Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

TRANSITION METAL CHEMISTRY
VII. CALCULATION OF CO STRETCHING FORCE CONSTANTS AND SEPARATION OF MESOMERIC AND INDUCTIVE EFFECTS FOR LM$(CO)_5$ COMPLEXES

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(Received November 30th, 1970)

SUMMARY

Refined values of the CO stretching force constants for monosubstituted metal pentacarbonyl complexes have been obtained by rigorous direct methods of calculation.

The following compounds have been treated by this method: manganese carbonyl complexes, halogenometal pentacarbonyls, some recently prepared aminocarbene complexes $[RHN(Me)C]Cr(CO)_5$, carbene pentacarbonyl compounds $[R(OC_2H_5)C]M(CO)_5$ ($R = CH_3$, n-C_4H_9 and $M = Cr$, W), phosphacarborane metal carbonyls of general formula $(CH_3)_4N[B_9H_{10}CHE \cdot M(CO)_5]$ with E = P, As and M = Mo, W, Cr and arsine pentacarbonyl complexes of Cr, Mo and W.

Using the more exact carbonyl stretching force constants obtainable from such calculations, relative σ and π Graham parameters for a series of LMn$(CO)_5$ compounds have been derived. The relative importance of σ and π bonding in some organotin derivatives is discussed.

CALCULATION OF FORCE CONSTANTS

Using the Cotton and Kraihanzel force field[1] and the orbital overlap theories outlined by Jones[2], a more exact method for the direct calculation of CO stretching force constants of complexes of the general formula LM$(CO)_5$ has recently been presented[3].

Previously, all papers dealing with calculations of force constants in the CO stretching region for substituted metal carbonyls used the Cotton and Kraihanzel approximative method which enabled only three of the five related force constants to be evaluated, and in an attempt to resolve this problem. Dalton *et al.*[4] have published some interesting interaction force constant relationships by introducing angular correction terms in the treatment of Jones[2]. As mentioned earlier this procedure does not improve the results.

If however, the interaction force constants relations and the rigorous algebraic

(*continued on p.* 394)

