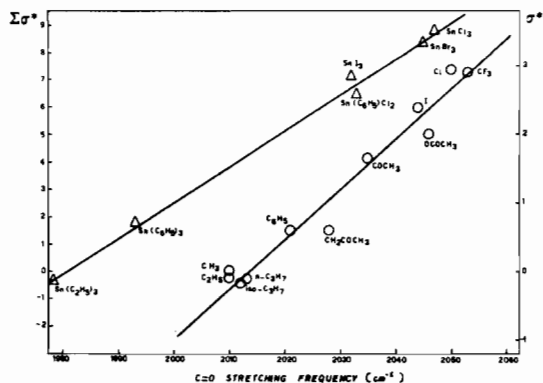


Figure 1. $\nu(\text{CO})$ (A'') of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$ (circles) and of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SnR}_3$ (triangles) against σ^* and $\Sigma\sigma^*$.

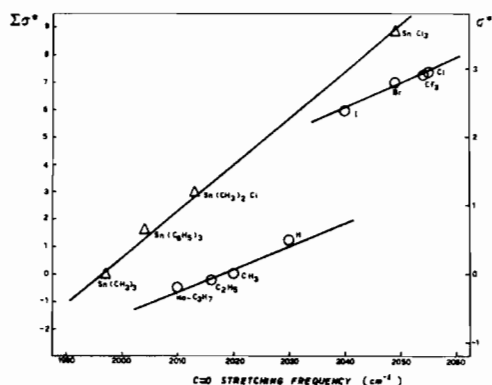


Figure 2. A_1 or A'' type carbonyl stretching frequency of $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{X}$ (circles) and of $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{SnR}_3$ (triangles) against σ^* and $\Sigma\sigma^*$.

carbonyl stretchings of the compounds above reported.

This proposition is confirmed by the linear correlation found between the same carbonyl stretchings and an entity, such as electronegativity, which is less sensitive than Taft's constants to steric requirements and secondary effects (Figure 3).

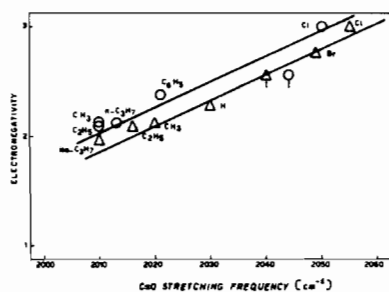


Figure 3. A'' type of carbonyl stretching frequency of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$ (circles) and of $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{X}$ (triangles) against the electronegativity of the X groups.

In order to have comparable figures we choose the group electronegativity calculated applying Pauling's method to thermochemical data of mercury organometallic compounds.¹⁶

When the carbonyl stretchings of compounds of the type $(\pi\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe-M}'\text{R}_3$ or $(\pi\text{-C}_5\text{H}_5)(\text{CO})_3\text{Mo-M}'\text{R}_3$

($M' = \text{Sn, Ge, Pb}$; $R = \text{halogen, Et, Me, Ph}$) are compared, a decreasing of the A_1 or A'' frequencies was found in the case of tin in the order $\text{Cl} > \text{Ph} > \text{Et} > \text{Me}$. This behaviour was previously explained by an increased π -acceptor properties of the tin atom in the order $\text{SnCl}_3 > \text{SnPh}_3 > \text{SnEt}_3 > \text{SnMe}_3$.⁷⁻¹¹

It seems, however that only inductive effects are again operative, probably through the σ bond, without changing the π bond, if any. Indeed nice linear correlations were found (Figures 1 and 2) between the sum of Taft's polar constants ($\Sigma\sigma^*$) of SnR_3 groups and A_1 or A'' stretching frequencies.

Besides, by passing from Sn to Ge and to Pb no appreciable variation of the values of carbonyl stretching frequencies was found (Tables III and IV).

The second series of compounds which was investigated have the general formula $(\text{CO})_5\text{MX}$ and $(\text{CO})_5\text{M-M}'\text{R}_3$ (see Table I).

Compounds of formula $(\text{CO})_5\text{MX}$ ($M = \text{Mn, Re}$) should have a C_{4v} symmetry, if no distortion is present; the carbonyl modes of stretching are of the type $A_1^{(1)}$, $A_1^{(2)}$ and E, according to Cotton's assignments.¹⁷

In Tables V and VI we have reported the frequencies of these absorptions with the relative assignments. In every case the $A_1^{(1)}$ carbonyl stretching which corresponds to the carbonyl vibration parallel to the four-fold axes in C_{4v} local symmetry and *trans* to X is well separated from the E stretching, which corresponds to the asymmetric vibration of the four carbonyls in the plane and *cis* to the X ligand.

As we have pointed out before,¹¹ the $A_1^{(1)}$ frequency should be most affected by change of X in *trans* position. It was now found that such a change is not only due to an inductive effect, because by plotting the $A_1^{(1)}$ frequency against Taft's polar constants σ^* of X groups we have not obtained any linear correlation.

However, good linear correlations were obtained by plotting $A_1^{(2)}$ or E frequencies against Taft's polar constants σ^* (Figures 4, 5, 6 and 7).

Similar linear correlations were also found between both these frequencies and the electronegativity of X groups.

It seems then that the X group in these compounds acts in a different way on *cis* or *trans* carbonyl groups;

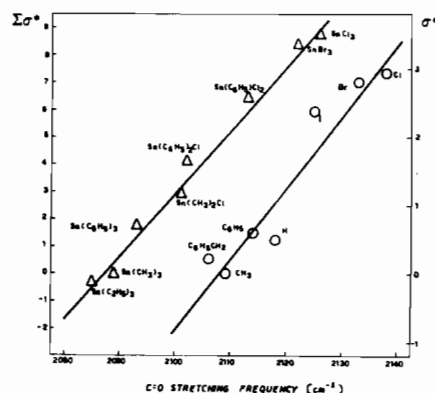


Figure 4. $A_1^{(2)}$ type of carbonyl stretching frequency of $\text{Mn}(\text{CO})_5\text{X}$ (circles) and of $\text{Mn}(\text{CO})_5\text{SnR}_3$ (triangles) against σ^* and $\Sigma\sigma^*$.

