Direct Carbon-13 Nuclear Magnetic Resonance Study of Boron Trifluoride Complexes with Alkyl and Cyclic Ketones

By **Anthony Fratiello,* Robert Kubo,** and **Stanley Chow,** Department of Chemistry, California State University, Los Angeles, Los Angeles, California 90032, U.S.A.

A study of the boron trifluoride complexes of the C_4—C_{10} cycloalkanones and nine alkyl ketones has been completed using a direct, low-temperature carbon-13 n.m.r. technique. At temperatures in the range −85 to −125 °C, exchange is slow enough on the n.m.r. time scale to permit the observation of separate ^{13}C resonance signals for bound and free ligand. The chemical shift displacements induced by complex formation were *ca.* 24 p.p.m. to lower field for the carbonyl group signal, and about an order of magnitude less, to higher and lower field, for the other carbon signals. Doublets were observed for the signals of bound ligand with several members of both series, a feature which is best interpreted in terms of a slow exchange of the BF_3 between the two sp^2 orbitals of the carbonyl oxygen atom. Some evidence is presented for the much greater stability of only one of these *cis*–*trans*-isomers in four of the alkyl ketone cases.

A VARIETY of thermodynamic and spectroscopic studies of boron trihalide complexes with organic molecules have been made to evaluate the energetics and stoicheiometry of complex formation, steric hindrance to complexation, and the relative basicities of the ligands.[1-22] An efficient approach involves n.m.r. measurements at temperatures low enough to slow exchange, thereby permitting the observation of separate resonance signals for bulk and co-ordinated ligand. Studies by ^{1}H, ^{11}B, ^{19}F,[23-31] and most recently ^{13}C [32-36] n.m.r. spectroscopy have been carried out for several sets of organic bases. Although ^{1}H and ^{19}F n.m.r. spectra are useful for determining the stoicheiometry of the complex and the extent of competitive complexation in mixtures of bases, the study of ^{13}C nuclei offers several advantages.[37,38] These include the sensitivity of ^{13}C nuclei to electron distribution changes induced by strong complex formation, the ability to study non-protonated functional groups, the appearance of well resolved single peaks in wide-band proton-decoupled spectra, and as will be demonstrated in this study, the ready detection of stereochemical features not easily observed in ^{1}H n.m.r. spectra. All these advantages were realized with the cycloalkanones and alkyl ketones chosen here, two groups which provide molecules of gradually increasing structural complexity.

EXPERIMENTAL

Methods.—Boron trifluoride and dichlorofluoromethane (Genetron) were Matheson CP grade. Dichloromethane and all ketones were reagent grade and they were dried over $CaSO_4$ before being used. BF_3 Was fractionated at −110 °C, and condensed *in vacuo* into the n.m.r. sample tube (Wilmad, 504PP) in liquid nitrogen. Vacuum line transfer also was necessary when Genetron was used as the solvent. The sample tubes were sealed, warmed in an acetone–dry ice-bath to dissolve all components, and stored in liquid nitrogen until the spectra could be recorded, usually within a day. Sample purity and the absence of any decomposition were verified by the ^{1}H and ^{13}C n.m.r. spectra.

^{1}H and ^{19}F n.m.r. spectra were recorded on Varian A-60 and HA-100 spectrometers, the latter operating at 94.1 MHz for ^{19}F nuclei. ^{13}C N.m.r. spectra were obtained at 22.6 MHz with a Bruker HX-90-E Fourier transform spectrometer, equipped with a Bruker–Nicolet data system, model B-NC-12. Pulses of *ca.* 5 μs width (7 μs produces a 90° tip angle) were applied at 1 s intervals. The ^{1}H nuclei were noise-decoupled at 90 MHz and a 2 000 Hz bandwidth. The base concentrations required 3 000—5 000 pulses for sufficient signal intensity, particularly for the carbonyl group peaks. Temperature studies from −150 to +200 °C are possible with the three instruments.

The ^{1}H, ^{13}C, and ^{19}F n.m.r. techniques used for the study of these complexes are similar in many respects to those described in more detail elsewhere.[23-30] However, at these natural abundance levels, ^{13}C measurements are more time consuming even with the accumulation capability provided by a Fourier transform accessory. Each sample required a series of calibration-type ^{13}C n.m.r. experiments to verify the slow exchange condition. After the temperature for maximum sensitivity and resolution had been determined, the final experiments were completed.

