stituted pyridine ligands to changes in covalency. The substituent could affect the ligand σ MO such as to alter the MO coefficients for the contributing carbons. However, the substituent effect would be expected to be localized, such that in the unsymmetrically substituted pyridines the MO coefficient and, hence, the contact shift for the two inequivalent *ortho* protons should be different if the substituent indeed significantly affects the σ MO. However, for $(3\text{-}C_2H_5\text{-py})_2CoX_2$, only one *ortho* resonance was found, with essentially identical line width as for $(py)_2CoX_2$, except some 300–400 cps further downfield, such that the changes in the σ MO appear negligible. It would be surprising if the 3 substituent would affect MO coefficients for the two *ortho* protons identically. The 4 substituents apparently do not affect ligand repulsions or structure, as might be anticipated. However, for the 3 position the shifts increase as both the size and the number of substituents increase. Molecular models indicate that 3 substituents could interfere with neighboring ligands, such that small but finite structural changes are sterically forced upon the complex. Such changes might well be small increases in the L–Co–L angles.[7] For the halogens, steric repulsions should increase $Cl < Br < I$, such that one mechanism can consistently explain both the anion and the substituent effects on covalency.

To test further the validity of this steric effect, it is instructive to inspect the shift distributions for the complexes more closely. Since the 4-H experiences upfield shifts, while the 4-CH_3 displays downfield shifts, both σ and π delocalization mechanisms are operative,[5,6] with the former dominant for the 2 and 3 positions, while the latter predominates for the 4 position. The dipolar shift is ignored, since the shift distributions here closely resemble those observed for pyridine in magnetically isotropic octahedral nickel complexes.[15] As the halogen is varied, the relative π to σ delocalization increases as $Cl < Br < I$, as evidenced by increasing ratio of shifts for the 4 position to the 2-H (shown in parentheses in Table I), again true for each substituent. As the pyridine substituent is varied, a similar increase in π to σ delocalization is observed, also increasing with increasing contact shift or covalency. Thus all characteristics of the shifts produced by varying the halide ion can also be produced by alkyl substitution on the pyridine. The evidence thus supports the contention that structural changes are primarily responsible for the observed covalency trends, though anion ligand field strength may have a secondary influence.[6] For these pyridine-type complexes, steric effects seem to account for the structural changes. Lack of X-ray data precludes a more detailed analysis of the steric effect on the covalency at this time. The ability of the substituents to simulate all of the effects of the halogens strongly suggests that the previously proposed simple MO model relating the ligand field strength to covalency is insufficient.

For the $((aryl)_3P)_2MX_2$ complexes, structural changes, ligand field strength of the anions, and sizable dipolar shifts complicate any detailed analysis.[1,3,6] For the $(HMPA)_2CoX_2$ complexes, structural variations can also account for the observed shift trends, since they resemble those of the pyridine complexes. Moreover, it is really not justified to neglect the dipolar shift as the source of the very small shifts as well as the trends. This was done[6] on the basis that HMPA is very similar to the halogens in ligand field strength. However, this appears to be an oversimplification, since if steric effects alter the tetrahedral angles, magnetic anisotropy in the order $Cl < Br < I$ can be expected.[1] In addition, separation of the observed shifts into contact and dipolar contributions for the $((aryl)_3P)_2MX_2$ complexes has indicated[1,16] that the magnetic anisotropy arises primarily from the D_{2h} distortion, which reflects the compression of the tetrahedron due to presumably steric effects, rather than the C_{2v} distortion, which reflects the difference in ligand field strength between phosphine and halogen. It is thus virtually impossible to ascertain the orgin of the small HMPA shifts with any confidence, much less the origin of their halide dependence.

Acknowledgments.—The financial support of NATO through a postdoctoral fellowship and the hospitality of the Swiss Federal Institute of Technology are gratefully acknowledged.

---

[15] J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

[16] G. N. La Mar, *ibid.*, **43**, 1085 (1965).

PHYSICAL CHEMISTRY LABORATORY
SWISS FEDERAL INSTITUTE OF
TECHNOLOGY
ZURICH, SWITZERLAND
GERD N. LA MAR

RECEIVED MAY 1, 1967

Recalculation of Force Constants in Carbon and Silicon Cobalt Tetracarbonyls[1,2]

Sir:

In a recent publication[3] we have reported values of $(k_e - k_a)$ where k_e and k_a are the force constants for the equatorial and axial carbonyl groups, respectively, in compounds of the type $RCo(CO)_4$ (R = organic or silicon-containing groups). It has been brought to our attention[4] that eq 3 in this paper,[3] $\lambda_E = (k_e - 2k_i)/\mu$, should be $\lambda_E = (k_e - k_i)/\mu$.[5,6] This equation together with eq 1[3] gives the relationship

$$k_e = \mu(\lambda_{A_1^e} + 2\lambda_E)/3$$

---

[1] This report is based on portions of a thesis to be submitted by A. P. Hagen to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] This research was sponsored by AFOSR(SRC)-OAR, USAF Contract No. AF 49(638)1519.

[3] A. P. Hagen and A. G. MacDiarmid, *Inorg. Chem.*, **6**, 686 (1967).

[4] The authors are greatly indebted to Professor F. G. A. Stone, Bristol University, England, who kindly brought this fact to their attention.

[5] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

[6] W. G. Fateley and E. R. Lippincott, *Spectrochim. Acta*, **10**, 8 (1957).

TABLE I[a]

VALUES OF $(k_e - k_a)^b$ in $RCo(CO)_4$

R	$10^2(k_e - k_a)$	R	$10^2(k_e - k_a)$
HCF_2CF_2	26	$(H_3CO)_3Si$	12
$F_3C(CF_2)_5CF_2$	24	Cl_3Si	6
$H_3C(g)$	20	F_3Si	5
H_3C	19	$(C_6H_5)_3Si$	4
F_3C	19	H_3CSiH_2	4
F_3CCF_2	19	H_3Si	3
H(g)	13	$(C\ H_5)_3Si$	−1
H	12	H_3CSiF_2	−2
C_6F_5	13	$(H_3C)_3Si$	−2

[a] For media in which spectra were determined, see ref 3.
[b] $(k_e - k_a)$ in millidynes per angstrom.

The values of $(k_e - k_a)$ reported in Table II of ref 3 have been recalculated using this relationship and are given in Table I. Two additional compounds, $H_3SiCo(CO)_4$[7] and $H_3CSiF_2Co(CO)_4$,[8] whose gas-phase infrared spectra in the CO stretching region have become available since the previous paper was written are also included.

The modified relationship slightly alters the relative magnitudes of the $(k_e - k_a)$ values only for $H_3CSiH_2Co(CO)_4$. The conclusions reached previously[3] remain unchanged. Indeed the modified relationship emphasized even more strongly the difference between carbon and silicon cobalt tetracarbonyls. Whereas the maximum $(k_e - k_a)$ value for a carbon cobalt tetracarbonyl was previously only twice that of the minimum value of a silicon cobalt tetracarbonyl, it is now very much greater than this. As can be seen from Table I the $(k_e - k_a)$ values for $H_3SiCo(CO)_4$ and $H_3CSiF_2Co(CO)_4$ fall within the range of values expected for silicon cobalt tetracarbonyls.

JOHN HARRISON LABORATORY
OF CHEMISTRY
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, PENNSYLVANIA 19104

A. P. HAGEN
A. G. MACDIARMID

RECEIVED JULY 12, 1967

---

(7) B. J. Aylett and J. M. Campbell, *Chem. Commun.*, 159 (1967).
(8) S. K. Gondal and A. G. MacDiarmid, unpublished observations, 1967.