High-Resolution Solid-State ^{119}Sn NMR Investigations of Organotin Halides R_3SnX and R_2SnX_2 (R = Alkyl, Aryl; X = Cl, Br)

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Solid-state ^{119}Sn CP/MAS NMR spectra have been obtained for four triorganyltin halides and seven diorganyltin dihalides. The solution-to-solid chemical shift changes are discussed in terms of the solid-state structures and, in the case of benzyl compounds, conformations. Unsymmetrical splittings in some of the spectra are explained as arising from residual dipolar and/or indirect coupling interactions between ^{119}Sn and ^{35}Cl, and the results are the first reported examples of this type. Some tin-119 CP/MAS results of general significance on other compounds are mentioned for the purpose of comparison.

Introduction

Organotin halides, R_3SnX and R_2SnX_2, have been known for a long time and have been used extensively as starting materials in organotin chemistry.[1] For some of these compounds the X-ray crystal structures have been determined.[2-6] and there is a considerable amount of data available from IR, Mössbauer, NQR, and solution-state NMR spectroscopy.[7-14] Despite this wealth of information there appears to be some difference of opinion concerning the solid-state structure of these compounds.[15] Depending on whether the emphasis in interpreting the crystallographic data has been laid on the full molecular geometry or on bond distances only, different conclusions have been drawn from very similar results. A similar picture emerges from previous Mössbauer studies. Large quadrupole splitting values have been explained in terms of coordination changes at the tin atom (penta- or hexacoordinated geometry to form polymeric chains in the solid state), but it has also been shown that these data can be explained satisfactorily by assuming a distorted tetrahedral geometry around tin.[3]

This situation prompted us to study some organotin halides, R_3SnX and R_2SnX_2, by means of solid-state ^{119}Sn NMR spectroscopy. Recently, this method has been shown to be a powerful tool in investigating the solid-state structures of organometallic compounds.[16-22]

Results and Discussion

(i) General Comments. Before discussing our solid-state ^{119}Sn CP/MAS results on specific compounds, it is necessary to comment on the observed parameters (i.e. $\delta(^{119}\mathrm{Sn})$, chemical shift anisotropies) in a general way in order to illustrate the expected ranges of data for different chemical situations. Such comments are necessary since to date surprisingly few reports on high-resolution solid-state ^{119}Sn NMR have appeared in the literature. In the solution state $\delta(^{119}\mathrm{Sn})$ covers a range of approximately 2000 ppm.[7] Therefore, substantial differences in $\delta(^{119}\mathrm{Sn})$ in solution versus solid state ($\Delta\delta(^{119}\mathrm{Sn}) = \delta(\mathrm{solid}) - \delta(\mathrm{solution})$) are to be expected in situations where the tin coordination number increases on going from solution (e.g. coordination number 4) to the solid state. For instance, for tricyclohexyltin hydroxide, $(C_6H_{11})_3SnOH$ (see Figure 1), $\delta(^{119}\mathrm{Sn})$ changes from +11.6 ppm for a dilute $CDCl_3$ solution to −217 ppm in the solid state. This dramatic increase in ^{119}Sn shielding (ca. 220 ppm), together with the extensive spinning sideband pattern for the solid-state spectrum, is fully in accord with the known X-ray crystal structures for Me_3SnOH and Ph_3SnOH,[23-25] showing hy-

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(1) Davies, A. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2.

(2) Cusack, P. A.; Smith, P. J.; Donaldson, J. D.; Grimes, S. M. *A Bibliography of X-ray Crystal Structures of Tin Compounds*; International Tin Research Institute: London, Publication No. 588.

(3) Ganis, P.; Valle, G.; Furlani, D.; Tagliavini, G. *J. Organomet. Chem.* **1986**, *302*, 165.

(4) Tse, J. S.; Lee, F. L.; Gabe, E. J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *42C*, 1876.

(5) Baxter, J. L.; Holt, E. M.; Zuckerman, J. J. *Organometallics* **1985**, *4*, 255.

(6) (a) Calogero, S.; Ganis, P.; Peruzzo, V.; Tagliavini, G. *J. Organomet. Chem.* **1979**, *179*, 145. (b) Calogero, S.; Ganis, P.; Peruzzo, V.; Tagliavini, G.; Valle, G. *J. Organomet. Chem.* **1981**, *220*, 11.

(7) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73.

(8) Long, G. J., Ed. *Mössbauer Spectroscopy Applied to Inorganic Chemistry*; Plenum: New York, 1984; Vol. 1.

(9) Davies, A. G.; Milledge, H. J.; Puxley, D. C.; Smith, P. J. *J. Chem. Soc. A* **1970**, 2862.

(10) Molloy, K. C.; Quill, K. *J. Chem. Soc., Dalton Trans.* **1985**, 1417.

(11) Blunden, S. J.; Searle, D.; Smith, P. J. *Inorg. Chim. Acta* **1986**, *116*, L31.

(12) Maddock, A. G.; Platt, R. H. *J. Chem. Soc. A* **1971**, 1191.

(13) Debye, N. W. G.; Linzer, M. *J. Chem. Phys.* **1974**, *61*, 4770.

(14) Maksyutin, Yu. K.; Khrapov, V. V.; Mel'nichenko, L. S.; Semin, G. K.; Zemlyanskii, N. N.; Kocheshkov, K. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, *3*, 602.

(15) See ref 3 and references given therein.

(16) Harris, R. K.; Sebald, A. *J. Organomet. Chem.* **1987**, *331*, C9.

(17) Harris, R. K.; Sebald, A., accepted for publication in *Magn. Reson. Chem.*

(18) Harris, R. K.; Packer, K. J.; Reams, P.; Sebald, A. *J. Magn. Reson.* **1987**, *72*, 385.

(19) Harris, R. K.; Packer, K. J.; Reams, P. *J. Mol. Struct.* **1986**, *141*, 13.

(20) Harris, R. K.; Sebald, A., to be submitted for publication.

(21) Harris, R. K.; Packer, K. J.; Reams, P. *Chem. Phys. Lett.* **1985**, *16*, 115.

(22) Harris, R. K.; Mitchell, T. N.; Nesbitt, G. J. *Magn. Reson. Chem.* **1985**, *23*, 1080.

(23) Davies, A. G., personal communication.

(24) Glidewell, C.; Liles, D. C. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *34B*, 129.

