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THE CARBONYL VIBRATION IN α-GROUP IV METAL KETONES*

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SUMMARY

Overend and Scherer's perturbation theory treatment (*Spectrochim. Acta*, 16 (1960) 773) of ν(CO) is applied to R_3MCOR' and R_3MCOMR_3 (M = C, Si, Ge, Sn). Corrected group frequencies, ν*(CO), which exclude effects extraneous to the CO bond (*e.g.* molecular geometry and potential energy contributions from internal coordinates other than the CO bond) and which reflect the true strength of the CO bond are calculated. Results are interpreted in terms of $Si(d_\pi) \leftarrow CO(\pi)$ interactions out-weighing silicon's $+I$ inductive effect in lowering ν(CO). Surprisingly, α-metal–CO electronic interactions appear to be of similar magnitude for C, Ge, and Sn. Our conclusions do not contradict the interpretation of the basicity order for the α-metal ketones in terms of relative inductive effects of M since the basicities depend on the availability of the non-bonding σ electrons of oxygen. In fact, the greater $+I$ of silicon may be expected to promote more effective $(d\text{–}p)\pi$ back-donation. A comment concerning the CO vibration in β-silyl ketones is given.

INTRODUCTION

Brook initially reported[1] that benzoyltriphenylsilane is yellow in contrast to the analogous carbon compound which is colorless. This observation has fired considerable enthusiasm[2,3] for attempting to understand the variations in the electronic properties of the carbonyl moiety upon substitution of silicon, germanium, or tin in a position α to this group. The infra-red carbonyl stretching frequency, ν(CO), of α-Group IV metal ketones is a good diagnostic for these compounds and is often used as supporting evidence for rationalization of their other electronic properties. Here, we present our efforts to improve our comprehension of the effects which metalloid substitution has on ν(CO) in these ketones.

Bathochromic shifts in ν(CO) vary over a wide range depending on the Group IV metal and its organic substituents[3-7]. To account for these shifts in a qualitative manner, the strong positive inductive effect of the metalloid relative to carbon has recently been considered to be of greater importance than $(nd\text{–}p)\pi$ interactions[5,7-9]

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as it appears consistent with the enhanced basicity[8] of the silyl and germyl ketones. More recently, Bock *et al*[2] have implied that, in view of the strong $+I$ effect of silicon and germanium which explains the basicities, a strong synergic interaction may be operative leading to significant withdrawal of electrons from the carbonyl group via $(d\text{–}p)\pi$ bonding, thus further weakening the CO bond. We have also pointed out[10] that a simple inductive effect argument completely collapses if applied to a comparison of acylgermanes and stannanes having the same organic moieties; the largest reported difference[5,7] in ν(CO) between germanium and tin derivatives in any one series is 3 cm^{-1}.

Sufficient experimental data are now available which may be used to improve significantly our understanding of the carbonyl vibration in the α-Group IV metal ketones. Below, we present a quantitative analysis of the observed CO stretching frequencies based on Overend and Scherer's treatment[11] for molecules XCOY. As the technique does not require a solution of the vibrational secular equation for the α-metal ketones, a complete vibrational assignment of the frequencies is not necessary.

The method provides an estimate of a "corrected" CO stretching frequency, ν^*(CO), which excludes effects extraneous to the CO bond, *e.g.* molecular geometry and potential energy contributions from internal coordinates other than the CO bond. The value of ν^*(CO), therefore, should reflect the true strength of the CO bond and direct electronic interactions between X, Y and the CO bond which affect the CO stretching force constant can be evaluated.

THE CALCULATION

In the original analysis[11] the perturbation treatment was applied to the CO stretching frequency of XCOY molecules which appear to have similar normal coordinates. X and Y represented diverse groups including CH_3, CN, CH_2Cl, CH_2Br, phenyl and the halogen atoms. Halford[12] has shown that if the α-substituents of a carbonyl group have masses equal to or greater than 12 amu, the CO stretching normal coordinate is quite insensitive to further increases in the masses of these substituents or to changes in the XCY angle. Furthermore, since the masses of atoms substituted β to the CO group have been shown[12] to have little effect on the value of ν(CO), only internal coordinates generated by nearest neighbor atoms are included in the treatment.