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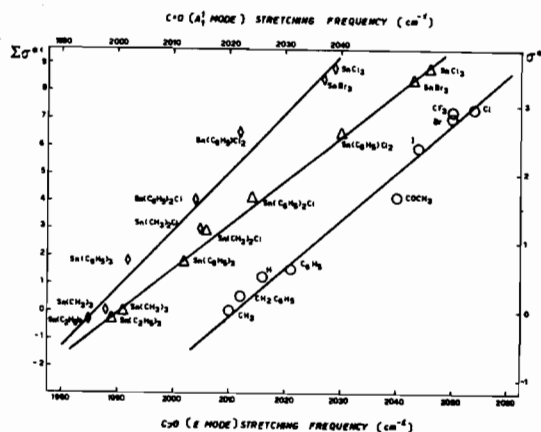


Figure 5. E type carbonyl stretching frequency of $\text{Mn}(\text{CO})_5\text{X}$ (circles), E type (triangles) and $\text{A}_1^{(1)}$ type (quadrangles) of $\text{Mn}(\text{CO})_5\text{SnR}_3$ against σ^* and $\Sigma\sigma^*$.

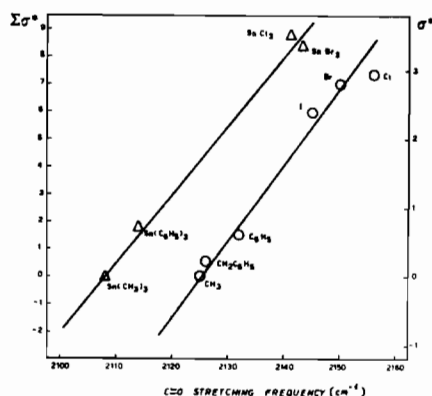


Figure 6. $\text{A}_1^{(2)}$ type carbonyl stretching frequency of $\text{Re}(\text{CO})_5\text{X}$ (circles) and of $\text{Re}(\text{CO})_5\text{SnR}_3$ (triangles) against σ^* and $\Sigma\sigma^*$.

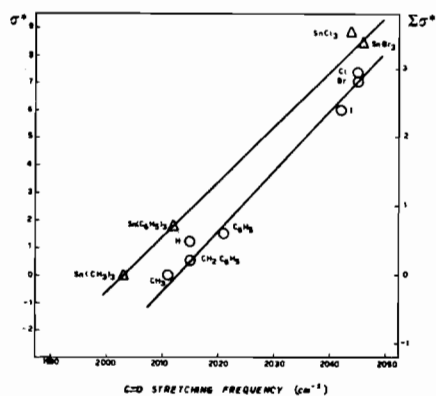


Figure 7. E type carbonyl stretching frequency of $\text{Re}(\text{CO})_5\text{X}$ (circles) and of $\text{Re}(\text{CO})_5\text{SnR}_3$ (triangles) against σ^* and $\Sigma\sigma^*$.

the *cis* carbonyl groups are affected only by the change of the average electronic density on the transition metal, while the *trans* group is affected, as expected,¹⁸ also by a strictly directional effect which could be a change in the π -bonding.

This hypothesis is supported by the linear correlations found between $\text{A}_1^{(1)}$ stretchings and the sum of Hammett's constants $\Sigma\sigma_{\text{H}}$ or of resonance constants

$\Sigma\sigma_{\text{R}}$. However the correlations were not very good for all the experimental points.

Compounds of formula $(\text{CO})_5\text{M}-\text{M}'\text{R}_3$ ($\text{M}' = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) should belong to the same C_{4v} local symmetry. However, (Tables V and VI), many of these compounds showed a degeneracy in that $\text{A}_1^{(1)}$ and E stretching frequencies were coincident, as we proposed before.¹¹

Table V. C-O stretching frequencies in $\text{Mn}(\text{CO})_5\text{X}$ molecules

X	Solvent	Assignments ^a		
		$\text{A}_1^{(2)}$	E	$\text{A}_1^{(1)}$
SnCl ₃	CH ₂ Cl ₂	2131 (w)	2045 (s)	2045 (s)
	cyclohex. ^b	2126	2046	2039
SnBr ₃	cyclohex. ^b	2122	2043	2037
	SnCl ₂ (C ₆ H ₅)	CH ₂ Cl ₂	2118 (w)	2029 (s)
cyclohex.		2114 (w)	2031 (s)	2022 (m,s)
SnCl(C ₆ H ₅) ₂	CH ₂ Cl ₂	2105 (w)	2012 (s)	2012 (s)
	n-hexane	2102 (w)	2015 (s)	2015 (s)
SnCl(CH ₃) ₂	cyclohex. ^b	2101	2006	2015
	Si(C ₆ H ₅) ₃	cyclohex. ^b	2098	2003
Ge(C ₆ H ₅) ₃	CH ₂ Cl ₂	2086 (w)	1993 (s)	1989 (s)
	cyclohex. ^b	2097	2006	2002
Sn(C ₆ H ₅) ₃	CH ₂ Cl ₂	2095 (w)	1999 (s)	1999 (s)
	cyclohex. ^b	2093	2002	2002
Pb(C ₆ H ₅) ₃	CH ₂ Cl ₂	2093 (w)	2002 (s)	2002 (s)
	cyclohex. ^b	2091	2003	2003
Sn(C ₂ H ₅) ₃	CH ₂ Cl ₂	2075 (w)	1981 (s)	1981 (s)
	n-hexane	2085 (w)	1989 (s)	1995 (m,s)
Pb(C ₂ H ₅) ₃	CH ₂ Cl ₂	2078 (w)	1981 (s)	1981 (s)
	n-hexane	2078 (w)	1987 (s)	1987 (s)
Sn(CH ₃) ₃	cyclohex. ^b	2089	1991	1998
	Cl	CCl ₄ ^c	2138 (w)	2054 (s)
Br	CCl ₄ ^c	2133 (w)	2050 (s)	2001 (m)
	I	CCl ₄ ^c	2125 (w)	2044 (s)
H	cyclohex. ^d	2117 (vw)	2016 (vs)	2007 (s)
	CH ₃	cyclohex. ^e	2109 (w)	2010 (vs)
C ₆ H ₅	cyclohex. ^e	2114 (w)	2021 (vs)	1997 (m)
	COCH ₃	CS ₂ ^f	2105	2040
CF ₃	KBr ^g	2155	2050	2016
	C ₆ H ₅ CH ₂	cyclohex. ^h	2106 (w)	2012 (s)

^a See ref. (17). ^b See ref. (9). ^c See ref. (42). ^d See ref. (43). ^e See ref. (44). ^f See ref. (45). ^g See ref. (46). ^h See ref. (22).