TABLE 1

OBSERVED CARBONYL STRETCHING MODES, ASSIGNMENTS AND FORCE CONSTANTS FOR $LM(CO)_5$ COMPOUNDS

Compound	Ref.	Frequencies (cm^{-1})				Force constants (mdynes/Å)				
		$A_1(1)$	$A_1(2)$	B_1	E	k_1	k_2	k_c	$k_{c'}'$	k_t
$(CH_3)_2ClSnMn(CO)_5$[a]	5	2101	2015	2039	2006	16.65_1	16.72_7	0.1978_9	0.2696_7	0.4675_6
$(CH_3)_3SnMn(CO)_5$[a]	5	2089	1998	2021	1991	16.30_8	16.49_8	0.2376_6	0.2431_6	0.4808_1
$(C_6F_5)_3SnMn(CO)_5$[a]	6	2116	2029	2059	2034	16.76_3	17.13_1	0.2082_1	0.2067_2	0.4149_3
$C_6H_5(C_6F_5)_2SnMn(CO)_5$[a]	6	2108	2020	2047	2020	16.63_6	16.92_7	0.2186_9	0.2218_4	0.4405_3
$(C_6H_5)_2C_6F_5SnMn(CO)_5$[a]	6	2101	2016	2038	2012	16.56_4	16.79_7	0.2278_1	0.2127_3	0.4405_4
$(C_6H_5)_2ClSnMn(CO)_5$[a]	6	2103	2018	2044	2018	16.59_7	16.87_9	0.2113_7	0.2133_6	0.4247_3
$C_6H_5Cl_2SnMn(CO)_5$[a]	6	2113	2023	2058	2031	16.68_2	17.08_5	0.1950_8	0.2230_4	0.4181_2
$C_6F_5COMn(CO)_5$[a]	7	2125	2017	2067	2042	16.53_9	17.27_6	0.2203_6	0.2075_3	0.4278_9
$C_6H_5COMn(CO)_5$[a]	7	2114	2002	2055	2021	16.38_1	16.98_5	0.2016_8	0.2799_7	0.4816_5
$C_2F_5COMn(CO)_5$[a]	7	2130	2023	2069	2039	16.68_7	17.26_8	0.2210_4	0.2489_7	0.4700_2
$CH_3(C_2H_5O)CCr(CO)_5$[b]	8	2064	1961	1983	1947	15.76_3	15.87_7	0.2747_7	0.2858_2	0.5605_9
$n\text{-}C_4H_9(C_2H_5O)CCr(CO)_5$[b]	8	2063	1958	1982	1947	15.69_6	15.87_4	0.2795_1	0.2778_1	0.5573_2
$CH_3(C_2H_5O)CW(CO)_5$[b]	8	2072	1958	1980	1945	15.67_5	15.89_3	0.3304_9	0.2775_3	0.6080_2
$n\text{-}C_4H_9(C_2H_5O)CW(CO)_5$[b]	8	2073	1957	1981	1945	15.66_7	15.89_9	0.3286_9	0.2855_3	0.6142_2
$Re(CO)_5I$[c]	9	2148	1981	2072	2031	16.03_3	17.28_6	0.2797_0	0.3398_5	0.6195_5
$Cr(CO)_5Br$[c]	9	2060	1851	1968	1933	13.93_8	15.72_4	0.3506_1	0.2758_3	0.6264_4
$Cr(CO)_5I$[c]	9	2054	1854	1967	1935	13.97_1	15.71_3	0.3326_8	0.2522_6	0.5849_3
$W(CO)_5Cl$[c]	9	2071	1817	1966	1913	13.52_1	15.58_5	0.3828_9	0.4153_4	0.7982_2
$W(CO)_5Br$[c]	9	2065	1841	1962	1928	13.77_7	15.68_5	0.3983_0	0.2672_0	0.6655_0
$W(CO)_5I$[c]	9	2063	1844	1962	1932	13.80_5	15.71_2	0.3942_2	0.2360_0	0.6302_2
$NH_2(Me)CCr(CO)_5$[d]	10	2063	1949	1964	1941	15.42_2	15.78_8	0.3841_5	0.1814_5	0.5655_9
$NH(Me)_2CCr(CO)_5$[d]	10	2058	1940	1970	1940	15.33_3	15.77_0	0.3265_0	0.2369_7	0.5634_8
$[(Et)NH(Me)C]Cr(CO)_5$[d]	10	2061	1938	1969	1938	15.30_4	15.76_2	0.3423_0	0.2446_9	0.5869_8
$[(CH_2Ph)NH(Me)C]Cr(CO)_5$[d]	10	2058	1938	1968	1941	15.27_4	15.77_7	0.3412_8	0.2132_2	0.5545_0
$[(i\text{-}Pr)NH(Me)C]Cr(CO)_5$[d]	10	2060	1940	1970	1940	15.33_0	15.77_9	0.3354_4	0.2369_7	0.5724_2
$[(C_6H_{11})NH(Me)C]Cr(CO)_5$[d]	10	2057	1936	1968	1936	15.28_5	15.72_3	0.3266_9	0.2523_8	0.5790_7
$[(t\text{-}Bu)NH(Me)C]Cr(CO)_5$[d]	10	2058	1918	1965	1936	14.96_1	15.72_6	0.3536_5	0.2285_5	0.5822_0
$[(p\text{-}NH_2C_6H_4)NH(Me)C]Cr(CO)_5$[d]	10	2058	1921	1966	1931	15.05_8	15.67_9	0.3370_0	0.2755_5	0.6125_5
$[(p\text{-}OMeC_6H_4)NH(Me)C]Cr(CO)_5$[d]	10	2058	1924	1969	1940	15.05_9	15.77_2	0.3364_9	0.2290_2	0.5655_1
$[(p\text{-}MeC_6H_4)NH(Me)C]Cr(CO)_5$[d]	10	2058	1938	1969	1938	15.30_8	15.74_9	0.3288_6	0.2446_9	0.5735_4