RESULTS

Although ^{13}C n.m.r. results are emphasized in this paper, ^{1}H and ^{19}F n.m.r. measurements were also carried out with these ketones. The cycloalkanone results have been described previously,[30] but in general, the ^{1}H n.m.r. data indicated 1 : 1 complex formation in all cases, and the ^{19}F data were used to evaluate the relative basicities of these ligands. Since the ^{1}H n.m.r. spectra of the BF_3–alkyl ketone mixtures were more complicated in most cases, detailed chemical shift measurements were not made. However, the resolution was good enough for intensity measurements which gave verification of 1 : 1 complex formation within 5% for all members of this series. The ^{19}F chemical shifts for these alkyl ketone complexes were not sufficiently different to

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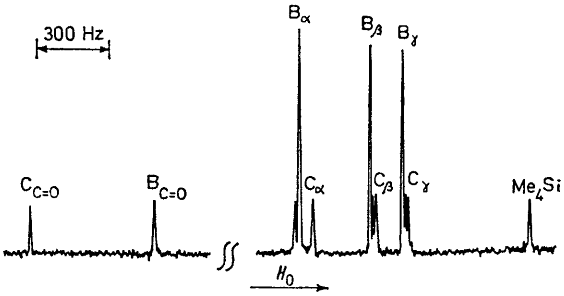
TABLE 1

Carbon-13 chemical shift data for BF_3 complexes of cycloalkanones

Ketone [a,b]	t/°C	δ/p.p.m.[e] C=O	α	β	γ	δ
C_4	−115 [d]	214.6 (+27.9)	47.6 (−1.3) (−2.6)	9.8 (+2.1)		
C_5	−85 [c]	221.9 (+24.8)	38.7 (+2.9) (+0.6)	23.4 (+0.3) (−0.9)		
C_5	−90 [d]	22.44 (+23.3)	39.0 (+2.7) (+0.6)	23.6 (+0.3) (−1.0)		
C_6	−90 [c]	213.9 (+24.9)	42.1 (−3.0)	27.2 (+0.7)	24.7 (−1.2)	
C_6	−120 [d]	216.3 (+23.3)	42.3 (−2.9)	27.2 (+1.1)	24.8 (−1.2)	
C_7	−85 [c]	216.9 (+23.6)	43.9 (+0.7) (−2.7)	30.4 (−0.6) (−1.2)	24.2 (−0.5) (−1.0)	
C_8	−90 [c]	220.9 (+24.0)	41.9 (−1.0) (−9.8)	26.7 (+1.2)	25.6 (−0.6)	24.3 (−1.7)
C_8	−90 [d]	221.9 (+23.4)	42.1 (−1.0) (−9.9)	27.0 (+1.1)	25.8 (−0.6)	24.6 (−1.9)
C_9	−85 [c]	220.5 (+23.3)	43.8 (−0.8)	27.8 (+0.6)	25.0 (+0.6)	24.1 (−2.4)
C_{10}	−90 [c]	216.6 (+22.0)	Not assignable			

[a] C_4—C_{10} = cyclobutanone to cyclodecanone. [b] Within 5%, the mole ratios of BF_3 : ketone : solvent, were 1 : 3.0 : 30 in all samples. This corresponds to a ketone concentration of *ca.* 1 M. [c] In methylene chloride. [d] In Genetron . [e] The chemical shifts of the bulk ligand were measured with respect to internal tetramethylsilane. The numbers in parentheses are the chemical shift differences, in p.p.m., between the co-ordinated and bulk ligand signals ($\delta_C - \delta_B$). A positive sign indicates a signal displacement to lower field in the complex.

permit a complete competitive basicity study. Specifically the ^{19}F chemical shifts of these complexes, all downfield from internal C_6F_6, were *ca.* 13.2 ± 0.2 p.p.m. in five cases; 12.3 and 14.2 p.p.m. for heptan-2- and -4-one, respectively; and doublets of unequal intensity at 13.0 and 12.8 p.p.m. for hexan-3-one and 13.6 and 13.3 p.p.m. for heptan-3-one.