Table VI. C-O stretching frequencies in $\text{Re}(\text{CO})_5\text{X}$ molecules

X	Solvent	Assignments		
		$\text{A}_1^{(2)}$	E	$\text{A}_1^{(1)}$
SnCl ₃	CH ₂ Cl ₂	2150 (w)	2046 (s)	2046 (s)
	cyclohex. ^a	2141	2044	2030
SnBr ₃	cyclohex. ^a	2143	2046	2030
	C(C ₆ H ₅) ₃	CH ₂ Cl ₂	2070 (w)	2009 (s)
Si(C ₆ H ₅) ₃		cyclohex. ^a	2118	2012
Ge(C ₆ H ₅) ₃	CH ₂ Cl ₂ ^e	2120 (w)	2010 (s)	1990 (sh,m)
	cyclohex. ^a	2118	2014	2000
Sn(C ₆ H ₅) ₃	CH ₂ Cl ₂	2116 (w)	2008 (vs)	2008 (vs)
	cyclohex. ^a	2114	2012	2003
Pb(C ₆ H ₅) ₃	cyclohex. ^a	2114	2015	2001
	Sn(CH ₃) ₃	cyclohex. ^a	2108	2003
Cl	CCl ₄ ^b	2156 (w)	2045 (s)	1982 (m)
	Br	CCl ₄ ^b	2150 (w)	2045 (s)
I	CCl ₄ ^b	2145 (w)	2042 (s)	1987 (m)
	H	cyclohex. ^c	2117 (w)	2015 (s)
CH ₃	cyclohex. ^d	2125 (w)	2011 (s)	1981 (m)
	C ₆ H ₅	CCl ₄ ^f	2132 (m)	2021 (vs)
COCH ₃	CCl ₄ ^f	2131 (wm)	2018 (vs)	2001 (ms)
	C ₆ H ₅ CH ₂	CCl ₄ ^f	2126 (m)	2015 (vs)

^a See ref. (9). ^b See ref. (42). ^c See ref. (43). ^d See ref. (44). ^e A weak band at 2045 cm^{-1} appeared always in the three different samples prepared by us. ^f See ref. (47).

(18) R. J. Angelici and F. Basolo, *J. Amer. Chem. Soc.*, **84**, 2495 (1962).

We have now surely confirmed such a degeneracy by studying the combination bands¹⁹ in some of these compounds (Table VII).

These bands were assigned by comparison with the spectra in the same region of pure SnPh_3Cl , $\text{Sn}(\text{C}_2\text{H}_5)_3\text{Cl}$ and PPh_3 . Absorptions due to phenyl groups may cause some little doubt on the assignments only in the case of the compound $\text{Sn}(\text{C}_6\text{H}_5)_3\text{Mn}(\text{CO})_5$.

equally distributed to *cis* and *trans* carbonyl groups via the metal-metal bond, without changing very much the π metal-metal bond, if any. Indeed no so good correlations were found by using Mammert's σ_{H} or resonance σ_{R} constants.

It is interesting to point out that no appreciable variation of the carbonyl stretching frequencies was found by passing from Si to Sn, Ge, Pb, but a lower

Table VII. Binary contributions of C–O stretching fundamentals

Compound	Solvent	Obs. frequencies	Assignments ^a	Calc. frequencies
$\text{Mn}(\text{CO})_5\text{Sn}(\text{C}_2\text{H}_5)_3$	film	4065 (sh, m)	$A_1^{(2)} + E$	4056
	liquid	4043 (s)	$B_1 + E$	$\nu B_1 + 1981$
		3972 (m)	$A_1^{(1)} + E$	3962
$\text{Mn}(\text{CO})_5\text{Sn}(\text{C}_6\text{H}_5)_3$	CCl_4	4085 (w)	$A_1^{(2)} + E$	4094
		4062 (m)	$B_1 + E$	$\nu B_1 + 1999$
	mull	3992 (w)	$A_1^{(1)} + E$	3998
<i>trans</i> - $\text{Mn}(\text{CO})_4\text{PPh}_3\text{Sn}(\text{C}_6\text{H}_5)_3$	CCl_4	3922 (m)	$B_1 + E$	$\nu B_1 + 1949$ (3935) ^b
		3980 (m)	$A_1 + E$	$\nu A_1 + 1949$ (3989) ^b

^a See ref. (19). ^b An i.r. spectrum recorded on very concentrated solution (CCl_4) showed these frequencies: 2041 (νw , νA_1), 1987 (νw , νB_1) and 1948 (νs , νE). If these assignments are exact, we have these calculated frequencies.

Table VIII. C–O stretching frequencies in $[\text{Mn}(\text{CO})_5]\text{SnR}_2$ ^a and *trans*- $\text{Mn}(\text{CO})_4\text{PPh}_3\text{SnR}_3$ ^b molecules

Compound	Solvent	Assignments		
		$A_1^{(2)}$	E	$A_1^{(1)}$
$[\text{Mn}(\text{CO})_5]_2\text{SnCl}_2$	CH_2Cl_2	2095 (s)	2029 (νs)	2003 (m)
$[\text{Mn}(\text{CO})_5]_2\text{Sn}(\text{C}_6\text{H}_5)_2$	CH_2Cl_2	2077 (s)	2003 (νs)	1979 (s)
<i>trans</i> - $\text{Mn}(\text{CO})_4\text{PPh}_3\text{SnCl}_3$	CH_2Cl_2	—	1995 (νs)	—
<i>trans</i> - $\text{Mn}(\text{CO})_4\text{PPh}_3\text{Sn}(\text{C}_6\text{H}_5)_3$	CH_2Cl_2	—	1949 (νs)	—

^a The assignments are made on the basis of local symmetry C_{4v} . However, in non polar solvents the spectra are more complex as reported for similar compounds (20). The nature of this behaviour will be discussed in a separated paper. ^b Apparent symmetry D_{4h} (see contents).