$[(p\text{-}HC_6H_4)NH(Me)C]Cr(CO)_5{}^d$	10	2057	1937	1972	1937	15.33_3	15.73_9	0.3026_0	0.2764_0	0.5790_0
$[(Me)_3NC]Cr(CO)_5{}^d$	10	2057	1930	1967	1930	15.23_2	15.66_2	0.3203_0	0.2913_0	0.6115_9
$[Et_2N(Me)C]Cr(CO)_5{}^d$	10	2056	1929	1966	1929	15.21_7	15.64_6	0.3201_4	0.2911_5	0.6112_9
$[(p\text{-}ClC_6H_4)NH(Me)C]Cr(CO)_5{}^d$	10	2060	1900	1967	1943	14.64_4	15.80_7	0.3639_4	0.1895_8	0.5535_2
$[(p\text{-}CF_3C_6H_4)NH(Me)C]Cr(CO)_5{}^d$	10	2058	1894	1970	1944	14.56_0	15.81_7	0.3414_9	0.2055_9	0.5470_8
$[7,8\text{-}B_9H_{10}CHP]Cr(CO)_5^{-\,c,f}$	11	2069	1925	1983	1943	15.16_1	15.87_6	0.3048_6	0.3172_6	0.6221_2
$[7,9\text{-}B_9H_{10}CHP]Cr(CO)_5^{-\,e,g}$	11	2067	1919	1982	1942	15.06_2	15.85_7	0.3019_6	0.3171_0	0.6190_6
$[7,8\text{-}B_9H_{10}CHP]W(CO)_5^{-\,c,g}$	11	2073	1920	1989	1941	15.15_8	15.88_2	0.2787_9	0.3811_0	0.6598_9
$[7,9\text{-}B_9H_{10}CHP]Mo(CO)_5^{-\,e,g}$	11	2077	1917	1989	1946	15.04_4	15.95_5	0.3124_6	0.3418_3	0.6542_9
$[7,9\text{-}B_9H_{10}CHP]W(CO)_5^{-\,e,g}$	11	2073	1911	1983	1939	14.95_8	15.85_8	0.3182_1	0.3486_3	0.6668_4
$[7,9\text{-}B_9H_{10}CHAs]Cr(CO)_5^{-\,e,g}$	11	2064	1912	1986	1953	14.89_0	15.96_3	0.2894_1	0.2626_1	0.5520_2
$[7,9\text{-}B_9H_{10}CHAs]Mo(CO)_5^{-\,c,g}$	11	2073	1907	1993	1947	14.91_3	15.95_7	0.2738_7	0.3661_5	0.6400_1
$[P(OCH_2)_3CC_5H_{11}]W(CO)_5{}^a$	12	2086	1964	1989	1958	15.71_6	16.10_4	0.3665_2	0.2471_9	0.6137_1
$[P(SCH_2)_3CC_5H_{11}]W(CO)_5{}^a$	12	2081	1965	1990	1960	15.73_1	16.10_3	0.3417_7	0.2394_0	0.5811_7
$[P(OCH_2)_3CC_4H_9]W(CO)_5{}^a$	12	2079	1966	1983	1952	15.76_0	16.00_0	0.3582_6	0.2464_4	0.6047_0
$W(CO)_5PH_3{}^d$	13	2083	1921	1984	1953	15.00_7	16.04_0	0.3826_3	0.2465_6	0.6291_9
$Mo(CO)_5PH_3{}^d$	13	2081	1925	1986	1956	15.06_6	16.06_4	0.3668_0	0.2389_1	0.6057_1
$Cr(CO)_5PH_3{}^d$	13	2075	1924	1982	1953	15.04_7	16.00_0	0.3585_0	0.2305_4	0.5890_4
$W(CO)_5AsH_3{}^d$	13	2078	1917	1982	1948	14.96_6	15.96_7	0.3643_4	0.2699_4	0.6342_8
$Cr(CO)_5AsH_3{}^d$	13	2072	1921	1982	1951	15.01_4	15.96_9	0.3425_4	0.2463_1	0.5888_5
$W(CO)_5AsPh_3{}^d$	13	2070	1939	1978	1939	15.38_9	15.82_6	0.3266_8	0.3086_2	0.6353_0