The ν(CO) frequency is most sensitive to variations in the force constants of angles and bonds neighboring the CO group. As the CO bond stretches, the normal coordinate governing ν(CO) contains changes in the CX and CY bond lengths and the XCY angle which contribute to the potential energy function and hence affect the magnitude of the carbonyl stretching frequency. These contributions are small compared to the work term arising from the distortion of the CO bond which accounts for the good carbonyl group vibration occurring in the region of 1600–1900 cm^{-1}. However, small variations within this range can not safely be ascribed to differences in the strengths of CO bonds as the contributions to the CO frequencies from potential energy terms not involving the CO internal coordinates are of comparable size.

The perturbation treatment expresses the characteristic group frequency of a molecule, ν_i' (here $\nu_i' = \nu'(\mathrm{CO})$, in terms of first order differences relative to the same characteristic frequency, ν_i^0, of a standard molecule

$$\nu_i' = \nu_i^0 + \sum_j (\partial\nu_i/\partial\phi_j)\Delta\phi_j + \sum_{\mathrm{X}} (\partial\nu_i/\partial\mu_{\mathrm{X}})\Delta\mu_{\mathrm{X}} + \sum_{\mathrm{XYZ}} (\partial\nu_i/\partial\alpha_{\mathrm{XYZ}})\Delta\alpha_{\mathrm{XYZ}} \cdots \tag{1}$$

where $\Delta\phi_j = \phi_j' - \phi_j^0$. The difference, $\Delta\phi_j$, compares the magnitudes of corresponding force constants of the molecule being treated and of the standard. Differences in the inverse atomic masses and the molecular angles are represented by $\Delta\mu_{\mathrm{X}}$ and $\Delta\alpha_{\mathrm{XYZ}}$. The terms including the force constants show the sensitivity of $\nu(\mathrm{CO})$ to variations in the potential energy functions of molecules (F matrix in the vibrational secular equation) whereas the last terms arise from kinetic energy effects (G matrix). The gradients, $(\partial\nu_i/\partial x_j)$, were determined[11] by applying perturbation theory to the vibrational secular equation of acetone. As the α-Group IV metal ketones are anticipated to have very similar carbonyl stretching normal coordinates and because these normal coordinates are expected to be more similar to acetone than those of the mixed halocarbonyls already tested[11], the use of acetone as a standard for these calculations appears particularly suitable. The $\partial\nu_i/\partial x_j$ calculated by Overend and Scherer are presented in Table 1. As $\Delta\mu_{\mathrm{X}}$ changes only slightly for masses greater than 12 amu, the values of $\partial\nu_i/\partial\mu_{\mathrm{X}}$ illustrate the relative insensitivity of $\nu(\mathrm{CO})$ to variations in the mass of X. On the other hand, the carbonyl stretching frequency is very sensitive to work terms involving the angles associated with the CO bond ($\partial\nu_i/\partial\phi_{\mathrm{CCC}}$ is 84.8 and $\partial\nu_i/\partial\phi_{\mathrm{CCO}}$ is 21.2 cm^{-1}A/mdyn).

TABLE 1

UREY–BRADLEY FORCE CONSTANTS AND FREQUENCY GRADIENTS OF ACETONE[a]

Parameters x_i	*Standard values*	$\partial\nu(\mathrm{CO})/\partial x_i$
$K(\mathrm{CO})$[b]	10.5	71.68
$K(\mathrm{CC})$	3.7	8.93
$H(\mathrm{CC})$	0.15	84.84
$H(\mathrm{OC})$	0.4	21.21
$F(\mathrm{CC})$	0.3	11.45
$F(\mathrm{OC})$	0.4	6.07
μ_{C}[c]	0.0666	68
α_{CCC}[d]	120°	−1.43

[a] From ref. 11.