The method of combination bands is particularly suitable for discriminating between the $A_1^{(1)}$ and the E frequency since the $A_1^{(2)} + E$ and the $A_1^{(1)} + E$ combination bands are well far away, much more than the original bands corresponding to the $A_1^{(1)}$ and E modes. The degeneracy of the $A_1^{(1)}$ and E stretchings is not completely accidental because it was present in compounds which differed for M' and R. In our opinion¹¹ in these compounds there is a much more extended delocalisation of the π bonds in a manner that the MR_3 groups affect the *trans* position and the *cis* position.

In contrast with other authors, a π contribution to the metal-metal bond could compete not only with the π bond of the *trans* CO which involves d_{xz} and d_{yz} orbitals, but also with the π bond of the *cis* CO which involves mainly the d_{xy} orbital, but also d_{xz} and d_{yz} orbitals.

For such a reason we thought that there was no strong directional effect of the MR_3 groups on the *trans* carbonyl groups or that this effect was somewhat lessened or less evident than that of the X groups previously described.

In fact all the 3 stretchings ($A_1^{(1)}$, $A_1^{(2)}$ and E) of molecules of the type $(\text{CO})_5\text{M}-\text{M}'\text{R}_3$ have been shown to be in linear correlation with the Taft's polar constant sum ($\Sigma\sigma^*$) of SnR_3 groups (Figures 4, 5, 6 and 7).

This means that inductive effects of R groups are

value of the same frequencies was found in the case of C (Tables V and VI).

We briefly investigated also the carbonyl stretching frequencies of the compounds of formula *trans* $\text{Mn}(\text{CO})_4\text{PPh}_3\text{SnR}_3$ (R = Cl, Ph) and $[\text{Mn}(\text{CO})_5]_2\text{SnR}_2$ (R = Cl, Ph) (Table VIII).

The i.r. spectra of these compounds confirmed what already found in the series above investigated. *Trans* $\text{Mn}(\text{CO})_4\text{PPh}_3\text{SnR}_3$ should belong to the C_{4v} point group and they should have 2 infrared active carbonyl stretchings, E and $A_1^{(2)}$.

However, they have always only one strong infrared absorption.

As we proposed in a previous paper,¹¹ it is not possible that the $A_1^{(2)}$ and E stretchings have the same value. Indeed in these compounds the $A_1^{(2)}$ stretching is of very low intensity; in a very concentrated solution two very weak bands appeared in the i.r. spectrum of *trans* $\text{Mn}(\text{CO})_4\text{PPh}_3\text{SnPh}_3$ at 2041 and 1987 cm^{-1} (Table VIII).

The band at higher frequency is the $A_1^{(2)}$ band; this assignment was found on the basis of combination bands (Table VII).

The band at 1987 cm^{-1} is probably the infrared forbidden B_1 band. The very weak intensity of the $A_1^{(2)}$ band showed that the selection rules for point group D_{4h} are "strong" in these compounds and that the effective symmetry is always almost D_{4h} , as we have first proposed.¹¹ In fact, in a strictly D_{4h} symmetry the $A_1^{(2)}$ vibration changes in the parent A_{1g}

(19) J. Lewis, A. R. Manning, J. R. Miller, M. J. Ware and F. Nyman, *Nature*, 207, 142 (1965).

vibration, which is infrared inactive, while the E vibration changes in the parent E_u which is still infrared active, without any appreciable variation of the intensity.

This behaviour confirms that the metal-metal bond in these compounds has a great tendency to transmit electronic effects in a manner as symmetrical as possible, since by changing R groups (e.g. Ph with Cl) on the tin atom there is not a change in the pattern of the spectrum, but only the expected change in the value of the frequencies in account of the different inductive effects of R groups.

C_{2v} symmetry or a lower symmetry is likely for $[Mn(CO)_5]_2SnR_2$ compounds, so that 8 infrared active CO stretchings are expected.

The carbonyl stretchings of these compounds had different patterns in different solvents.²⁰ However, in some solvents like $CHCl_3$ or CH_2Cl_2 the coupling between the two different carbonyl moieties is not strong, so that a C_{4v} site symmetry is likely for $Mn(CO)_5$ groups (Table VIII). The assignments were made on the basis of the intensity and value of the frequencies.

In these compounds the degeneracy of vibrations of type $A_1^{(1)}$ and E, which was previously found for the non bridging compounds, disappeared and the $A_1^{(2)}$ and $A_1^{(1)}$ frequencies were found at a lower value, while the E frequency was nearly unchanged.

It can be deduced here that the bridging groups SnR_2 have a directional effect on the CO in the *trans* position of $Mn(CO)_5$ moieties and that the Mn-Sn bond order is probably a little less than that found in non bridging compounds, probably because the tin atom can share its 5d orbitals between two manganese atoms. However, it seems that many factors affect the infrared spectra of compounds with two bridging metal-metal bonds. In fact in the series $[(\pi-C_5H_5)Fe(CO)_2]_2M'R_2$ ($M' = Sn, Ge$) and $[(\pi-C_5H_5)Mo(CO)_3]_2SnR_2$ no linear correlations were found between carbonyl stretchings and any σ constants sum of R groups.

A complete study of the i.r. spectra of these and related compounds will be reported in a forthcoming paper.²⁰

Incidentally, a similar inductive mechanism was shown to be operative in some pentacoordinated compounds of formula $(CO)_4CoMR_3$ ($M = Si, Ge, Sn, Pb$; $R = Et, Ph, Cl, OCH_3$ when $M = Si$). These compounds having a trigonal bipyramidal coordination showed on the ground of a local C_{3v} symmetry 3 bands ($2A_1 + E$). We assume that $A_1^{(1)}$ is the vibration parallel to the tertiary axis and $A_1^{(2)}$ the symmetrical vibration in the trigonal plane. By plotting the frequencies of $A_1^{(1)}$, $A_1^{(2)}$ and E vibrations against the sum of Taft's polar constants, three linear correlations (Figure 8) were obtained, showing that also in this case and with a trigonal bipyramidal coordination the inductive effects of R groups are transmitted through the σ metal-metal bond.*

The correlations of E and $A_1^{(1)}$ vibrations showed a nearly equal slope, which possibly means that the inductive effects are nearly equally distributed in the *cis* and *trans* position of the SiR_3 group.

