Revised Carbonyl Stretching Force Constants in Triphenylgermaniumpentacarbonylmanganese and Related Compounds

Sir:

In order to obtain approximate carbonyl stretching force constants in metal carbonyl derivatives (limited in the present context to $LMn(CO)_5$ species), it is usually assumed that interactions of carbonyl stretching vibrations with other vibrations of the molecule can be ignored. This is the CO-factored force field or energy factoring model. Even those most concerned with rigor in force constant calculations consider that the CO-factored values of the *primary* force constants (as distinguished from the interaction force constants) are useful for comparative purposes, assuming an error of 0.1 mdyn/Å.[1]

TABLE I

OBSERVED AND CALCULATED CARBONYL STRETCHING BANDS IN ^{13}CO-ENRICHED $(C_6H_5)_3GeMn(CO)_5$

	All ^{12}CO				Axial ^{13}CO		Single radial ^{13}CO[c]		
	$A_1^{(2)}$	$A_1^{(1)}$	B_1	E	A_1	A_1	A′ [$A_1^{(2)}$]	A′ [B_1]	A′ [E]
Obsd[a]	2097.5 (3)	2001 (5, sh)	2033 (0.8)	2006.5 (10)	2084 (0.2)	1974 (2)	2091 (1)	2029 (0.8)	1969 (1, sh)
Calcd[b]	2097.3	2002.7	2033.6	2005.8	2082.3	1972.1	2092.9	2028.2	1970.0

[a] Cyclohexane solution, CO–DBr calibration, values in cm^{-1}. Approximate relative *transmittance* of bands is given in parentheses relative to the most intense band as 10. [b] Using force constants listed in Table II. [c] Vibrations of this molecule must be classified under the C_s point group. They may formally be correlated with those of the parent all-^{12}CO molecules of C_{4v} symmetry as indicated in brackets.

A simple and widely used procedure for calculating approximate force constants is due to Cotton and Kraihanzel;[2] the CK method is based on several assumptions as well as that of CO factoring itself. Recently, ^{13}CO-enriched compounds have been used to derive CO-factored force constants without additional assumptions (other than the neglect of anharmonicity).[3–5] In the compounds examined to date (L = H, Cl, Br, I, CH_3, and CF_3) the primary force constants from the latter method have been in reasonable agreement with the CK values. In particular, the CK assumption that $k_1 < k_2$ has been borne out.[6]

We wish to draw attention to some unexpected results we have obtained during studies of ^{13}CO-enriched derivatives of the type $(C_6H_5)_3MMn(CO)_5$ (M = Ge, Sn).[7] Observed and calculated band positions for the various isotopic species of $(C_6H_5)_3GeMn(CO)_5$ are shown in Table I. Force constants for this and related molecules are collected in Table II. It is apparent that for the phenyl derivatives, $k_1 > k_2$, contrary to the CK requirement, and that the difference of *ca.* 0.3 mdyn/Å is significant.[8]

Previously, CK constants for these derivatives[9,10] were used in a discussion of the nature of the metal–metal bond, when it was inferred from the k_1 values, which were among the largest calculated, that ligands such as $(C_6H_5)_3Ge$ were accepting π-electron density from the transition metal.[10] Later, the approach based on CK force constants was extended to take account of both inductive and π-bonding effects.[11]

TABLE II

CO-FACTORED FORCE CONSTANTS[a]

	k_1	k_2	k_c	k_c'	k_t
$(C_6H_5)_3GeMn(CO)_5$	16.87	16.58	0.39	0.10	0.33
$(C_6H_5)_3SnMn(CO)_5$	16.81	16.50	0.37	0.12	0.34
$Br_3GeMn(CO)_3$	16.87	17.35	0.21	0.19	0.43
$Br_3SnMn(CO)_5$	16.94	17.28	0.24	0.16	0.42

[a] Values in mdyn/Å. Force constant designations are as given by Cotton and Kraihanzel[2] and as used by other workers.[3–5]

Fortunately, and perhaps fortuitously, it would appear that earlier conclusions[10,11] about the π-bonding ability of $(C_6H_5)_3M$ ligands are qualitatively unaltered by the revised force constants. Indeed, it seems appropriate to revise upward our estimate of the π-acceptor capability of the $(C_6H_5)_3M$ group.[12] This would also make understandable the breakdown of the CK method for these particular ligands. The origin of the premise that $k_1 < k_2$ lies, of course, in the hypotheses (a) that the ligand L interacts most strongly with the axial carbonyl group and (b) that the ligand L makes a smaller demand for d_π electrons than a carbonyl group. We consider it more likely that (b) breaks down, so that in fact the $(C_6H_5)_3M$ ligands may

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[1] L. H. Jones, *Inorg. Chem.*, **7**, 1681 (1968).

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

[3] H. D. Kaesz, T. Bau, D. Hendrickson, and J. M. Smith, *ibid.*, **89**, 2844 (1967).

[4] P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *ibid.*, **89**, 2851 (1967).

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

[6] The force constant designations are as in ref 2; k_1 refers to the carbonyl group *trans* to the ligand L, and k_2, to the radial carbonyl groups (*cis* to L).

[7] Owing to the very slow exchange of $(C_6H_5)_3MMn(CO)_5$ with ^{13}CO, these compounds were synthesized from ^{13}CO-exchanged $ClMn(CO)_5$[8] by the sequence

$$ClMn(CO)_5 \xrightarrow{Na\text{–}Hg} Mn(CO)_5^- \xrightarrow{(C_6H_5)_3MX} (C_6H_5)_3MMn(CO)_5$$

Phenyl cleavage from the latter using HBr in *n*-hexane afforded the $Br_3MMn(CO)_5$ derivatives. Assignments and calculations were carried out by the procedure used by Kaesz, *et al.*, with an adaptation of their program.[3,4] We thank Professor Kaesz for generous assistance in the early stages of our work.

[8] A second feature of the force constants of Table II is that the interaction force constants for the phenyl derivatives are not interrelated in even approximately the expected way.[2] The significance of this feature is not clear at present, in view of the suggested large uncertainty in the interaction force constants.[1]

[9] CK force constants for the compounds of Table II from ref 10 and the present work are as follows (compound, k_1, k_2, k_i): $(C_6H_5)_3GeMn(CO)_5$, 16.33, 16.70, 0.23; $(C_6H_5)_3SnMn(CO)_5$, 16.34, 16.64, 0.23; $Br_3GeMn(CO)_5$, 16.86, 17.33, 0.21; $Br_3SnMn(CO)_5$, 16.88, 17.26, 0.20. The assignments of the ^{12}CO fundamentals on which these calculations were based are confirmed by the present calculations.

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

[11] W. A. G. Graham, *ibid.*, **7**, 315 (1968).

[12] For $(C_6H_5)_3SnMn(CO)_5$, σ and π parameters[11] become −1.21 and 0.94, respectively, using the revised constants and appropriate values[3] for $CH_3Mn(CO)_5$ as reference.

even exceed CO in π-acceptor capability in these compounds; this circumstance was presumably not considered likely when the CK approach was formulated. The force constants in Table II for $Br_3SnMn(CO)_5$, on the other hand, agree very well with CK values.[9] One can perhaps attribute the reduced π acceptance of this ligand to Br→Sn back-donation.[11] However, it will be necessary to examine ^{13}CO-enriched spectra for many more such compounds to arrive at a less speculative interpretation of the relation of force constants to chemical bonding.

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