[b] Units are mdyn/A and cm^{-1} A/mdyn.

[c] Units are amu^{-1} and cm^{-1} amu.

[d] Units are deg and cm^{-1}/deg.

A corrected group frequency, ν_i^* can be defined[11] as:

$$\nu_i^* = \nu_i^0 + (\partial\nu_i/\partial\phi_k)\Delta\phi_k \tag{2}$$

where in our case ϕ_k is the CO force constant. In this way, ν_i^* represents a pure CO stretching frequency of a molecule relative to that of acetone. Variations in ν_i^* can then be interpreted in terms of changes in the electronic character of the CO bond due to the various α substituents. Combining the above equations allows a direct evaluation of ν_i^*.

$$\nu_i^* = \nu_i' - \sum_{j \neq k} (\partial \nu_i / \partial \phi_j) \Delta \phi_j - \sum_{\mathrm{X}} (\partial \nu_i / \partial \mu_{\mathrm{X}}) \Delta \mu_{\mathrm{X}} - \sum_{\mathrm{XYZ}} (\partial \nu_i / \partial \alpha_{\mathrm{XYZ}}) \Delta \alpha_{\mathrm{XYZ}} \cdots$$

or

$$\nu_i^* = \nu_i' - \Delta \nu_i \tag{3}$$

It remains to estimate force constants for the α-Group IV metal ketones. As the standard parameters of acetone were estimated from the Urey–Bradley force field calculation of Miyazawa[13] it is desirable to transfer Urey–Bradley force constants from molecules similar to the α-Group IV metal ketones. Few force constant calculations for molecules containing Si, Ge, and Sn atoms have been reported thus far, most of these concentrating on a vibrational description of the silyl, germyl and stannyl groups. For this reason the C–M stretching force constants were transferred from the CH_3MH_3[14–16] molecules where M = C, Si, Ge and Sn, and adjusted (Table 2) such that the C–C force constant of ethane agrees with the Urey–Bradley constant (K(CC) = 3.7 mdyn/A) for acetone. The choice of the bending force constants is more critical because the CO stretching frequency is extremely sensitive to their magnitudes. Unfortunately, bending force constants for angles defined by CM and CO bonds have not been reported, to our knowledge. However, all the Urey–Bradley bending constants used in ref. 11 for acetone and acetyl fluoride are constant within 0.2 mdyn/A. Furthermore, these bending constants for a series of esters[17] are within 0.15 mdyn/A of those for acetone and acetyl fluoride. This invariance in these bending force constants for the first row substituents suggests that the bending constants for the silicon and germanium derivatives may be reasonably estimated from the corresponding values of acetyl chloride and bromide, respectively. On the assumption that the bending force constants in the α-Group IV metal ketones vary through the series in a regular manner, the force constants (H's) given in Table 2 are obtained. Estimations of the force constants for the bis-(α-Group IV metal) ketones were

TABLE 2

UREY–BRADLEY FORCE CONSTANTS, INVERSE MASSES AND ANGLES OF THE α-GROUP IV METAL KETONES, TOGETHER WITH THE CALCULATED VALUES OF $\Delta\nu$(CO)[a]

–MCOM′–:	*–SiCOC–*	*–GeCOC–*	*–SnCOC–*	*–SiCOSi–*	*–GeCOGe–*
K(CM)	2.6	2.3	2.1	2.6	2.3
K(CM′)	3.7	3.7	3.7	2.6	2.3
H(MM′)	0.07	0.05	0.03	0.04	0.02
H(OM)	0.15	0.10	0.05	0.15	0.10
H(OM′)	0.4	0.4	0.4	0.15	0.10
F(MM′)	0.17	0.17	0.17	0.14	0.14
F(OM)	0.22	0.16	0.10	0.22	0.16
F(OM′)	0.40	0.40	0.40	0.22	0.16
μ_M	0.0356	0.0138	0.0084	0.0356	0.0138
$\mu_{M'}$	0.0666	0.0666	0.0666	0.0356	0.0138
$\alpha_{MCM'}$	120°	120°	120°	120°	120°
$-\Delta\nu$(CO)	27	34	39	48	61