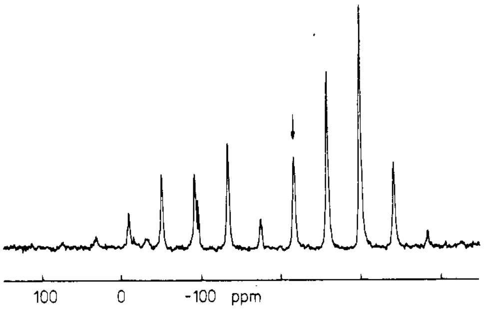


Figure 1. 74.63-MHz CP/MAS ^{119}Sn NMR spectrum of tricyclohexyltin hydroxide. Spectral parameters: contact time, 1 ms; recycle delay, 10 s; number of transients, 750. The vertical arrow indicates the centerband.

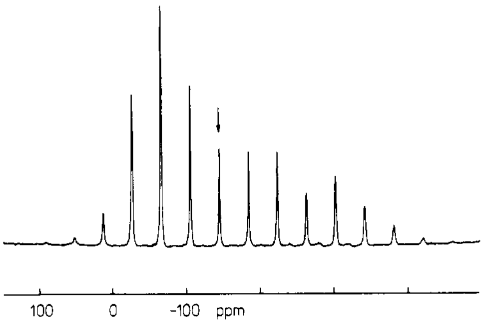


Figure 2. 74.63-MHz CP/MAS ^{119}Sn NMR spectrum of dibenzyltin diphenylacetylide. Spectral parameters: contact time, 1 ms; recycle delay, 10 s; number of transients, 2120. The vertical arrow indicates the centerband.

Table I. ^{119}Sn CP/MAS and Solution-State NMR Data for Some Triorganyltin Halides, R_3SnX

compound	$\delta(^{119}Sn)$ solid	$\delta(^{119}Sn)$ solution[a]	$\Delta\delta$[b]
Ph_3SnCl (II)	$\left\{\begin{matrix}-33^c\\-35\end{matrix}\right\}$	-44.7 ($CDCl_3$)[d]	~10
$(PhCH_2)_3SnCl$ (III)	+105	+52.5 ($CDCl_3$)	52.5
c-Hex_3SnCl (IV)	+82	+66.2 (C_6D_6)[d]	15.8
c-Hex_3SnBr (V)	+94	+79.2 ($CDCl_3$)	14.8

[a] The solvent is indicated in parentheses. [b] $\Delta\delta = \delta(^{119}Sn(solid)) - \delta(^{119}Sn(solution))$. [c] Reams, P. Ph.D. Thesis, University of Durham, 1986. [d] Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73.

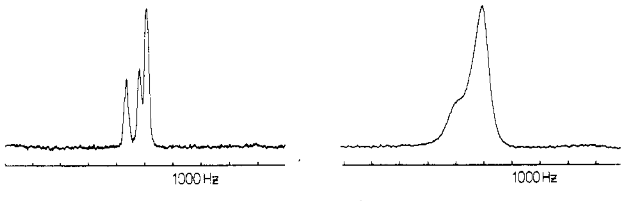
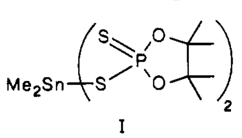


Figure 3. 74.63-MHz CP/MAS ^{119}Sn NMR spectra of (left) tribenzyltin chloride and (right) tricyclohexyltin chloride. Only the centerbands are shown, on expanded scale to show the fine structure caused by residual interactions of ^{119}Sn with ^{35}Cl. The markers are at 1-kHz intervals. There are few spinning sidebands. Spectral parameters: contact time, 1 ms; recycle delay, 10 s; number of transients, 528 (left), 1510 (right).

droxy-bridged polymeric structures. In fact, the solid-state NMR data for both Me_3SnOH and Ph_3SnOH[18,19] are very similar to those for $(C_6H_{11})_3SnOH$. Similarly, for Me_3SnF and n-Bu_3SnF, an increase in ^{119}Sn shielding by approximately 150 ppm from the solution to the solid state has been observed.[21] The polymeric nature of these two compounds is confirmed by the X-ray crystal structure of Me_3SnF,[26] and it is further corroborated by the observation of an AX_2-spin system in the solid state, where the ^{119}Sn resonance is split into a 1:2:1 triplet, indicating apparently equal coupling (on the NMR time scale) to two fluorine nuclei. On the other hand, even slight changes in the geometry around tin can induce quite substantial solution-to-solid chemical shift differences. This is illustrated by the ^{119}Sn NMR data[27] for compound I which is known to be monomeric both in solution and in the solid state ($\delta(^{119}Sn(CH_2Cl_2))$ -210, $\delta(^{119}Sn(solid))$ -257). Thus chemical shift changes $|\Delta\delta(^{119}Sn)|$ of the order of 50 ppm have to be considered as fairly moderate; i.e., they do not necessarily have to be explained by an increase in the coordination number in the solid state but may be due merely to minor changes in the molecular geometry. The familiar "sagging pattern"[7] for plots of ^{119}Sn solution-state NMR chemical shifts versus n in compounds R_nSnX_{4-n} (n = 0–4) is relevant in this context. The biggest deviations from linearity in these plots are observed when n = 2 or 3, which coincides with those cases where the largest deviations from regular tetrahedral geometry can be expected. One might be tempted to relate the occurrence of extensive spinning sideband patterns in ^{119}Sn CP/MAS spectra to the formation of polymers, i.e. to trigonal-bipyramidal or distorted octahedral geometries at the tin. However, we have observed[20] substantial ^{119}Sn chemical shift anisotropy even for a tetraorganylstannane $R_2SnR'_2$, $(PhCH_2)_2Sn(C{\equiv}CPh)_2$, as is shown in Figure 2. There is no indication of the formation of a polymer in the solid state for this compound ($\delta(^{119}Sn(CDCl_3))$ -175.3,[28] $\delta(^{119}Sn(solid))$ -146), but departure of the molecular geometry from regularly tetrahedral to distorted tetrahedral (point group C_{2v}) accounts for the observed spinning sideband pattern.