Carbon-13 n.m.r. spectrum at −85 °C of a 1.0 : 3.0 : 30 mole ratio mixture of BF_3, cycloheptanone, and methylene chloride. The spectrum is the accumulation of 2 000 pulses obtained at 22.6 MHz on a Bruker HX-90-E Fourier transform spectrometer. The signals arising from bulk (B) and co-ordinated (C) ketone molecules are identified

The ^{13}C chemical shift data for all cyclic and alkyl ketones are presented in Tables 1 and 2, respectively, and a representative spectrum is shown in the Figure. The cycloalkanones are designated as C_4—C_{10} for cyclobutanone to cyclodecanone, respectively. Each entry represents measurements with at least two samples. Dichloromethane was used as the solvent for several of the cycloalkanones, but for temperatures below — 100 °C, or to avoid viscosity problems, Genetron was used. A comparison of results for the same ketone in both solvents, specifically, C_5, C_6, and C_8 in Table

TABLE 2

Carbon-13 chemical shift data for BF_3 complexes of alkanones

Ketone [a,b]	t/°C	δ_B (p.p.m.) [c] C-1	C-2	C-3	C-4	C-5	C-6	C-7
Propan-2-one	−125	31.7 (+1.7) (−2.3)	211.4 (+23.4)	31.7 (+1.7) (−2.3)				
Butan-2-one	−110	30.3 (−2.3)	212.9 (+22.8)	37.0 (+3.2)	7.5 (−0.7)			
Pentan-3-one	−125	7.7 (+2.0) (−1.0)	35.9 (+0.8) (−1.2)	216.2 (+24.4)	35.9 (+0.8) (−1.2)	7.7 (+2.0) (−1.0)		
Pentan-2-one	−110	30.4 (−2.2)	213.3 (+22.1)	45.8 (+2.1)	17.0 (−0.8)	13.7 (−0.7)		
Hexan-3-one	−120	7.6 (+2.1) (−0.8) [d]	36.0 (+1.0) [d] (−1.4)	214.9 (+23.7) [d] (+24.5)	44.4 (+1.4) (−1.6) [d]	17.3 (+2.8) [d] (−1.3) [e]	13.8 (+0.6) [d] (−0.9) [e]	
Heptan-4-one	−105	13.8 (+0.6) (−0.8)	17.2 (+3.1) (−1.1)	44.8 (−0.3) (−1.7)	214.5 (+23.5)	44.8 (−0.3) (−1.7)	17.2 (+3.1) (−1.1)	13.8 (+0.6) (−0.8)
Hexan-2-one	−120	30.5 (−2.3)	213.1 (+22.5)	43.9 (+2.4)	25.7 (−1.0)	22.5 (−0.7)	14.6 (< −0.3)	
Heptan-3-one	−115	7.6 (−0.8)	36.1 (+0.9) [d] (−1.5)	215.6 (+23.0) [d] (+23.9)	42.8 (−1.4)	26.1 (+2.6) [d] (−0.5)	22.7 (+0.8)	14.5 (−0.3)
Heptan-2-one	−115	30.4 (−2.2)	213.5 (+21.7)	44.0 (+2.3)	23.5 [f] (−0.9) [g]	31.5 [f] (−0.7)	23.5 (−0.3) [g]	14.6 ~0

[c] The solvent was Genetron in all samples. [b] Within 5%, the mole ratios of BF_3 : ketone : Genetron, were 1 : 3.0 : 30 in all samples. This corresponds to a ketone concentration of *ca.* 1M. [c] This bulk ligand chemical shifts, δ_B, were measured with respect to internal tetramethylsilane. The numbers in parentheses are the chemical shift differences in p.p.m., between the co-ordinated and bulk ligand signals ($\delta_C - \delta_B$). A positive sign indicates a signal displacement to lower field in the complex. [d] This signal was more intense than the other doublet component. [e] This signal was barely observable. [f] This assignment may be reversed. [g] This assignment may be reversed.

1, reveals a small difference only in the carbonyl group resonance position. In Tables 1 and 2, the bulk ketone chemical shifts, δ_B, measured with respect to internal tetramethylsilane, are given, and in parentheses, the separation between each peak and the same signal in the complex, $\delta_C - \delta_B$, is shown. The δ_B values are accurate to *ca.* 0.1 p.p.m. Signal assignments were made by reference to published results, when available,[38-40] and by internal comparisons among members of each series. The small differences, generally *ca.* 1 p.p.m., between our δ_B results and those reported previously, can be attributed to solvent and temperature effects. Complete assignments of all bulk and co-ordinated ligand signals were possible in most cases.