[a] Units are mdyn/A, amu^{-1}, cm^{-1} for force constants, inverse masses, and frequency correction factors, respectively.

similarly obtained from the corresponding data for the dihaloketones[11]. The Urey–Bradley non-bonded force constants (*F*'s) were extrapolated from those for the acetyl halides. Although these constants are quite different for acetone and acetyl fluoride, this difference is expected to decrease with the heavier α substituents. Finally, the dependence of ν'(CO) on the non-bonded constants is much smaller than on the bending force constants which are critical in the calculation of ν^*(CO).

Assuming a 0.2 mdyn/A error in each of these estimated force constants, this analysis indicates that deviations in ν^*(CO) of 32 cm^{-1} or more in any series of molecules are probably significant*. Although the actual errors in the force constants may exceed this estimate, the relative values of ν^*(CO) calculated by this treatment will be essentially correct if the force constants vary in a regular manner as assumed above.

The inverse masses**, μ_X, the interbond angle, $\alpha_{MCM'}$ and the calculated correction term, $\Delta\nu$(CO) from eqn. 3, are also listed in Table 2. Although bond angles are available[9] from single crystal data for acetyltriphenylsilane ($\alpha_{CCSi} = 124°$) and acetyltriphenylgermane ($\alpha_{CCGe} = 119°$), due to the lack of structural data for the other systems considered here, we have chosen all $\alpha_{MCM'} = 120°$ in our calculations. Employment of the experimental value for α_{CCSi} would only emphasize further the uniqueness of the acylsilanes compared to the other ketones as will be seen below.

RESULTS

Values of ν^*(CO) for the α-Group IV metal and bis-(α-Group IV metal) ketones are presented in Table 3. Since the correction term, $\Delta\nu$(CO), is negative (M = Si, Ge, Sn, Table 2) these values of ν^*(CO) are higher than the corresponding observed frequencies, ν'. Also, the range of frequencies for any given series is smaller for ν^*(CO) than for ν' since $\Delta\nu$(CO) is defined as zero for ketones with two carbon atoms α to the CO bond. For each series of α-metal ketones, ν^*(CO) for the silicon derivative lies more than 32 cm^{-1} below ν^*(CO) for its carbon analog. These differences are considered significant on the basis of our error estimate.

Those ketones (M = Ge, Sn) with alkyl groups bonded directly to the carbonyl carbon have ν^*(CO) values which fall surprisingly close to ν^*(CO) for the corresponding carbon compounds. This behavior of ν^*(CO) is clearly not anticipated upon inspection of the observed CO stretching frequencies where values of ν' for the heavier α substituents are in close proximity to those of the Si compounds and are well separated from those of the carbon analogs.

A somewhat different behavior emerges from the relative values of ν^*(CO) if a phenyl group is attached directly to the CO bond. These values for both benzoyltriphenylgermane and benzoyltriphenylstannane lie nearly 32 cm^{-1}—our limit of

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* Overend and Scherer assume an error of 0.1 mdyn/A which implies that deviations of 18 cm^{-1} or more are meaningful. Our error values are less optimistic because the bending and non-bonded force constants are extrapolated from values used by Overend and Scherer and the stretching force constants are estimated from values derived from valence force field calculations.

** According to Overend and Scherer's prescription, the effective mass of carbon is taken as 12 amu unless there are hydrogens bonded directly to it, in which case the masses of the hydrogens are added. We have chosen, for simplification however, an effective mass of 15 amu for any carbon. This difference causes an insignificant change of 1 cm^{-1} in the results.