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(ii) Triorganyltin Chlorides, R_3SnCl. Table I lists the solid- and solution-state ^{119}Sn NMR data for the compounds R_3SnCl (R = Ph (II), $PhCH_2$ (III), C_6H_{11} (IV)), together with those for tricyclohexyltin bromide (V) and the solution-to-solid chemical shift differences $\Delta\delta(^{119}Sn)$. The 74.63- MHz ^{119}Sn CP/MAS spectra of III and IV are shown in Figure 3. Inspection of the data in Table I and of the spectra makes several features apparent. (a) The $\Delta\delta(^{119}Sn)$ values for II and IV are very small. All three chlorides II–IV experience deshielding on going from solution to the solid state. (b) The $\Delta\delta(^{119}Sn)$ value for $(PhCH_2)_3SnCl$ (III) is unusually large. (c) No spinning sidebands at all, or a few spinning sidebands of very low intensity, are observed for II–IV, when spectra were obtained with spinning speeds of 3.0–3.5 kHz. (d) For R_3SnCl (II–IV), an unsymmetrical shape is observed for the centerband, with resolved lines in the cases of II and III. (e) A doubling of the centreband structure is observed for Ph_3SnCl (II). This is made clear by spectra obtained at two magnetic fields (see below); moreover, these spectra show substantial changes in the residual splittings mentioned under (iv).

The very small $\Delta\delta(^{119}Sn)$ values of approximately 10–15 ppm for II and IV are a clear indication that no association occurs in the solid state for these compounds. Compounds

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(25) Ho, Y. K.; Zuckerman, J. J. *J. Organomet. Chem.* **1975**, *96*, 41.

(26) Yasuda, K.; Kawasaki, Y.; Kasai, N.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1216.

(27) Huber, F.; Harris, R. K.; Saxena, A.; Sebald, A. to be submitted for publication.

(28) Kerschl, S. Ph.D. Thesis, University of Munich, 1986.

R_3SnCl are known to be monomeric in solution in noncoordinating solvents, with a coordination number of $n = 4$ and tetrahedral geometry (though slightly distorted). Any change of the coordination number toward higher coordination in the solid state would probably be accompanied by a substantial increase in the ^{119}Sn shielding. The slight decrease in ^{119}Sn shielding in the solid state is of the same order of magnitude as solvent effects of noncoordinating solvents on $\delta(^{119}Sn)$ in solution, e.g. $\delta(^{119}Sn)$ for Me_3SnCl: +159 (benzene, $CHCl_3$), +153.5 (cyclohexane), +155.1 (CH_2Cl_2), +165.8 (CCl_4). This interpretation of the ^{119}Sn NMR data is confirmed by the findings from X-ray crystal structure determinations for II[4] and IV.[6] In both cases the authors arrived at the conclusion that Ph_3SnCl and $(C_6H_{11})_3SnCl$, respectively, are monomeric in the solid state. For II the shortest intermolecular Sn–Cl distances are 6 Å, while the intramolecular Sn–Cl bond length is 2.41 Å.[4] The difference between inter- and intramolecular Sn–Cl distances is less pronounced for IV (3.30 Å versus 2.41 Å[6]), but the very similar $\Delta\delta(^{119}Sn)$ values for II and IV support the interpretation of 3.30 Å as a nonbonding intermolecular distance. Previously, the large quadrupole splitting value in the Mössbauer spectrum of IV had led to the conclusion that IV is pentacoordinated in the solid state. The X-ray crystal structure of II[4] also explains why two chemical shifts are observed in the ^{119}Sn CP MAS spectrum of Ph_3SnCl: the unit cell contains two crystallographically independent molecules with rather similar geometrical data. This, in turn, is consistent with the very similar $\delta(^{119}Sn)$ values for the two centerbands (−33 and −35 ppm) and the almost identical appearance of the two multiplets observed. The fact that no spinning sidebands, or only few spinning sidebands of very low intensity, are observed is another indication of the almost tetrahedral geometry around tin in the solid state. The deviations from ideal tetrahedral geometry are very moderate for Ph_3SnCl (II) ($\angle$C–Sn–C = 112.3°, $\angle$C–Sn–Cl = 106.4°[4]) and account for the low-intensity spinning sidebands. The complete absence of spinning sidebands for IV is somewhat more surprising; after all, the bond angles C–Sn–Cl are 101.9° and 101.4° and C–Sn–C 115.0° and 119.0°, respectively.[6]

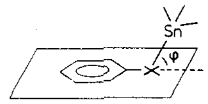

Figure 4. The conformation of compounds involving the part structure PhXSn (X = CH_2, S, etc.).

Table II. ^{119}Sn CP/MAS and Solution-State NMR Data for Some Diorganyltin Dihalides, R_2SnX_2

	$\delta(^{119}Sn)$		
compound	solid	solution[a]	$\Delta\delta$
Me_2SnCl_2 (VI)	+74.5	+137.0 (CH_2Cl_2)[b]	−62.5
Et_2SnCl_2 (VII)	+82.0	+121.0 (CH_2Cl_2)[b]	−39
n-Bu_2SnCl_2[c] (VIII)	+84[d]	+123.4 (CH_2Cl_2)[e]	−39
Bz_2SnCl_2 (IX)	+55.0	+36.4 (CH_2Cl_2)	+19
c-Hex_2SnCl_2 (X)	+7[d]	+73.8 ($CDCl_3$)	−67
c-Hex_2SnBr_2 (XI)	+82	+70.7 ($CDCl_3$)	11
Me_2SnBr_2 (XII)	+90[d]	+70.0 ($CHCl_3$)[b]	20

[a] The solvent is indicated in parentheses. [b] Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73. [c] In the first publication on ^{119}Sn CP/MAS NMR (Lippmaa, E. T.; Alla, M. A.; Pekh, T. J.; Engelhardt, G. *J. Am. Chem. Soc.* **1978**, *100*, 1929) a ^{119}Sn CP/MAS spectrum is mentioned, though these results appear somewhat ambiguous in the light of the information available now. [d] Broad resonances. [e] Smith, P. J.; Tupčiauskas, A. P. *Annu. Rep. NMR Spectrosc.* **1978**, *8*, 291.