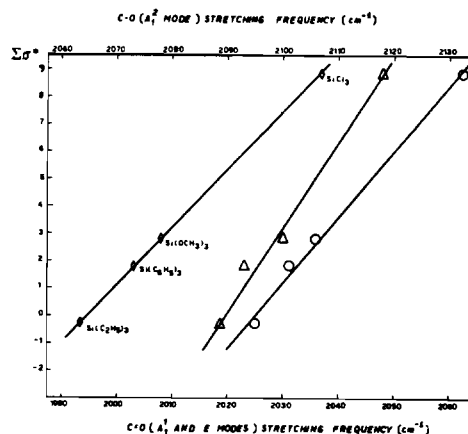


Figure 8. E type (quadrangles), $A_1^{(2)}$ type (triangles) and $A_1^{(1)}$ type (circles) carbonyl stretching frequency of $Co(CO)_5SiR_3$ against $\Sigma\sigma^*$.

Infrared spectra: M-C stretching region. We studied only the M-C stretchings of compounds of the type $M(CO)_5M'R_3$ (Table IX) because it is difficult to assign M-C stretchings in cyclopentadienyl derivatives.

Table IX. $\nu(Mn-CO)^a$ modes in $Mn(CO)_5X$ molecules

X	Solvent	Assignments		
		$A_1^{(2)}$	E	$A_1^{(1) e}$
$SnCl_3$	nujol	403 (vw)	450 (m)	530 (vw) 450 (m)
$SnCl_2(C_6H_5)$	nujol	400 (w)	460 (w)	533 (vw) 460 (s)
$SnCl(C_6H_5)_2$	nujol	400 (w)	465 (s)	543 (vw) 465 (s)
$Ge(C_6H_5)_3$	nujol	395 (m)	478 (m)	— 478 (m)
$Sn(C_6H_5)_3$	nujol	410 (w)	477 (s)	556 (w) 480 (s)
$Pb(C_6H_5)_3$	nujol	405 (w)	472 (m)	553 (w) 472 (m)
$Sn(C_2H_5)_3$	nujol	409 (w)	479 (m)	545 (w) 479 (m)
$Pb(C_2H_5)_3$	nujol	410 (w)	476 (m)	543 (w) 476 (m)
Cl ^b	nujol	^d	403 (m)	^d
Br ^b	nujol	—	415 (s)	—
I ^b	nujol	—	419 (s)	—
H ^c	cyclohex.	—	462 (m)	—
CH_3^e	CCl_4	—	462.7 (m)	—
$C_6H_5^e$	CCl_4	—	455 (m)	—
$CH_2C_6H_5^c$	CCl_4	—	457.8 (m)	—

^a $\delta(MnCO)$ modes were found in the expected 500-700 cm^{-1} region. ^b See ref. (21). ^c See ref. (22). ^d Other bands were described but it was impossible to give any assignment. ^e The assignment is made tentatively; in nearly all the compounds a weak band in the region 520-550 cm^{-1} appeared. This band could be as well assigned to the $A_1^{(1)}$ mode, but, because of the high value of the frequency, an assignment as a bending mode is also probable.

In compounds of formula $M(CO)_5X$ ($M = Re, Mn$) the only band which can be surely assigned is the strong E vibration;^{21,22} the $A_1^{(1)}$ and $A_1^{(2)}$ vibrations, which should now appear in the following sequence of frequencies, $A_1^{(1)} > E > A_1^{(2)}$ can be weak or medium and their assignments can be made only tentatively on

(20) S. Cenini, R. Ugo and F. Bonati, to be published.
(*) Some similar correlations were recently obtained by Graham and coworkers (see ref. 28).

(21) M. A. Bennett and R. J. H. Clark, *J. Chem. Soc.*, 5560 (1964).
(22) R. W. Cattrell and R. J. H. Clark, *J. Organomet. Chem.*, 6, 167 (1966).

the basis of the similar pattern of the many reported spectra (see Tables IX and XI).

We found that also in this region a linear correlation is obtained by plotting the frequency of E stretchings against Taft's polar constants σ^* (Figure 9).

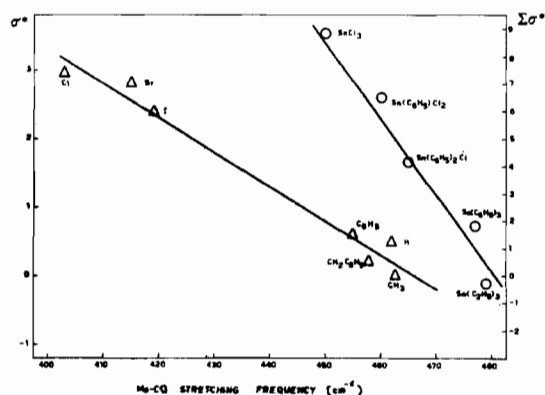


Figure 9. E type Mn-C stretching frequency of $\text{Mn}(\text{CO})_5\text{X}$ (triangles) and of $\text{Mn}(\text{CO})_5\text{SnR}_3$ (circles) against σ^* and $\Sigma\sigma^*$.

A similar pattern was obtained using electronegativity instead of Taft's polar constants. It seems then that the E metal-carbon vibrations are affected only by inductive effects as the carbonyl stretchings.

In compounds of the type $\text{M}(\text{CO})_5\text{M}'\text{R}_3$ the assignments of the metal-carbon stretchings were made tentatively on the basis of the patterns, which were similar to those of $\text{M}(\text{CO})_5\text{X}$ compounds (Table IX). Also in this case the strong E vibration is the only one which can be assigned satisfactory; however, the reported spectra have a very similar pattern so that $\text{A}_1^{(1)}$ and $\text{A}_1^{(2)}$ stretchings can be assigned reasonably to some typical absorptions which are always present in the expected region.

Some authors²² have previously claimed that any linear correlation was not found, in these compounds, between ν_{CO} and $\nu_{\text{M-C}}$. However, both types of stretching frequencies should be sensitive to the same factor, namely inductive effects. It was then probable that a linear correlation should exist between ν_{CO} and $\nu_{\text{M-C}}$; indeed such correlation was nicely obtained, with our assignments, by plotting these two types of stretchings (Figure 10).

We have then briefly studied the low frequency region of some *trans* substituted compounds and of compounds with bridging metal-metal bonds (Table X).