TABLE 3

OBSERVED[a] (ν') AND CORRECTED (ν^*) GROUP FREQUENCIES (cm^{-1}) FOR THE CARBONYL STRETCHING VIBRATION IN α-GROUP IV METAL KETONES

	Ph_3MCOCH_3		$Ph_3MCOC(CH_3)_3$		Ph_3MCOPh	
M	ν'[b]	ν^*	ν'[b]	ν^*	ν'[b]	ν^*
C	1710	1710	(1694)	(1694)	1692[c]	1692
Si	1644[c]	1671	1628	1655	1618[c]	1645
Ge	1669	1703	1652	1686	1628[c]	1662
Sn	1670	1709	1655	1694	1627	1666

	$(CH_3)_3MCOPh$		$(CH_3)_3MCOCH_3$		$(CH_3)_3MCOC(CH_3)_3$	
M	ν'	ν^*	ν'	ν^*	ν'	ν^*
C	1680[d]	1680	1711[f]	1711	1691[h]	1691
Si	1618[c]	1645	1645[g]	1672	1638[g]	1665
Ge	1629[e]	1663	—	—	—	—

	$(CH_3)_3MCOM(CH_3)_3$		$Ph_3MCOMPh_3$	
M	ν'	ν^*	ν'	ν^*
C	1691[h]	1691	(1690)	(1690)
Si	1555[i]	1603	1555[i]	1603
Ge	—	—	1616[i]	1677

[a] In CCl_4 solutions. Values in parentheses are our estimates. [b] Refs. 5 and 7. [c] Also reported in ref. 4. [d] Ref. 18. [e] Ref. 8. [f] Ref. 19. [g] Ref. 20. [h] Ref. 21. [i] Ref. 22.

significant differences in $\nu^*(CO)$—below that for benzoyltriphenylmethane. Also $\nu^*(CO)$ for benzoyltrimethylgermane is equidistant from the values for benzoyltrimethylmethane and benzoyltrimethylsilane.

Although the data for the bis(α-metal) ketones are limited, it seems astonishing that the correction term $\Delta\nu$ is large enough for the germanium derivative to shift $\nu^*(CO)$ to within 13 cm^{-1} of $\nu^*(CO)$ for its carbon analog. This datum serves to highlight both the differences between silicon and germanium and the significant resonance interaction between the carbonyl group and an α-phenyl ring which will be discussed below.

The CO stretching force constants reflect the strength of the CO bond*. These values for the ketones can, in principle, be calculated from equation (2), $K(CO) \equiv \phi_k$, using our values for $\nu^*(CO)$ and the appropriate standard parameters for acetone. However, as all the experimental data, ν', have been obtained in carbon tetrachloride solution, before we can calculate $K(CO)$ we are required to correct for solvent effects

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* Strictly, the stretching force constant is a measure of the curvature of the potential energy curve at the bottom of the potential well; it is the depth of this well which is directly related to bond strength. However, a larger force constant may be considered as an indication of a stronger bond in a series of related molecules (ref. 31).

which are known to perturb gas phase frequencies. Since these perturbations are often comparable to the frequency differences being considered, the force constants uncorrected for solvent effects are not presented here*. Fortunately, observed frequency shifts for various non-metal substituted ketones similar to the carbon members of the series being studied appear to be essentially constant[19]. Hence, although the absolute values of ν^*(CO) will change with corrections for solvent effects, we expect that the relative values of ν^*(CO) and thus of K(CO) will remain unaffected.

DISCUSSION

From the striking similarity in ν^*(CO) values for the alkyl ketones (M=C, Ge, Sn) we infer that α-carbon, germanium, or tin affect the CO bond strength to the same degree. Therefore, a simple inductive effect argument based on relative electronegativities is clearly unacceptable for explaining the observed stretching frequencies. To account for the significant lowering of ν^*(CO) for all the silicon derivatives it is simplest to assign a major role to $\mathrm{Si}(3d_\pi)\leftarrow\mathrm{CO}(\pi)$ interaction in weakening the carbonyl bond. This is certainly in accord with Bock and Seidel's analysis[23] of the variations of the C≡C stretching frequencies in silyl acetylenes from which they concluded that $(d\text{–}p)\pi$ interaction predominates over silicon's $+I$ effect when silicon is directly attached to the multiple bond. As this implies silicon–carbon double bond character we note that the X-ray crystal structure determination[9] of acetyltriphenylsilane shows, if anything, a Si–C bond length slightly longer than a "normal" Si–C single bond. Trotter[9] ascribes this lengthening to important contributions from nonbonded structures such as $\mathrm{Ph_3M^+ : C(O^-)CH_3}$. This apparent contradiction, however, should be considered while keeping in mind that solid state effects may provide more favorable conditions for stabilization of charge separation (*e.g.* via dipole–dipole interactions) than would a non-ionizing medium such as carbon tetrachloride in which the infrared data were obtained. It is worth noting that in the series of carboxylic acids[24], $\mathrm{Ph_3MC(O)OH}$, ν(CO) significantly drops by 36, 21 and 21 $\mathrm{cm^{-1}}$ for M=C, Si, Ge respectively, upon changing the solvent medium from carbon tetrachloride to potassium bromide.