DISCUSSION

In a previous ^1H n.m.r. study of BF_3–cycloalkanone complexes,[30] and in the ^1H measurements carried out with the alkyl ketones in this study, it was observed that the bound ligand shift displacements are all to lower field, generally are *ca.* 0.5 p.p.m. for the α-CH_2 protons, and are attenuated markedly with distance from the interaction site. As seen in Tables 1 and 2, the ^{13}C shift displacements are much larger, and upfield in some cases at sites other than the carbonyl. This reflects the greater number of factors which can affect the electronic environment of ^{13}C nuclei. As anticipated, the largest signal displacement for both series of ketones occurred with the carbonyl group resonance of the complex, *ca.* 24 p.p.m. downfield from the bulk ligand peak. The magnitude of this shift displacement is comparable to that observed for the carbonyl group of acetone in sulphuric acid solution,[41,42] and must result from a similar inductive effect. Resonance contributions from structures such as C^+–$O^- \cdots BF_3$ could account for the extensive deshielding of this carbon nucleus. However, it is unusual that the magnitude of the signal displacement does not depend on the strength of the BF_3 complex. In a previous study of acetone hydrogen-bond complexes, a high dependence of the carbonyl ^{13}C resonance position on acid strength was noted, with shifts ranging from 2 to 40 p.p.m. downfield from pure acetone. One can compare the cycloalkanone relative basicities toward BF_3, determined by direct measurement, with their carbonyl group signal displacement induced by complex formation. The relative basicities,[30] with $\delta_C - \delta_B$ values in parentheses, are $C_8(24.0) > C_5(24.8) > C_7(23.6) > C_6(24.9) \simeq C_9(23.0) > C_{10}(22.0) \gg C_4(27.9)$. Thus, base strength,[30,43] or presumably, the strength of the complex, does not appear to be the dominant factor in these shift displacements. In fact, the greatest signal displacement was observed for the complex of C_4, the weakest base by far of the cycloalkanone series, and probably, of both series.

Another interesting result, illustrated in the Figure for the BF_3 complex of cycloheptanone, is the appearance of doublets for the bound ligand signals for several members of both series of ketones. This observation was made for co-ordinated C_4(α-C), C_5, C_7, and C_8(α-C) in the cycloalkanone group, and propan-2-one, pentan-3-one, heptan-4-one, hexan-3-one, and heptan-3-one among the alkyl ketones. One process which can account for these results with both groups is a slow exchange of the BF_3 between the two vacant sp^2 orbitals of the carbonyl oxygen atom. This *cis–trans*-isomerization has been proposed to explain the appearance of doublet ^1H n.m.r. patterns for BF_3–alkyl ketone complexes [11,22] and the BF_3 complexes of cyclohexanone and cycloheptanone.[30] This process also was invoked to explain doublets in the ^{13}C n.m.r. spectra of the BF_3 complex of cyclohexenone,[33] pentan-3-one,[34] and two cyclic ketones.[34] Although ring inversions are possible for the cycloalkanones, such processes can be ruled out here for several reasons. The rigid structure of C_4 and C_5 precludes inversion with these molecules. On the other hand, slow exchange of BF_3 between the two oxygen sp^2 orbitals would produce doublets for the α-C and β-C of C_5, but only for the α-C of C_4. As seen in Table 1, the observation of doublets for these carbons and a single peak for the β-C of C_4 is consistent with this prediction. Although a chair–chair interconversion is possible for C_6, and even more complicated conformational processes for the larger cycloalkanones, prior studies again would rule out slow inversions as the cause of the spectral results here. Anet and his co-workers were able to slow chair–chair interconversion for deuteriated C_6 only at −185 °C, and calculated $\Delta G^\ddagger$ *ca.* 4 kcal mol^{-1} for this process.[44] Similarly, ring inversion of C_8 is slow on the n.m.r. time scale in the range −135 to −160 °C with $\Delta G^\ddagger$ *ca.* 8 kcal mol^{-1}.[45,46] These measurements have not been possible for C_7, presumably because of an extremely low energy barrier to inversion. It does not seem likely that complexation would increase $\Delta G^\ddagger$ sufficiently in these molecules to cause a slowing of inversion at the much higher temperatures of this study.