The unusually large $\Delta\delta(^{119}Sn)$ value of 52 ppm for $(PhCH_2)_3SnCl$ (III) deserves a special comment. Similarly unusual $\Delta\delta(^{119}Sn)$ values have also been found for $(PhCH_2)_2Sn(C{\equiv}CPh)_2$ (29 ppm, see Figure 2) and for $(PhCH_2)_2SnCl_2$ (IX) (19 ppm, see below). Abnormally high shielding for ^{119}Sn in benzyltin compounds in solution is commonly observed (e.g. $Me_2Sn(C{\equiv}CPh)_2$, −147.6 ppm; $(PhCH_2)_2Sn(C{\equiv}CPh)_2$, −175.3 ppm; Me_3SnCl, +164.2 ppm, $(PhCH_2)_3SnCl$, +52 ppm; $(Me_3Sn)_2S$, +87.0 ppm, $((PhCH_2)_3Sn)_2S$, +26.9 ppm[7,29]). The fact that benzyltin compounds are normally better shielded than their methyl analogues is certainly not expected on grounds of electron-withdrawing properties of R as a normal substituent effect. This abnormal solution-state behavior of benzyltin compounds has been shown to be due to hyperconjugative interaction between the π orbitals of the phenyl moiety and the Sn–C σ bond.[30-33] This electronic interaction also explains unusually large long-range coupling constants $^5J(^{119}Sn^{13}C_{aryl})$ in benzyltin compounds. UV photoelectron spectroscopy has proved the existence of such hyperconjugative interaction for $Me_3Sn(CH_2Ph)$ in the gas phase.[34] Recently, UV photoelectron spectroscopy established the same type of interaction between the phenyl π orbitals and the Sn–C σ bond for Me_3SnSPh.[35] For this compound interaction between the π orbitals and the sulfur lone-pair orbitals might have been another alternative. Coherent with these findings, the solution-state ^{119}Sn chemical shifts for Me_3SnSPh (+90.5 ppm) and Me_3SnSMe (+90 ppm)[7] are the same within experimental error, which would not be expected on grounds of the −SMe versus −SPh electronegatively. Clearly, such hyperconjugative interaction requires that the molecule adopts a special conformation (perhaps suitably time-averaged): see Figure 4. The possibility of conjugation of the phenyl π orbitals and the Sn–X σ bond (X = S, or X = CH_2 for benzyl) will depend on the dihedral angle ψ. A maximum effect is to be expected for $\psi = 90°$. From comparison of $^3J(^{119}Sn^{13}C)$ data in different benzyltin compounds with fixed molecular geometry a Karplus-type relationship has been found.[31] For instance, a dihedral angle $\psi = 60°$ has been estimated for $Me_3Sn(CH_2Ph)$ in solution. In the gas-phase and in solution—with a high degree of motional freedom—such a special conformation can be easily adopted. Obviously, in the solid state a conformation allowing this σ–π interaction is no longer the most favorable. Packing in the crystal apparently leaves the benzyl groups in a conformation where the extra shielding influence of the hyperconjugative interaction is lost. Unfortunately, the X-ray crystal structure is not known for any of the three benzyltin compounds studied here. Variable-temperature ^{119}Sn NMR spectroscopy in solution has shown a decrease of ^{119}Sn shielding with decreasing temperature for benzyltin compounds.[30] The loss of this special "benzyl effect" in the solid state puts R = benzyl in the "correct" order as a normal substituent with $\delta(^{119}Sn(solid))$ for R = benzyl > cyclohexyl > Ph. The magnitude of the "benzyl effect"

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(29) Kerschl, S.; Wrackmeyer, B.; Männig, D.; Nöth, H.; Staudigl, R. *Z. Naturforsch.*, in press.

(30) Kitching, W.; Drew, G.; Adcock, W.; Abeywickrema, A. W. *J. Org. Chem.* **1981**, *46*, 2252.

(31) Doddrell, D.; Kitching, W.; Bullpitt, M.; Lee, C.-H.; Mynott, R. J.; Considine, J. L.; Kuivila, H. G.; Sarma, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 1640.

(32) Bullpitt, M.; Kitching, W.; Adcock, W.; Doddrell, D. *J. Organomet. Chem.* **1976**, *116*, 187.

(33) Adcock, W.; Gupta, B. D.; Kitching, W.; Doddrell, D. *J. Organomet. Chem.* **1975**, *102*, 297.

(34) Bischof, P. K.; Dewar, M. J. S.; Goodman, D. W.; Jones, T. B. *J. Organomet. Chem.* **1974**, *82*, 89.

(35) Cauletti, C.; Grandinetti, G.; Sebald, A.; Wrackmeyer, B. *Inorg. Chim. Acta* **1986**, *117*, L37.

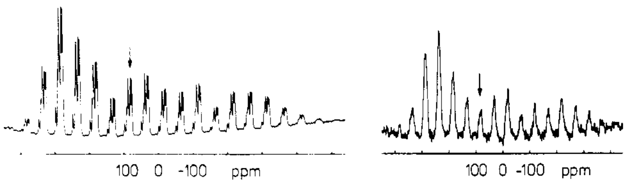

Figure 5. 74.63-MHz CP/MAS ^{119}Sn NMR spectra of (left) Et_2SnCl_2 and (right) Bu_2SnCl_2. Spectral parameters: contact time, 1 ms; recycle delay, 8 s; number of transients, 3600 (left), 400 (right). The vertical arrows indicate the centerbands.

(and consequently its loss in the solid state) parallels the number of benzyl groups per molecule; i.e., the effect is larger for $(PhCH_2)_3SnCl$ than for $(PhCH_2)_2SnX_2$ (X = Cl, C≡CPh).

(iii) Diorganyltin Halides R_2SnX_2. In Table II the solid- and solution-state ^{119}Sn NMR data for five dichlorides, R_2SnCl_2 (VI–X), and two dibromides (XI and XII) are given, including solution-to-solid chemical shift differences $\Delta\delta(^{119}Sn)$. Figure 5 shows some representative ^{119}Sn CP/MAS spectra for Et_2SnCl_2 and n-Bu_2SnCl_2. Opinions about the solid-state structures of diorganyltin dihalides, R_2SnX_2, are far more diverging than for the corresponding triorganyltin halides, R_3SnX. There have been considerable discussions in the literature[15] whether in the solid state isolated molecules in strongly distorted tetrahedral surroundings are present or whether polymers with the tin in a pseudooctahedral environment are formed by intermolecular Cl bridges. One reason for the uncertainties is that it is difficult to decide if the intermolecular Sn–Cl bond distances, often found to be of the order of 3.3 Å, represent a bonding interaction or not. Perhaps Ph_2SnCl_2 can serve as an example to illustrate the dispute: the original data from X-ray crystallography were interpreted in terms of isolated molecules in the solid.[36] Later on these data were reinterpreted as indicative for strong intermolecular association, in order to account better for Mössbauer spectroscopic results.[37] X-ray crystal structures are known for compounds VI,[9] VII,[38] and X.[3] In all three cases only one crystallographic type of molecule per unit cell is found, consistent with the observation of one centreband in each ^{119}Sn CP MAS spectrum. Generally, for all VI, VII, and X compounds severe distortions from regular tetrahedral geometry around tin occur. The bond angles Cl–Sn–Cl are 93° for Me_2SnCl_2, 96° for Et_2SnCl_2, 96.8° for $(C_6H_{11})_2SnCl_2$, and bond angles C–Sn–C of 123.5, 134.0, and 131.0°, respectively, are found. The data from Table II may be used to attempt an interpretation of the solid R_2SnCl_2 structures, as seen by NMR spectroscopy.