The fact that the disilanyl ketones, $\mathrm{Ph_5Si_2COCH_3}$ and $\mathrm{Ph_5Si_2COPh}$, exhibit $n\rightarrow\pi^*$ electronic transitions and carbonyl stretching frequencies equal to their respective monosilyl analogs (Table 3) has been offered[25] as evidence against Si–CO-(π) bonding. The UV data, however, may only reflect insignificant $(d\text{–}p)\pi^*$ interactions and Ramsey[26] has offered alternate explanations for the constant $n\rightarrow\pi^*$ transition energy. Here, we are considering ground state interactions between a vacant d orbital of a metalloid and the filled π orbital of the carbonyl group. According to our treatment, β substituents do not affect the value of $\Delta\nu$. Thus, a β-silyl group can only influence the carbonyl stretching frequency via electronic interactions. The fact that the observed frequencies for the disilanyl ketones are the same as for the corresponding monosilyl compounds suggests that the β-silyl group is electronically inert with respect to ν(CO). However, for a series of β-silyl ketones with carbon α to the carbonyl group, the sensitivity of ν(CO) to the silyl group is clearly established[4b]. For

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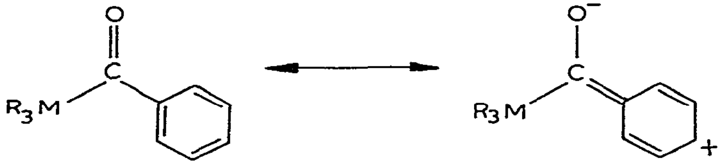
* The CO stretching force constant for the α-metal ketones should be similar to that for acetone: 10.5 mdyn/A (ref. 13).

these compounds evidence has been presented[6] for intramolecular interaction between the β-silicon and the carbonyl group although the nature and magnitude of such interactions were not resolved. An assessment of intramolecular interactions in these β-silyl ketones can be obtained by a simple calculation which shows that the closest approach non-bonded distance between the β-silicon and the carbonyl oxygen in, for example, $(CH_3)_3SiCH_2COCH_3$ is well within the sum of their Van der Waals radii while for a disilanyl ketone the closest approach exceeds their sum*. This at least implies little if any intramolecular interaction of the through-space type between β-Si and the CO group in the disilanyl compounds.

A closer examination of the data in Table 3 for the α-methyl and α-t-butyl ketones shows a consistently lower value ($\sim 15\ cm^{-1}$) for ν' and ν^* in the latter series. This probably arises from steric interaction of the t-butyl group which would be manifested in an increase of the MCC bond angle[28]. Had we chosen this angle more realistically, *i.e.* greater than 120°, we would have obtained a larger $\Delta\nu(CO)$ which would lift $\nu^*(CO)$ for these compounds even closer to $\nu^*(CO)$ for the α-methyl ketones.