In compounds of formula *trans* $\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{SnR}_3$ which, as we have previously demonstrated, could belong to a local D_{4h} symmetry only the Mn-C stretching

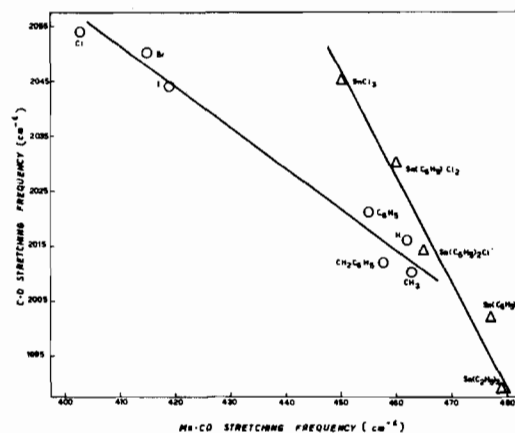


Figure 10. E type carbonyl stretching frequency against E type Mn-C for $\text{Mn}(\text{CO})_5\text{X}$ (circles) and for $\text{Mn}(\text{CO})_5\text{SnR}_3$ (triangles).

of type E was easily assigned. As expected, the values of this frequency are higher when $\text{R} = \text{Ph}$ than when $\text{R} = \text{Cl}$.

A similar conclusion was found for the E stretching mode (assuming a C_{4v} local symmetry) of the bridged compounds.

In these compounds the values of the E stretching frequencies were higher or equal to those of the related non-bridged compounds.

Although shifts of similar frequencies in this region are less evident than in carbonyl region, this seems to give partial support to the fact that the Mn-Sn bond order in bridged derivatives could be a little lower than in non bridged compounds.

Table XI. $\nu(\text{Re-CO})$ modes ^a in $\text{Re}(\text{CO})_5\text{X}$ molecules

X	Solvent	Assignments		
		$\text{A}_1^{(2)}$	E	$\text{A}_1^{(1) c}$
SnCl_3	nujol	410 (m)	375 (s)	515 (m, w) 375 (s)
$\text{C}(\text{C}_6\text{H}_5)_3$	nujol	435 (w)	395 (s)	535 (w) 395 (s)
$\text{Ge}(\text{C}_6\text{H}_5)_3$	nujol	425 (w)	393 (m)	525 (w) 393 (m)
$\text{Sn}(\text{C}_6\text{H}_5)_3$	nujol	422 (m)	395 (s)	520 (m) 395 (s)
Cl^b	nujol	431 (w)	346 (s)	484 (w) 346 (s)
Br^b	nujol	431 (w)	351 (s)	493 (w) 351 (s)
I^b	nujol	434 (w)	360 (s)	496 (w) 360 (s)

^a See note (a) on Table IX. ^b See ref. (21). ^c See note (e) on Table IX.

Table X. $\nu(\text{Mn-CO})$ ^a modes in $[\text{Mn}(\text{CO})_5]_2\text{SnR}_2$ ^b and *trans*- $\text{Mn}(\text{CO})_4\text{PPh}_3\text{SnR}_3$ ^b molecules

Compound	Solvent	Assignments		
		$\text{A}_1^{(2)}$	E	$\text{A}_1^{(1) c}$
$[\text{Mn}(\text{CO})_5]_2\text{SnCl}_2$	nujol	399 (w)	465 (m)	552 (w) 465 (m)
$[\text{Mn}(\text{CO})_5]_2\text{Sn}(\text{C}_6\text{H}_5)_2$	nujol	405 (w)	473 (m)	542 (w) 473 (m)
<i>trans</i> - $\text{Mn}(\text{CO})_4\text{PPh}_3\text{SnCl}_3$	nujol	—	464 (m)	—
<i>trans</i> - $\text{Mn}(\text{CO})_4\text{PPh}_3\text{Sn}(\text{C}_6\text{H}_5)_3$	nujol	—	491 (m)	—

^a See note (a) on Table IX. ^b See footnotes on Table VIII. ^c See note (e) on Table IX.

N.m.r. spectra. We investigated the possibility of correlating the hydrogen chemical shift of cyclopentadienyl ring of compounds of the type $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ and $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}$ (see Tables III and IV) with some properties of the X group like electronegativity or some σ constants.

In fact, the variation of the values of these chemical shifts should reflect the interaction of antibonding orbitals of the ring with non bonding electrons on the metal. It is reasonable to suppose that the energy of non bonding electrons is mainly affected by the nature of X groups.

However, the possible effects of long range shieldings due to a group asymmetry, the influence of restricted rotation of a bulky R_3M -group around the M-M' bond or the effect due to the ring current of the phenyl rings might also be operative.

Studies of this type were reported in compounds of formula $(\pi\text{-C}_5\text{H}_5)_2\text{TiX}_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{H}_4\text{-X})_2$ ²³ and quite nice correlations were obtained.

By comparing the chemical shifts of $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ and $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}$ compounds with Taft's polar constants of X groups some nearly linear correlations have been obtained (Figures 11 and 12).

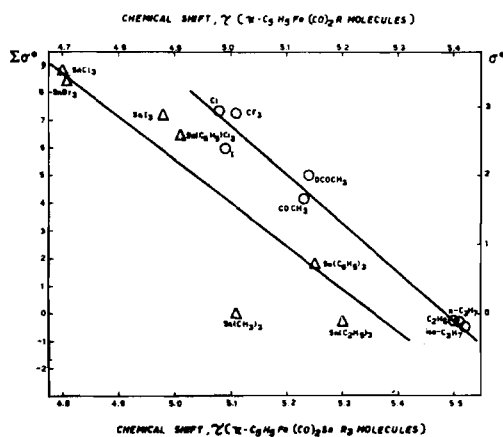


Figure 11. ^1H chemical shift of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ (circles) and $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SnR}_3$ (triangles) compounds against σ^* and $\Sigma\sigma^*$.

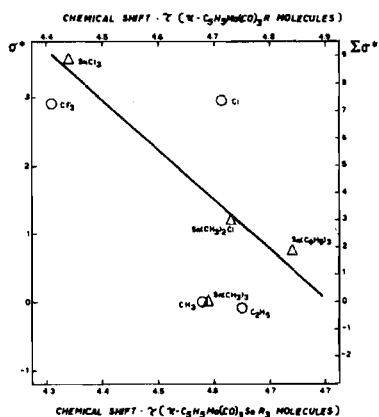


Figure 12. ^1H chemical shift of $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{R}$ (circles) and of $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{SnR}_3$ compounds (triangles) against σ^* and $\Sigma\sigma^*$.