Generally, for all R_2SnCl_2 compounds investigated (see Figure 5) extensive spinning sideband patterns are observed. This finding can only be explained by a generally more severely distorted geometry at tin (consistent with the X-ray data mentioned above) as compared to triorganyltin compounds, R_3SnX, though it needs to be borne in mind that distortions affecting shielding anisotropy may be electronic rather than geometric. Again, as has been discussed before for $(PhCH_2)_3SnCl$ (III), compound IX, $(PhCH_2)_2SnCl_2$, presents an exceptional $\Delta\delta(^{119}Sn)$ value. For R = Me, Et, n-Bu and C_6H_{11}, ^{119}Sn shielding in the solid state is increased by 50 ± 10 ppm in comparison to solution-state data. This increase in the ^{119}Sn shielding could be an indication of intermolecular association, although the magnitude of the effect is very moderate. It may be helpful to bear in mind that Me_2SnCl_2 and Et_2SnCl_2 are solid at room temperature— in the complete absence of intermolecular association one might well expect these compounds to be liquids. According to ^{119}Sn CP/MAS spectroscopy, by comparison with ^{119}Sn solution-state NMR and based on chemical shift arguments, diorganyltin dichlorides, R_2SnCl_2, are best described as weakly associated in the solid state.

For some of the dichlorides (R = Me, Et, Bz) the centerbands and sidebands show distinctive fine structure, which will be discussed in section iv below. Other dichlorides (such as n-Bu_2SnCl_2) merely show broad lines, which would conceal any such splittings.

(iv) Interactions of ^{119}Sn with ^{35}Cl. Finally, the splitting patterns observed for the monochlorides (II and III) and for some dichlorides (VI, VII, and IX) have to be explained. There are several possible explanations. (a) There could be different independent molecules per unit cell—this possibility is ruled out by the known X-ray crystal structures for II, IV, VI, VII, and X.[3,4,6,9,38] (b) Polymorphism is not uncommon for organometallic compounds—this is highly unlikely as explanation for this case since basically the same splitting pattern is observed for all three R_3SnCl compounds (II–IV). (c) The presence of impurities—but this can be excluded since all three compounds, II–IV, gave a single ^{119}Sn resonance in solution. (d) The splitting could be due to interaction with the adjacent quadrupolar ^{35}Cl or ^{37}Cl nucleus (spin $^3/_2$, natural abundances 75%). This last explanation has to be explored in more detail. Effects arising from interactions with neighboring quadrupolar nuclei have been observed before in solid-state CP/MAS spectra of spin 1/2 nuclei. Splitting and/or broadening due to neighboring ^{14}N nuclei has been reported for ^{13}C spectra,[39,40] broadening of the solid-state ^{13}C resonances due to adjacent ^{35}Cl has been mentioned,[41] and splitting of the ^{31}P resonances in phosphine–copper complexes has been analyzed as interaction between ^{31}P and ^{63}Cu.[42] Splittings in ^{31}P solid-state spectra arising from interactions with $^{35/37}$Cl have been noted for PCl_5.[43] The cases discussed here are the first to be reported for ^{119}Sn NMR, though our work has been mentioned in symposium proceedings.[44] Two possible types of interaction have to be considered—(i) indirect (scalar) coupling (J coupling) and (ii) direct (dipolar) coupling—though, of course, both types may be present in a given case. In principle, variable field studies can distinguish between these two interactions.[42] In the limiting high-field case for purely indirect coupling, a quartet of four equally intense, equally spaced (by $|J|$) lines will be observed. For purely dipolar coupling at high field a single resonance would be observed. As far as we are aware, there are no reported data in the literature for (Sn,Cl) indirect coupling, either isotropic values or anisotropies. If an average Sn–Cl bond length of 2.5 Å for organotin chlorides is assumed, a dipolar coupling constant ^{119}Sn–^{35}Cl of approximately 300 Hz can be calculated. Although this coupling is much smaller than the usually

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[36] Green, P. T.; Bryan, R. F. *J. Chem. Soc. A* **1971**, 2549.

[37] Bokii, N. G.; Struchkov, Yu. T.; Prok'iev, A. K. *J. Struct. Chem.* **1972**, *13*, 619.

[38] Alcock, N. W.; Sawyer, J. T. *J. Chem. Soc., Dalton Trans.* **1977**, 1090.

[39] Groombridge, C. J.; Harris, R. K.; Packer, K. J.; Say, B. J.; Tanner, S. F. *J. Chem. Soc., Chem. Commun.* **1980**, 175.

[40] Naito, A.; Ganapathy, S.; McDowell, C. A. *J. Chems. Phys.* **1981**, *4*, 5393.

[41] Fleming, W. W.; Fyfe, C. A.; Lyerla, J. R.; Vanni, H.; Yamouri, C. S. *Macromolecules* **1980**, *13*, 460.

[42] Menger, E. M.; Veeman, W. S. *J. Magn. Reson.* **1982**, *46*, 257.

[43] Harris, R. K.; Root, A. *Mol. Phys.*, accepted for publication. Root, A. Ph.D. Thesis, University of East Anglia, 1986.

[44] Harris, R. K. Proceedings of the Second Conference on Modern Methods of Radiospectroscopy, Reinhardsbrunn, German Democratic Republic, 1985.

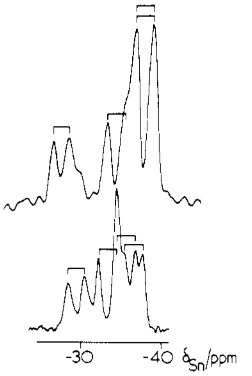

Figure 6. CP/MAS ^{119}Sn NMR spectra of Ph_3SnCl: above, 74.63 MHz; below, 111.86 MHz (on the same scale in ppm). Only the centerbands are shown, at expanded scale. The linkages indicate the crystallographic splittings. Spectral parameters: contact time, 1 ms; recycle delay, 20 s; number of transients, 480.