If a phenyl group is substituted α to the CO bond as in Ph_3MCOPh and $(CH_3)_3MCOPh$, the $\nu^*(CO)$'s for M = C, Ge, Sn no longer form a well-defined group. As it is apparent that the phenyl group is responsible for the decreases in ν' of 18 and 31 cm^{-1} in going from acetyltriphenylmethane to its benzoyl analog and from acetyltrimethylmethane to its benzoyl analog, respectively, decreases of a similar nature must be operative in the other ketones but to somewhat differing degrees. The further diminutions in CO bond strength with phenyl substitution may reflect the relative importance of resonance structures involving the phenyl ring. The largest frequency variation (47 cm^{-1}) within any one series of the mono-α-metal ketones in Table 3 occurs between the carbon and silicon substituents of Ph_3MCOPh. The CO bond of the silicon derivative may be weakened through both $(d\text{-}p)\pi$ bonding and resonance with the phenyl group, both effects tending to remove π electron density from the CO bond. The importance of resonance interaction with the phenyl ring is further substantiated by the $\nu^*(CO)$ values calculated by Overend and Scherer[11] for the acetyl and benzoyl halides. Each series of halides has values of $\nu^*(CO)$ which vary by less than 26 cm^{-1} although the substitution of phenyl for methyl in any given halide results in a decrease of $\nu^*(CO)$ by more than 50 cm^{-1}.



The considerable difference between $\nu^*(CO)$ for the bis-α-silyl ketones and the approximately equal $\nu^*(CO)$'s for the germanium and carbon analogs (Table 3) is essentially double that for the alkyl α-metal ketones. This suggests that a simple

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* For the model systems SiCCO and SiSiCO the following parameters were employed: ∠CCO and ∠SiCO 120°; ∠SiCC and ∠SiSiC 109.5°; $r(C{=}O)$ 1.20 Å; $r(Si{-}C)$ 1.86 Å; $r(Si{-}Si)$ 2.30 Å. The calculated distances of closest β-Si–O approach are 2.8 Å (SiCCO) and 3.4 Å (SiSiCO). We estimated the sum of the Si and O Van der Waals Radii as 3.3 Å (ref. 27).

additive effect of α-silicon substitution may be operative on the CO stretching frequency*. It may, therefore, be possible to predict the carbonyl stretching frequency for mixed bis-α-metal ($M \neq C$) ketones which are as yet unknown to our knowledge.

Previous interpretations of the carbonyl stretching frequency have been correlated[5,7-9] with the basicity data[8] (R_3MCOPh; $M = Si > Ge > C$) by emphasizing the role of the inductive effect of M. Therefore, it is important to point out that our interpretation of $\nu(CO)$ remains consistent with the basicity data as well as being more satisfactory regarding $\nu(CO)$. It should be remembered that the basicities reflect the availability of the non-bonding electrons on oxygen which occupy orbitals orthogonal to the carbonyl π system. Although the greater $+I$ of silicon leads to the higher basicity and would be expected to result in a decrease in the strength of the CO σ bond, further reduction of the CO bond strength may be achieved synergically via $M(d) \leftarrow CO(\pi)$ bonding in favorable cases. As the generally accepted order[29] of $(d\text{–}p)\pi$ bonding is $Si > Ge > Sn$, the most favored systems are the acylsilanes for which we observe the lowest values of $\nu^*(CO)$ (or $\nu'(CO)$). The $\nu(CO)$ values for the series Ph_3MCOCH_3 suggest, not surprisingly, that $(d\text{–}p)\pi$ bonding is less important for germanium and tin than for silicon. In order to assess in more detail the differences in the electronic interactions between tin and germanium α to a carbonyl group it would be useful to have basicity data for α-tin ketones; these are unavailable at present.

The importance of $(d\text{–}p)\pi$ bonding ($d_\pi\text{–}p_\pi^*$ interaction) in determining electronic properties dependent on the excited states of the α-Group IV metal ketones is well established[2,30]. Our analysis appears to provide strong evidence, at least for silicon, that $(d\text{–}p)\pi$ bonding ($d_\pi\text{–}p_\pi$ interaction) also plays a major role in the ground state.

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* This additive effect of adjacent metalloids is also observed in the lowering of the $n \rightarrow \pi^*$ electronic transition from that of the carbon analog (ref. 3, p. 134).

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