[a] In cyclohexane. [b] In pentane. [c] Powdered solid. [d] In hexane. [e] In acetonitrile. [f] As tetrabutylammonium salt. [g] As tetramethylammonium salt.

method described in Part III of this series are used, all the CO stretching force constants of monosubstituted metal carbonyls $LM(CO)_5$ may be calculated with great precision. This method has now been applied to a second series of $LM(CO)_5$ compounds and the results are presented in Table 1.

The calculations were mainly carried out in double precision on an IBM 360 type 30 computer of the Digital Computing Laboratory of the University of Ghent.

SEPARATION OF INDUCTIVE AND MESOMERIC EFFECTS

CO stretching frequencies and force constant shifts in substituted metal carbonyls are currently interpreted in terms of the differences in π bonding ability between the ligands[14], although in some infrared studies[15] it has been suggested that is the σ bonding ability of the ligand and not its π bonding capacity which is the principal factor in determining the CO stretching frequencies of the complex.

In a particularly interesting paper[16], Graham has assumed that inductive effects operating through the ligand–metal σ bond, and ligand–metal π bonding, are both important in determining the carbonyl stretching force constants in complexes of the type $LM(CO)_5$ (M = Mo, Mn).

In order to separate the inductive and mesomeric effects, the following simple relations have been suggested by Graham:

$$\Delta k_1 = k'_1 - k_1 = m \cdot \Delta\sigma + n \cdot \Delta\pi$$
$$\Delta k_2 = k'_2 - k_2 = \Delta\sigma + \Delta\pi$$

with $m = 1$ and $n = 2$. In these equations k'_1 and k_1 are the stretching force constants of the carbonyl group *trans* to L in the compound considered and in the reference compound respectively, while k'_2 and k_2 are the related stretching force constants of the carbonyl groups *cis* to L. $\Delta\sigma$ and $\Delta\pi$ are the differences between the σ inductive and π acceptor properties of the ligands. The coefficient $m = 1$ is introduced to allow for the assumption that the inductive effect of the ligand operates equally over all five CO groups, whereas the coefficient $n = 2$ simply arises from the splitting of the over-all change in the π portion according to the treatment of Jones[2].

Using these equations the σ and π parameters for a series of pentacarbonylmanganese derivatives $LMn(CO)_5$ have been calculated, some of them for the first time. As the required experimental stretching force constants k_1 and k_2 are closely related to the interaction force constants, and since the calculation method[3] used here allows the direct evaluation of all five of the most important CO force constants, all in perfect agreement with the vibrational data, the parameters presented in Table 2 are considered more accurate.

Despite the increased accuracy, however the magnitude acid variation of σ and π donor-acceptor properties is very similar to that found by Graham[16]. However, $HMn(CO)_5$ is preferred as the reference compound over $CH_3Mn(CO)_5$ as force constant values for the former have been calculated exactly using the isotopic substitution method[17].

It is pertinent to query the justification for the calculation of force constants to nine significant figures, despite the fact that from such calculations it is possible to

TABLE 2

σ AND π BONDING PARAMETERS FOR PENTACARBONYLMANGANESE COMPLEXES $LMn(CO)_5$[a]