By using Hammett's constant σ_{H} or resonance constant σ_{R} we did not obtain any linear correlation, which however were obtained using electronegativities.

Once demonstrated in this way that mainly polar effects are operative on the variation of the chemical shift of the cyclopentadienyl ring, we investigated compounds of the type $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SnR}_3$ and $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{SnR}_3$.

Linear correlations between the chemical shifts of the cyclopentadienyl ring and the Taft's polar constants sum ($\Sigma\sigma^*$) of R groups were obtained (Figures 11 and 12).

By using Hammett's constant σ_{H} or resonance constant σ_{R} the obtained correlations were not so straight.

It is interesting to point out that in the bridged compounds $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SnR}_2$ and $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2\text{SnR}_2$ the correlations between chemical shifts and $\Sigma\sigma^*$ of R groups were not so good as those obtained with the non bridged compounds.

The correlations here found confirm again that inductive effects of R groups are mainly operative on the electronic density of the transition metal through the σ metal-metal bond, as pointed out from infrared spectra.

In the above reported correlations the experimental values of the $\text{Sn}(\text{CH}_3)_3$ group are far away from the straight line; on the contrary this discrepancy was not found in the infrared correlations. It seems that the $\text{Sn}(\text{CH}_3)_3$ group shows a complex behaviour when nuclear magnetic phenomena are involved.

Indeed the position of the methyl resonance was found to shift towards lower fields passing from $\text{Sn}(\text{CH}_3)_4$ to $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Sn}(\text{CH}_3)_3$ and $\text{Mn}(\text{CO})_5\text{-Sn}(\text{CH}_3)_3$.⁹ On the ground of inductive effects only a shift towards higher field was expected. On the basis of this and our results it is clear that there are many mechanisms, other than those due to inductive effects, which attend to the general trends of chemical shifts of methyl group of compounds having $\text{Sn}(\text{CH}_3)_3$ group bound to a transition metal.

Dipole moments. In Table XII we have reported the dipole moments in benzene or dioxane solution of compounds of formula $(\text{CO})_5\text{Mn-M}'\text{Ph}_3$ ($\text{M}' = \text{Sn, Ge, Pb}$), *trans*- $\text{PPh}_3(\text{CO})_4\text{MnSnR}_3$ ($\text{R} = \text{Cl, Ph}$) and $(\text{CO})_5\text{-MnSnCl}_3$.

The crystal structures of many of these compounds have been reported²⁴ and in every case no appreciable

Table XII.

Compound	μ^b	μ 20%	μ calc. $\text{Mn-M}'^a$
$\text{Mn}(\text{CO})_5\text{SnCl}_3$	7.21	7.17	2.41 - 3.21
$\text{Mn}(\text{CO})_5\text{Ge}(\text{C}_6\text{H}_5)_3$	1.45	1.01	0.45 - 0.75
$\text{Mn}(\text{CO})_5\text{Sn}(\text{C}_6\text{H}_5)_3$	1.60	1.16	0.60 - 0.90
$\text{Mn}(\text{CO})_5\text{Pb}(\text{C}_6\text{H}_5)_3$	1.87	1.39	0.77 - 1.07
<i>trans</i> - $\text{Mn}(\text{CO})_4\text{PPh}_3\text{Sn}(\text{C}_6\text{H}_5)_3$	6.60	6.47	1.9 - —
<i>trans</i> - $\text{Mn}(\text{CO})_4\text{PPh}_3\text{SnCl}_3$	12.81	12.76	4.3 - 4.8

^a Extreme values by taking $\mu_{\text{Mn-CO}}$ between 0.5-0.8 D, $\mu_{\text{M}'-(\text{C}_6\text{H}_5)_3}$ between 0.1-0.2 D, $\mu_{\text{M}'-\text{Cl}_3}$ between 3.4-4 D and $\mu_{\text{Mn-PPh}_3}$ equal to 4.5 D. ^b In Debye units.

(24) (a) B. P. Kilbourn, T. L. Blundell and H. M. Powell, *Chem. Comm.*, 444 (1965) and references therein; (b) R. F. Bryan, *Chem. Comm.*, 355 (1967) and references therein.

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distortion was found from the regular octahedral co-ordination of the manganese atom.

Owing to the good knowledge of the stereochemistry of the above reported compounds we calculated the partial moment $\mu_{Mn-M'}$, from the dipole moment μ found for compounds of formula $(CO)_5Mn-M'Ph_3$, using the following formula:

$$\mu_{Mn-M'} = \mu - \mu_{Mn-CO} - \mu_{M'(C_6H_5)_3}$$

where $Mn-C=O$ was taken equal to 0.5-0.8 D and $M'-(C_6H_5)_3$ equal to 0.1-0.2 D.²⁵

The obtained values are reported in Table XII.

The polarity of the bond is $Mn-M'$ in every case; by substituting the *trans* CO with PPh_3 the total moment increased, as expected. In fact the polarity of the $Mn-P$ bond is $Mn-PPh_3$ with the partial moment 4.5 D.²⁶

On the other side, also the partial moment $Mn-Sn$ increased, possibly because of the higher electronic density of the manganese by substituting the CO group with PPh_3 .

In the compound of formula $(CO)_5MnSnCl_3$ the partial moment $Mn-Sn$ had the same polarity but it was higher. (2.3 against 0.6-0.9 D).

By substituting the *trans* CO with PPh_3 the partial moment increased, as previously found, of nearly 1.5-2 D.

It seems then that the $Mn-M'$ bond is of low polarity but extremely polarisable; the polarity and the polarisability increased in the order $Si < Ge < Sn < Pb$. This order is confirmed by considering the dipole moments of $(CO)_4CoM'R_3$ compounds reported by other authors.¹⁰

If a non distorted trigonal bipyramidal coordination is considered and if the polarity of the $Co-M'$ bond is, as we have demonstrated for the $Mn-M'$ bond, $Co-M'$, the following partial moments can be calculated (Table XIII).

Table XIII.