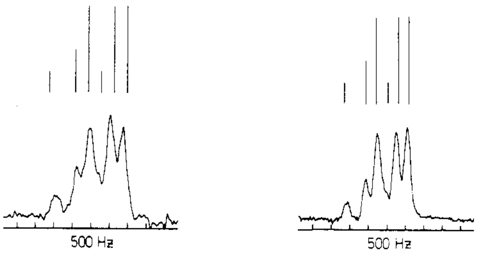

Figure 7. 74.63-MHz CP/MAS ^{119}Sn NMR spectrum of (left) Bz_2SnCl_2 and (right) Et_2SnCl_2: expansion of the centerbands. The stick plots indicate the 1:2:4:1:4:4 splitting patterns as discussed in the text. The spectral parameters are as for Figure 5 (left).

achieved spinning speeds of 3.0–3.5 kHz, it will not be completely averaged by magic-angle spinning when the spin states of the quadrupolar nucleus are no longer quantized along the z axis (i.e. axis of the external magnetic field). This situation arises when the Zeeman and the quadrupole interactions for the quadrupolar nucleus are of the same order of magnitude. In other words, it is most likely for nuclei with large quadrupole moments, such as ^{35}Cl. Similarly, *anisotropy* in the indirect (J) coupling will not be entirely removed by MAS in such circumstances.

For the commonly observed (^{13}C, ^{14}N) situation, a 1:2 or 2:1 broadened doublet is often observed in the ^{13}C spectrum, the true chemical shift being approximately located at the centre of gravity of the band. Our ^{119}Sn spectrum of $(PhCH_2)_3SnCl$ at 74.63 MHz shows a 1:1:2 pattern, with the high-frequency spacing approximately twice the low-frequency spacing. We therefore anticipate that the central line will be a good estimate of the chemical shift, and this is the value listed in Table I. We have obtained spectra of Ph_3SnCl at two different applied magnetic fields (Figure 6). The 74.63-MHz spectrum of Ph_3SnCl (Figure 6a) is complicated by a crystallographic splitting (see above), but it can be interpreted as a doubled-up 1:1:2 pattern like that of $(PhCH_2)_3SnCl$. At 111.86 MHz for Ph_3SnCl the total range of the spectrum (Figure 6b) is actually reduced (in ppm) from that of 74.63 MHz (but is not constant in Hz), confirming that residual dipolar (and/or indirect anisotropic) splittings play a role. The splitting complexity is actually greater at the higher magnetic field. However, this is consistent with Menger and Veeman's figures, and it is expected that in principle four lines will generally be present (corresponding to the four spin states of ^{35}Cl), together with the doubling due to crystallographic effects. This is in accord with observations at both frequencies providing some overlapping is assumed. The central pair of peaks in the 74.63-MHz spectrum remain at the same δ values (within experimental error) in the higher field spectrum, confirming that the middle line of a 1:1:2 pattern is a good approximation to the true chemical shift. The appearance of the spectra suggests to us that isotropic indirect (^{119}Sn, ^{35}Cl) coupling is significant, probably being comparable in magnitude to the dipolar coupling. Menger and Veeman suggest that frequently the central splitting will give a rough value for the indirect coupling, leading us to postulate $|J_{SnCl}| \approx 220$ Hz, which in turn leads to a ratio of the dipolar to indirect coupling constants of ca. 1.4. The interplay of direct and indirect coupling between a spin 1/2 nucleus and a spin 3/2 nucleus (^{31}P–^{63}Cu) has been analyzed quantitatively in some circumstances by Veeman et al.[42] Following this analysis in a very qualitative way, the appearance of the ^{119}Sn CP/MAS spectra for R_3SnCl can be best explained by a combination of direct and indirect coupling ^{119}Sn–^{35}Cl. Use of known ^{35}Cl quadrupole coupling constants from literature[45] to roughly locate the Sn–Cl compounds on Veeman's graphic analysis plots enables a prediction of a three-line-spectrum with a 1:1:2 splitting pattern to be made. For Ph_3SnCl two ^{35}Cl nuclear quadrupole resonances are observed, at 16.750 and 16.985 MHz, respectively. This yields nuclear quadrupole coupling constants χ of 33.500 and 33.970 MHz for the two different crystallographic sites of Ph_3SnCl. These data may be used to calculate the parameter K

$$K = -\left[\frac{3e^2 q_{zz} Q}{4S(2S-1)} \Big/ \gamma_S \hbar B_0 \right]$$

for Veeman's analysis (with $\chi = e^2 q_{zz} Q/\hbar$ and $\gamma_S = 2\pi\nu_L/B_0$, where $\nu_L = 19.618$ MHz at 4.7 T). Thus, for Ph_3SnCl values for the parameter K of 0.427 and 0.433 are obtained. This suggestion nicely matches the observed ^{119}Sn spectra. At the present stage no more detailed conclusions concerning the magnitude (and the sign) of the indirect coupling constant have been drawn. A full analysis of the ^{119}Sn spectra at different magnetic field strengths, however, should yield such information. The presence of a second Cl isotope with similar properties to ^{35}Cl has not been taken into account. Chlorine-37 is 25% naturally abundant and has spin $^3/_2$ and a similar quadrupole moment and magnetic moment to those of ^{35}Cl. The presence of this second Cl isotope is not expected to perturb the spectra greatly.

Our interpretation of the splitting patterns for the monochlorides I and II may be extended to those of the dichlorides. It appears reasonable to apply the same successive splitting methods to the residual dipolar/indirect coupling patterns discussed herein as are used for simple solution-state first-order NMR spectra. Such an approach, which essentially amounts to a convolution of the effects of coupling to different nuclei, has already been used satisfactorily[46] in the case of residual dipolar splittings in the spectrum of a ^{13}C nucleus interacting with two ^{14}N spins. In that case the nitrogens in question were nonequivalent. For the ^{119}Sn/^{35}Cl situation examined here, it appears the chlorines in Me_2SnCl_2, Et_iSnCl_2, and $(PhCH_2)_2SnCl_2$ may be treated as equivalent (though possibly this may be an artefact of strong interactions between the chlorines themselves). A 1:1:2 repetition of the 1:1:2 splitting pattern, with equal coupling, should produce a 1:2:4:1:4:4 spectrum with equal spacings except

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[45] Green, P. J.; Graybeal, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 4305.

[46] Harris, R. K.; Jonsen, P.; Packer, K. J. *Magn. Reson. Chem.* **1985**, *23*, 565.