L	k_1	k_2	Δk_1	Δk_2	$\Delta\sigma$	$\Delta\pi$
$(CH_3)_2SnCl$[5]	16.651	16.727	0.191	−0.153	−0.497	0.344
$(CH_3)_3Sn$	16.308	16.498	−0.152	−0.382	−0.612	0.230
Br_3Sn[4]	16.984	17.188	0.524	0.308	0.092	0.216
$(C_6H_5)_3Ge$[4]	16.439	16.665	−0.021	−0.215	−0.409	0.194
$(C_6H_5)_2SnC_6F_5$	16.564	16.797	0.104	−0.083	−0.270	0.187
$(C_6H_5)_2SnCl$	16.597	16.879	0.137	−0.001	−0.139	0.138
$C_6H_5Sn(C_6F_5)_2$	16.636	16.927	0.176	0.047	−0.082	0.129
$(C_6H_5)_3Pb$	16.346	16.646	−0.114	−0.234	−0.354	0.120
$(C_6H_5)_3Sn$	16.314	16.643	−0.146	−0.237	−0.328	0.091
$(C_6H_5)_3Si$	16.345	16.680	−0.115	−0.200	−0.285	0.085
$(C_6F_5)_3Sn$	16.763	17.131	0.303	0.251	0.199	0.052
$(CH_3)_2SnCl$[4]	16.406	16.792	0.054	−0.088	−0.122	0.034
$(C_6H_5)_3Ge$[5]	16.318	16.711	−0.142	−0.169	−0.196	0.027
$(C_6H_5)SnCl_2$	16.683	17.085	0.223	0.205	0.187	0.018
H[b]	16.460	16.880				
Br_3Sn[5]	16.823	17.253	0.363	0.373	0.383	−0.010
$HCFClCF_2$	16.543	17.301	0.083	0.421	0.759	−0.338
$HCCl_2CF_2$	16.528	17.292	0.068	0.412	0.756	−0.344
HCF_2CF_2	16.549	17.329	0.089	0.449	0.809	−0.360
$N_3C_3F_2$	16.509	17.296	0.049	0.416	0.783	−0.367
cyclo-C_4F_5	16.594	17.383	0.134	0.503	0.872	−0.369
cyclo-C_6F_9	16.604	17.398	0.144	0.518	0.892	−0.374
C_4F_5	16.494	17.289	0.034	0.409	0.784	−0.375
NC_5F_4	16.505	17.310	0.045	0.430	0.815	−0.385
HCF_2CFCl	16.534	17.345	0.074	0.465	0.856	−0.391

[a] All spectra were measured in cyclohexane solution. Force constants have been taken from parts III and VII of this series. [b] Reference.

reproduce the experimental values for the wave numbers perfectly to within 1×10^{-10} cm^{-1}.

The experimental precision in determining the force constants is, of course, not nearly so high. Indeed, on the assumption that they are mutually independent, root mean square errors m (standard deviations σ) of ± 1 cm^{-1} in each of the four bands in a typical case of $LM(CO)_5$ compounds, change the values of k_1 and k_2 by m equal to 0.029 and 0.013 mdynes/Å, and of k_c, $k_{c'}$ and k_t by m equal to 0.010, 0.011 and 0.0065 mdynes/Å respectively. Actually such an experimental precision is an upper limit, since it pre-supposes the comparison of spectra obtained under the most favorable conditions and in one and the same solvent. The corresponding uncertainties for the σ and π parameters are easy to evaluate.

The progression of σ and π parameters in some tin derivatives, as reported in Table 3, is one interesting aspect of the results. A comparison of the parameters found by Graham[16] on the basis of the Cotton and Kraihanzel approximate force constant calculation method (needing only three frequencies) with those derived from the rigorous algebraic approach presented here (using all four frequencies) suggests that