Compound	$\mu_{calc.} \delta_{Co-M'}$
$Co(CO)_4SiCl_3$	0.35 - 0.65
$Co(CO)_4Si(C_2H_5)_3$	0.25 - 0.65
$Co(CO)_4Si(C_2H_5)_2$	0.47 - 0.87
$Co(CO)_4Ge(C_2H_5)_3$	0.74 - 1.14
$Co(CO)_4Sn(C_2H_5)_3$	1.05 - 1.45
$Co(CO)_4Pb(C_2H_5)_3$	1.85 - 2.25

^a See footnote on Table XII and by taking $\mu_{M'-Cl} = 1.7$ D when $M' = Si$. The dipole are in Debye units.

Although the absolute values did not agree completely with those above obtained (Table XII), the order of the polarity is still the same.

It is interesting to point out that by substituting on the Si atom C_6H_5 and C_2H_5 groups with Cl there is not

any appreciable variation of the value of the $Co-Si$ partial moment, which agrees with a low polarisability of such a bond.

Conclusion

The nature of the metal-metal interaction in the series of compounds here investigated have been the subject of many discussions.

The general physical trends of this type of metal-metal bond (e.g. high *trans*-effect, high stability) have been always explained in term of $d_{\pi}-d_{\pi}$ interactions between the filled d orbitals of the transition metals and the unfilled d orbitals of IV group B elements. It is well known that empty d orbitals have an interesting role in the chemistry of Si, Ge and Sn, but up to now there is no sure evidence of strong π interactions in transition to group IV metal bonds.

Indeed the distances found in such metal-metal bonds are not far away from the sum of covalent single bond radii²⁴ although the single bond radii of transition metals are not very well known, and there is no appreciable difference in the $Mn-Sn$ distance in compounds of the type $Mn(CO)_5SnR_3$, when $R = C_6H_5$ or when $R = CH_3$.²⁴

Parshall⁷ described the $SnCl_3^-$ ligand as very weak σ donor and a strong π acceptor «only» on the basis of its high *trans* effect.

However the *trans*-effect could be explained equally well by a very polarisable strong σ bond.²⁷ Indeed ligands such as H^- or CH_3^- showed very high *trans*-effect also if they do not have the possibility of a π interaction with the transition metals.

The correlations here found demonstrate clearly that the effect of R groups bound to the group IV metals are transmitted to the transition metal only by a purely inductive mechanism through a very polarisable σ metal-metal bond.

On the ground of our results the great variations (e.g. carbonyl stretchings) found by passing from $M'Cl_3$ to $M'(CH_3)_3$ ($M' = Si, Sn, Ge$) can not be attributed to an inductive effect of halogen substituents which could increase the electron affinity of empty d_{π} orbitals of group IV metals,²⁸ but mainly to an inductive effect which should change the effective electronegativity of group IV metals, and subsequently the s character of the tin atom for use in the σ metal-metal bond.

Indeed by substituting a methyl group with a chlorine on the tin atom bound to $Mn(CO)_5$ ⁹ or $Co(CO)_4$,²⁸ moieties there is a decrease of the tin-hydrogen coupling constant. Following the interpretation of Graham and coworkers,⁹ this means that the tin orbital bonding to transition metal is mainly changed in the s character and has increased its s character as expected by a change of electronegativity. On the other side, as pointed out by Stone and coworkers,⁸ filled p orbitals of halogens could compete with filled d orbitals of the transition metals in using vacant d orbitals of the group IV metals and this mechanism should decrease and not increase the π acceptor properties of the group IV metals.

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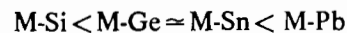
(28) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 5, 981 (1967).

Recent works²⁹ suggested that π interaction is not very strong in bonds such as phosphorus to transition metal bond. Such bonds are very dependent on the over-all electron state of both parts of the complex molecule which are connected through the bond. This means that donor-acceptor capacities of «soft» ligands, such as tertiary phosphines, are not constant, but depend on the chemical structure of the ligand (e.g. the true electronegativity of the phosphorus atom) and also on the electronic state of the transition metal.

We suggest that a similar behaviour can be attributed to the heterogeneous metal-metal bonds here studied. In fact these bonds are very sensitive to the chemical structure of the ligand as shown by the many correlations here reported and to the electronic state of the transition metal as shown by the variation of polarity by substituting a carbonyl group bound to the transition metal with a tertiary phosphine.

We believe that π interaction is less important in these metal-metal bonds than σ interaction; indeed our suggestions are supported also by the following points.

On the contrary no appreciable change in the carbonyl stretchings was found by passing from Si to Ge, to Sn and to Pb (although force constants should be a better criterium) and, generally speaking, the Si compounds are usually less stable than Ge and Sn compounds. Besides the polarity and polarisability of the metal-metal bonds seem to increase in the order



The heterogeneous metal-metal bonds here studied are not very polar but very polarisable as suggested before³⁰ on the basis of infrared and Raman intensities of metal-metal vibrations and the mean features of the metal-metal bond seem to depend mainly on the apparent electronegativity of group IV metal.

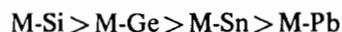
This latter suggestion is confirmed by the constant values of apparent electronegativities of SnR_3 groups (Table XIV) calculated by using data obtained from complexes with different transition metals and different stereochemistry.

Table XIV. Apparent electronegativity of SnR_3 groups

	$SnCl_3$	$SnBr_3$	$Sn(CH_3)_2Cl$	$Sn(C_2H_5)_3$	$Sn(CH_3)_3$	$Sn(C_2H_5)_3$
from iron	2.90	2.85	—	1.65	—	1.30
from molybdenum	2.80	—	1.94	1.62	1.56	—
from manganese ^a	2.61	2.50	1.94	1.62	1.60	1.50
from manganese ^b	2.73	2.68	2.05	1.98	1.80	1.68
from rhenium ^a	2.55	2.60	—	1.90	1.75	—
from rhenium ^b	2.86	2.90	—	2.13	1.95	—
average value	2.74	2.70	1.97	1.81	1.73	1.49

^a Variations of the stretching frequency $\nu_{C=O}$ ($A_1^{(2)}$). ^b Variations of the stretching frequency $\nu_{C=O}$ (E).

Owing to the nearly equal electronegativity of Si, Ge, Sn and Pb any π interactions should increase the stability and change the polarity of the metal-metal bond in the order



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Our results confirm Nyholm's and Lewis first suggestions^{3,4} of the stability of heterogeneous metal-metal bonds associated with the s character of the bonding atomic orbitals.

Acknowledgments. We wish to thank C.N.R. for financial support.

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