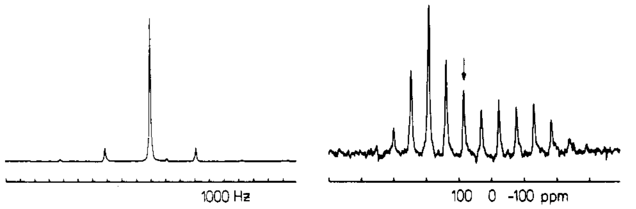

Figure 8. 74.63-MHz CP/MAS ^{119}Sn NMR spectra of (left) tricyclohexyltin bromide and (right) dicyclohexyltin dibromide. The markers for the $(C_6H_{11})_3SnBr$ spectrum are at 1-kHz intervals. The centerband for $(C_6H_{11})_2SnBr_2$ is indicated by an arrow. Spectral parameters: contact time, 1 ms; recycle delay, 10 s; number of transients, 240 (left), 1510 (right).

that the first one is twice the others. Such a pattern is consistent with the observed spectra (Figure 7). The central line of unit intensity, which is at the center of gravity of the band and has been used as the best estimate of the chemical shift in Table II is not fully resolved from the other peaks. If polymeric chains are formed by compounds R_2SnCl_2 in the solid state (as is the case for Me_3SnF,[26] for instance), it might be expected that the chlorines would become nonequivalent and that more complicated splitting patterns would be observed than is actually the case. This comment provides a little corroboration for the conclusions tentatively expressed earlier regarding the structures of the compounds R_2SnCl_2.

Another question concerning the appearance of ^{119}Sn CP/MAS spectra for the compounds R_3SnCl and R_2SnCl_2 arises. Why is the splitting clearly observed in some cases (II, III, VI, VII, and IX) while only unresolved broadening, though with the same overall shape and similar overall line width, is obtained for other compounds (IV, VIII, and X)? Generally, splitting due to ^{119}Sn–^{35}Cl interaction can only be observed when the ^{35}Cl relaxation is sufficiently slow. The ^{35}Cl relaxation is closely linked to molecular motion: slow molecular motion can provide a very efficient relaxation mechanism for ^{35}Cl. In the limiting case, very fast relaxation of the quadrupolar nucleus will lead to "self-decoupling". Since splittings due to interaction with ^{35}Cl are observed for the compounds II–IV, it is therefore likely that molecular motion is fairly restricted—too restricted to provide a suitable relaxation mechanism for the ^{35}Cl nucleus. However, significantly faster ^{35}Cl relaxation rates would not be expected for all three of the compounds lacking the fine structure in the ^{119}Sn spectra. It is possible that matters are compounded by molecular motion interfering with the effects of proton decoupling or magic-angle spinning.

(v) Organotin Bromides, R_3SnBr and R_2SnBr_2. Table I contains NMR data for tricyclohexyl bromide (V), and information on two dibromides, R_2SnBr_2 ($R = C_6H_{11}$ (XI) and Me (XII), is included in Table II. The solid-state ^{119}Sn spectra are shown in Figure 8. In some ways these results parallel those for the corresponding chlorides. Thus the $\Delta\delta(^{119}Sn)$ value for V is small (14.8 ppm) and positive, and there are only a small number of weak sidebands in the solid-state spectrum. These results are consistent with the suggestion that, as for the monochlorides, no association occurs for R_3SnBr in the solid (the compounds are known to be monomeric in solution in noncoordinating solvents) and almost tetrahedral geometry is preserved. However, the solid-state spectrum of V (Figure 8a) consists of a very sharp centerband resonance ($\Delta\nu_{1/2}$ = 100 Hz) of symmetrical shape; no broadening or splitting is observed. Residual dipolar/indirect coupling effects due to ^{79}Br obviously do not occur, and it may be concluded that this is a case of fast relaxation of the halogen and thus of self-decoupling.

The solid-to-solution shifts for the two dibromides are, like that for $(C_6H_{11})_3SnBr$ but unlike those for the dichlorides VI, VII, VIII, and X, small and positive (i.e. slight deshielding in the solid state). The low electronegativity of bromine makes intermolecular interactions less likely than is anticipated for the dichlorides. Indeed, the ^{119}Sn NMR data suggest that the tin in compounds XI and XII preserves a tetrahedral geometry (albeit, perhaps, distorted) in the solid state. However, extensive spinning sidebands are observed in the ^{119}Sn solid-state spectra for these compounds, as in the case of the dichlorides. The X-ray crystal structure of XI is known[3] and shows the asymmetric unit is a single molecule, which is consistent with the spectrum. The latter is not, however, a very positive piece of evidence, since the ^{119}Sn lines for XI ($\nu_{1/2}$ = 500 Hz) and XII ($\nu_{1/2}$ = 1200 Hz) are broad (like those for the chlorides VIII and X and, presumably, for similar reasons) though, given the relative sharpness of the single signal for V, there would appear to be some anomalies in this situation.

Conclusions

It has been shown that ^{119}Sn CP/MAS spectroscopy is a valuable tool for the discussion of the structures of organotin halides in the solid state. It is concluded that for R_3SnX and R_3SnX_2 (X = Cl, Br), there are no gross changes in coordination between the solution and solid states. However, for benzyl compounds it appears that there are considerable differences in conformation, resulting in the shielding effect of hyperconjugative interaction being lost in the solid state. Unsymmetrical 1:1:2 splittings for two compounds R_3SnCl are attributable to residual dipolar/indirect coupling interactions of ^{119}Sn with directly bonded ^{35}Cl. It has been shown that for some of the dichlorides, R_2SnCl_2, such residual interactions result in 1:2:4:1:4:4 multiplets (with the first spacing twice the others, and the chemical shift being at the central weak peak) when the two chlorines are considered as equivalent.

Experimental Section

Most of the solid-state ^{119}Sn spectra were obtained by using a Bruker CXP 200 NMR spectrometer at ambient probe temperature (ca. 30 °C) and 74.63 MHz. Two different rotor systems were used at different times: an Andrew-Beams "mushroom" type for early spectra of Ph_3SnCl and a double-bearing version for other spectra. Each contains ca. 300–400 mg of material. The higher field solid-state spectrum was obtained at 111.86 MHz with a Varian VXR 300 spectrometer at ca. 28 °C and a Doty wide-bore 7-mm probe. Delrin rotors were used on the Andrew-Beams probe, whereas the spectra on the double-bearing probe were obtained by using alumina or zirconia rotors. Typically, spectral parameters were as follows: contact time, 1 ms; recycle delay between 8 and 15 s (except for Ph_3SnCl where it was 20 s): number of transients between 240 and 3600. Spinning speeds were between 2.8 and 3.8 kHz for the best spectra. Generally, spectra were rerun at lower speeds (and fewer transients) to establish the position of the centerband(s), which is (are) indicated in the figures by a vertical arrow. The magic angle was set by using the ^{79}Br resonance of KBr,[47] by replacement. A sample of $(C_6H_{11})_4Sn$ was generally used to set the Hartmann–Hahn matching condition, as described elsewhere.[17]

Solution-state ^{119}Sn spectra were obtained where necessary by using a Bruker AC 250 spectrometer at 93.28 MHz and ca. 30 °C. Gated decoupling was employed to suppress the NOE. Pulse angles of 30° were typical, together with 5-s recycle delays.