TABLE 3

INFLUENCE OF FORCE CONSTANTS CALCULATION METHODS ON σ AND π PARAMETERS FOR $(R_{3-n}SnX_n)Mn(CO)_5$

$R_{3-n}SnX_n$	$\sigma_1{}^a$	$\sigma_2{}^b$	$\pi_1{}^a$	$\pi_2{}^b$
$(CH_3)_3Sn$	−0.612	−0.84	0.230	0.51
$(CH_3)_2SnCl$	-0.497^c	−0.66	0.344	0.56
	-0.122^d		0.034^d	
CH_3SnCl_2	^{f}	0.02	^{f}	0.23
$SnCl_3$	$0.383^{e,f}$	0.18	$-0.010^{e,f}$	0.31
$(C_6H_5)_3Sn$	−0.328	−0.59	0.091	0.41
$(C_6H_5)_2SnCl$	−0.121	−0.38	0.140	0.43
$C_6H_5SnCl_2$	0.187	−0.04	0.018	0.29
$SnCl_3$	$0.383^{e,f}$	0.18	$-0.010^{e,f}$	0.31
$(C_6H_5)_3Sn$	−0.328	−0.59	0.091	0.41
$(C_6H_5)_2SnC_6F_5$	−0.270	−0.52	0.187	0.49
$C_6H_5Sn(C_6F_5)_2$	−0.082	−0.31	0.129	0.41
$Sn(C_6F_5)_3$	0.199	−0.27	0.052	0.51

[a] σ_1, π_1: σ and π parameters obtained in this study. [b] σ_2, π_2: Graham σ and π parameters. [c] Ref. 5. [d] Ref. 4. [e] $SnBr_3$. [f] Force constants calculations for these compounds could not be made as the B_1 mode of these derivatives has not, as yet, been assigned.

the significance of differences in force constants in series of related compounds is not so absolute as generally stated. It appears that particular trends in the π parameter may be reversed by applying another, more exact, method of calculation.

The increasing trend in the σ parameter with progressive chlorine or C_6H_5 substitution is as expected. The overall effect of this progressive substitution means that the substituted tin group becomes a weaker σ donor ligand with every new substitution. As a result of this effect the contraction of the filled d orbitals of manganese will progressively increase, reducing their overlap with the antibonding π orbital on carbon monoxide and hence increasing the CO stretching frequency. At the same time, the excess negative charge built up on manganese by donor σ bonding, and available for back donation to the ligand, should decrease.

The changes and fluctuations in the π parameter are not so clear-cut. With the introduction of the first electronegative substituent (chlorine or C_6F_5 group) in the R_3Sn ligand, the π parameter appears to rise, suggesting that there should be an increase in π electron withdrawal from manganese to tin. This result, however, does not fit the expected synergic character in the metal–ligand bond, although the change in the π parameter also results in an increase of ν(CO).

Tin itself has d_π orbitals which could be sensitive to electronegative substituents, and for this reason, the first chlorine or C_6F_5 substituent could cause a contraction of these tin d_π orbitals, increasing their π bonding with the manganese atom. This could be a possible explanation for the observed increase of the π parameter.

The second substitution, however, gives rise to a drop of the parameter for π acceptor ability, in agreement with the synergic interaction, while the third substitution leads to an increase of the Graham π parameter, when the approximate evaluation method is used, but yields a further decrease of the π parameter if the rigorous direct calculation method is applied. The latter effect is more logical than the former, for if this result is accepted, decreases of the π parameter after a second and third substitution could be interpreted as a result of the contribution of two simultaneous processes, (a) a further contraction of the tin d_π orbitals beyond the ideal extent for overlap with the manganese d orbitals, and (b) a back donation from the electronegative substituent to tin[19], which also would reduce the π acceptor capacity of tin with respect to the manganese atom. Such a suggestion agrees with a partial decrease of ν(CO), which is evidently cancelled by a greater potential increase of ν(CO) due to the inductive effect.

In general, these results point out the relative importance of the σ donor effect at the expense of the mesomeric effect.

Finally, it should be stated that, as suggested by Gay and Graham[20], it will be necessary to examine the IR spectra of isotopic enriched species in order to arrive at less speculative interpretations regarding the relation of CO stretching force constants to chemical bonding. However, this refinement does not eliminate the need to integrate both ν(M–C) and ν(M–L) in the carbonyl stretching force constants calculations.

ACKNOWLEDGEMENT

The authors wish to thank Prof. Dr. C. C. Grosjean for permission to use the computing facilities of his institute and Miss. Lic. R. M. De Caluwe and Dr. H. Steyaert for executing the computer programs. They also wish to express their gratitude to Dr. E. V. Van den Berghe for many helpful discussions.

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