A correlation of these ^{13}C n.m.r. results with the ^1H data for these ketone complexes is not entirely satisfactory. Doubling of the ^1H spectral patterns for co-ordinated propan-2-one [47] and pentan-3-one [13] have been described elsewhere, but no further ^1H shift studies for the alkyl ketones were made here. However, detailed proton resonance experiments with the BF_3 complexes of C_4—C_{10} in our laboratories revealed such doubling only for co-ordinated C_6 and C_7 in this series.[30] The ^1H patterns for co-ordinated C_4 and C_5 were well resolved with no sign of additional multiplicity, and the ^{13}C spectrum of BF_3–C_6 remained unchanged even at −140 °C. In view of these facts, one may conclude that by coincidence, the

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specific hydrogen atoms in C_4 and C_5, and carbon atoms in C_6, are electronically, but not structurally, equivalent.

The alkyl ketone results clearly demonstrate the importance of steric effects in the complexing process. Bound ligand doublet patterns were observed for propan-2-one, pentan-3-one, heptan-4-one, hexan-3-one, and heptan-3-one. This indicates that complexing can occur at either oxygen sp^2 orbital if the two orbitals are sterically equivalent, or if bulky alkyl groups appear on both sides of the carbonyl group. The areas of the doublet components were essentially equivalent, and only one bound carbonyl signal was observed in the ^{13}C n.m.r. spectra of the three symmetrical ketones mentioned above. However, non-equivalent doublets and two carbonyl signals were recorded for the BF_3 complexes of hexan-3-one and heptan-3-one. Two ^{19}F signals also were observed for the last two complexes, corresponding to the unequal electronic environments experienced by BF_3 in these cases.

Singlet co-ordinated ligand patterns were recorded with the four remaining ketones, which have a methyl group combined with a bulkier alkyl group. It does not seem reasonable that exchange of the BF_3 between the two oxygen sp^2 orbitals could be more rapid in these cases, producing one averaged set of ligand signals. A more likely possibility is the greater stability of one conformational isomer, that with the BF_3 co-ordinated at the oxygen orbital close to the methyl group.

Support for this choice is provided by the BF_3–propan-3-one results, *i.e.*, the appearance of methyl group ^{13}C signals at +1.7 and −2.3 p.p.m. from the bulk acetone methyl peak. The $\delta_C - \delta_B$ value of −2.3 p.p.m. corresponds almost exactly to that obtained for the methyl group shift displacement of these four ketones, specifically, butan-2-one (−2.3), pentan-2-one (−2.2), hexan-2-one (−2.3), and heptan-2-one (−2.2 p.p.m.). Also, since the 3-carbon is a CH_2 group in each of these molecules, the shift displacements should be analogous at this site. A $\delta_C - \delta_B$ value of *ca.* +2.2 p.p.m. was observed for these carbons in three cases, with only butan-2-one deviating from this pattern. This last result is not surprising since the 4-carbon in butan-2-one is a CH_3 group rather than a CH_2 as in the other ketones.

The negative sign of the CH_3 carbon sign displacements for these four ketones also is consistent with this single isomer proposal. It has been shown that steric crowding of a carbon site results in increased shielding and an upfield shift.[38,48–51] For example, for alkyl C–H bonds, Grant and his co-workers[48,49] interpreted this in terms of a steric polarization of the carbon valence electrons by a non-bonding interaction. A similar interaction could occur between the alkyl groups of these ketones, and the bulkier, more polarizable BF_3. If so, the results of Table 2 permit a separation of shifts due to inductive and steric effects in the methyl ketones. From the results for acetone and the other four methyl ketones, δ_{ind} is *ca.* +1.7 and *ca.* +2.5 p.p.m., respectively, for CH_3 and CH_2 groups bonded to carbonyl. For the same molecules, δ_{steric} is *ca.* −4 p.p.m. for a CH_3 group bonded to a carbonyl, provided the observed upfield displacement of −2.3 p.p.m. is the resultant of δ_{ind} plus δ_{steric}.

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