Spectra have been referenced to the signal for Me_4Sn, the replacement technique being employed.

The benzyl compounds, Me_2SnCl_2, and Et_2SnCl_2 came from the laboratory of B. Wrackmeyer, whereas Ph_3SnCl was obtained

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[47] Frye, J. S.; Maciel, G. E. *J. Magn. Reson.* 1982, *48*, 125.

from the Johnson Matthey Research Centre. The cyclohexyl compounds were synthesized following published methods.[48]

Note Added in Proof. Since this manuscript was prepared, further work has been carried out (Molloy, K. C.; Tagliavini, G.; Ganis, P.; Furlani, D. *Inorg. Chim. Acta*, in press) on the solid-state structure of dicyclohexyltin dichloride, and the conclusions regarding tin coordination presented here were reinforced. The solid-state ^{119}Sn NMR spectra of five compounds, including Ph_3SnCl and Et_2SnCl_2, have been reported (Komoroski, R. A.; Parker, R. G.; Mazany, A. M.; Early, T. A. *J. Magn. Reson.* 1987, *73*, 389). The effects of residual dipolar coupling to chlorine are mentioned but not explained in detail. The isotropic chemical shifts appear to have been incorrectly reported (loc. cit. Table I).

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Registry No. II, 639-58-7; III, 3151-41-5; IV, 3091-32-5; V, 3023-92-5; VI, 753-73-1; VII, 866-55-7; VIII, 683-18-1; IX, 3002-01-5; X, 3342-69-6; XI, 2954-94-1; XII, 2767-47-7; c-Hex_3SnOH, 13121-70-5; $(PhCH_2)_2Sn(C{\equiv}CPh)_2$, 111113-25-8.

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[48] Krause, E.; Pohland, R. *Ber. Dtsch. Chem. Ges.* 1924, *57*, 532.

Unidentate vs Bidentate Acyl Coordination: Reactions of High-Spin Iron(II) Alkyls with Carbon Monoxide and the Crystal Structure of the Bidentate Acyl $Fe(\eta^2\text{-}COC_6H_2Me_3)Br(CO)(dippe)$

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The carbonylation of the 14-electron high-spin iron(II) dialkyls FeR_2(dippe), dippe = 1,2-bis(diisopropylphosphino)ethane, leads to formation of the zerovalent iron carbonyl $Fe(CO)_3$(dippe) (**1**) and, for R = CH_2CMe_3, 2,2,6,6-tetramethyl-4-heptanone. When monoalkyl derivatives FeRX(dippe) are carbonylated, acyl-containing species are formed, and products containing unidentate or bidentate acyls have been isolated depending on the CO pressure and the identity of the alkyl group. Thus, when the carbonylation of $Fe(CH_2CMe_3)X$(dippe) is caried out by using approximately 2 equiv of CO, $Fe(\eta^2\text{-}COCH_2CMe_3)X(CO)$(dippe), **2a** (X = Br) and **2b** (X = Cl), are formed. The products **2a** and **2b** contain a bidentate acyl (ν_{COR} = 1591 and 1596 cm^{-1}, respectively) and only one terminal carbonyl ligand. Reaction of $Fe(CH_2CMe_3)X$(dippe) with excess CO at 3 atm gives $Fe(\eta^1\text{-}COCH_2CMe_3)X(CO)_2$(dippe), **4a** (X = Br) and **4b** (X = Cl), each of which contains a unidentate acyl (ν_{COR} = 1634 and 1630 cm^{-1}, respectively) and two carbonyl ligands. The major isomer formed in the latter reaction has been determined by ^{13}C and ^{31}P NMR spectroscopy to possess mutually trans acyl and halide ligands while the minor isomer has mutually trans carbonyl and halide ligands. Carbonylation of the iron(II) mesityl $Fe(C_6H_2Me_3)Br$(dippe) gives only the bidentate acyl product $Fe(\eta^2\text{-}COC_6H_2Me_3)Br(CO)$(dippe) (**3**) even with excess CO. The infrared absorption at 1525 cm^{-1} for the bidentate mesityl acyl is much lower in frequency than for the bidentate neopentyl acyls due to conjugation with the aromatic ring. Of the five isomers possible for this stoichiometry, **3** adopts a structure in which the carbonyl ligand is trans to the oxygen atom of the acyl group, as shown by ^{13}C and ^{31}P NMR data. This is confirmed by the X-ray crystal structure of **3**, which shows that the Fe center is six-coordinate and that the acyl group is indeed bidentate, with Fe–C_{acyl} = 1.85 (1) Å and Fe–O_{acyl} = 1.99 (1) Å. Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions a = 10.470 (10) Å, b = 17.659 (16) Å, c = 15.259 (18) Å, β = 100.34 (8)°, V = 2775 (5) Å^3, Z = 4, R_F = 8.2%, and R_{wF} = 8.1% for 1969 independent reflections. A review of structural parameters for bidentate acyls of transition metals is given, and a comparison of the bonding in **3** with other molecules reveals that the Fe–O distance is unusually short as a result of steric "compression" from one of the ortho methyl groups of the mesityl substituent.

Introduction

Unsaturated species are the key intermediates in virtually all chemical reactions and catalytic processes involving transition-metal complexes. We have recently reported the synthesis and characterization of a series of tetrahedral, 14-electron organoiron compounds of stoichiometry FeR_2(dippe) and FeRX(dippe), where dippe is 1,2-bis(diisopropylphosphino)ethane and R is a β-stabilized alkyl.[1] The steric bulk of the dippe ligand allows the isolation of these unusual high-spin organoiron compounds in contrast to other phosphines such as PMe_3 or dmpe that invariably form octahedral, low-spin iron(II) species. We now describe the reactions of the highly coordinately unsaturated complexes FeR_2(dippe) and FeRX(dippe) with carbon monoxide to yield ketones and iron acyls as insertion products.

Most of the acyl complexes in the literature adopt unidentate coordination geometries,[2,3] whereas the first

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[1] Hermes, A. R.; Girolami, G. S. *Organometallics* 1987, *6*, 763–768.

[2] Wojcicki, A. *Adv. Organomet. Chem.* 1973, *11* 8–145.

0276-7333/88/2307-0394$01.50/0