syn−*anti* Conversion in Octahedral Bis(β-diketonato)diorganotin(IV) Derivatives Containing Fluorinated 4-Acyl-5-pyrazolonato Donors

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Six-coordinate organotin derivatives L_2SnR_2 [L = 3-methyl-1-(4-trifluoromethylphenyl)-4-R^3-C=O-5-pyrazolonato (R^3 = CH_3, L = L^1; R^3 = C_6H_5, L = L^2; R^3 = CF_3, L = L^3; R = CH_3, *n*-C_4H_9, C_6H_5)] have been synthesized and characterized by analytical and spectroscopic (^1H, ^{13}C, ^{119}Sn, and ^{19}F NMR, IR) techniques. Partial dissociation of one ligand in chlorohydrocarbon solvents gives rise to cationic five-coordinate L-(solvent)-diorganotin(IV) complexes. The X-ray crystal structure of bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]diphenyltin (**6**) shows the metal in a distorted octahedron (skewed trapezoidal bipyramidal) with the two β-diketonato donors in *syn* positions, a C–Sn–C bond angle of 165.2(2)° and two sets of tin–oxygen bonds [2.141(5) and 2.139(3) Å for Sn–O(pyrazolonato) and 2.250(4) and 2.272(5) Å for Sn–O(acyl)]. Surprisingly, the recently reported dimethyltin derivative has the *anti* configuration, in contrast to expectations based on all previous experience. Large scale Hartree–Fock (HF) and Density Functional Theory (DFT) calculated structures for the *anti* configuration of bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin show good agreement with the experimental structure obtained from X-ray methods. The hypothetical *syn* configuration of bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin was also studied theoretically and both methods also predict characteristic structural features, such as: (from HF) a C–Sn–C bond angle of 150.0°, Sn–O(pyrazolonato) bond lengths of 2.088 and 2.084 Å and Sn–O(acyl) bond lengths of 2.385 and 2.401 Å. Results from the *syn* calculated structures suggest that intramolecular repulsive F···F interactions contribute to the *syn*–*anti* conversion.

Introduction

Organotin compounds have varied applications, including their use as boat paint additives to prevent attack by microorganisms,[1] and as insecticides and fungicides.[2−3] They are also effective antitumor agents.[4−8] We are particularly interested in organotin derivatives of 4-acyl-5-pyrazolones because these ligands possess several sites for substitution, allowing for a systematic analysis of their effects on the subsequent biological activity. So far, only the variation at R^3 has been fully explored (Figure 1).[9−20]

Recently, we have modified the R^1 position and synthesized some organotin derivatives, with R^1 = methyl[21] (usually it is a phenyl group), that possess an increased solubility in water and alcohols, an important feature for biological applications. Since halogen-substituted anions induce stronger biological activity in their organotin derivatives, both as antitumor agents[5−8] and as insecticides,[22] and, in particular, fluorine substituents have been reported to strongly influence the antitumor activity,[23−26] we then synthesized a ligand with R^1 = *p*-CF_3-Ph (Figure 2). This chemical modification results in a ligand with a lower donating ability of the O(pyrazolonato) atom and a greater ring-electron delocalization in the crystalline compound bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin. However, its structure rather unexpectedly has an *anti* configuration,[27] the first to be observed.

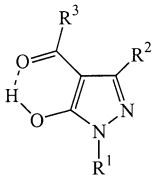

Figure 1. Proligands

Since the *anti* configuration was obtained after a seemingly subtle change in a peripheral area (substitution of a CF_3 group for a H atom in the *para* position of R^1 phenyl), we discuss the *syn*−*anti* variation after analyzing the theoretically calculated *syn* molecular structure and supporting experimental data. Large-scale ab initio calculations were performed on these metal complexes as a large number of atoms is involved.

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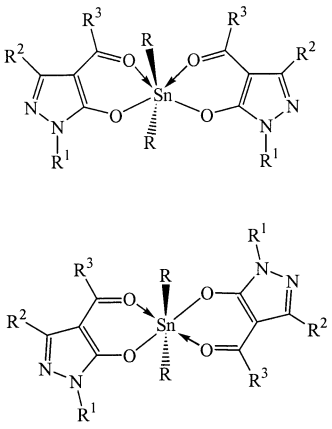


Figure 2. (top) *syn* configuration (normally observed in bis(4-acyl-5-pyrazolonato)diorganotin complexes; (bottom) *anti* configuration

A related *cis*−*trans* conversion has been reported by Gielen[28,29] and us,[11−13,17−19,21] for analogous monoorganotin(IV) β-diketonates in solution. However, in the case of diorganotin(IV) acylpyrazolonates, the *syn*−*anti* variation seems also to be feasible in the solid state, as previously demonstrated by multinuclear NMR spectroscopy and Mössbauer studies.[11,17]

Results and Discussion

We analyzed other diorganotin derivatives containing related ligands and the same R^1 (*p*-CF_3-Ph) substituent in an attempt to explain why the unexpected *anti* configuration of bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin is the form experimentally observed (described in Exp. Sect.). Since a previous diphenyltin derivative of a related 4-acyl-5-pyrazolonato showed less octahedral deformation than usual,[17] we selected bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]diphenyltin **6** from the compounds synthesized, and determined its molecular structure by X-ray diffraction methods.

Diffraction Study of $(L^2)_2SnPh_2$, 6

The crystal structure is formed from well-separated discrete molecules with no imposed crystallographic symmetry (Figure 3). The six-coordinate metal is surrounded by four O atoms from the two anionic chelating pyrazolonato ligands, and two C atoms from the phenyl groups, in a distorted octahedral arrangement so that the ligands have their equivalent arms facing one another (*syn* configuration), a geometry normally observed for bis(4-acyl-5-pyrazolonato)-diorganotin complexes. The relatively small octahedral distortion, described later in Table 1, is similar (although a bit larger) to that of another diphenyltin derivative, namely bis[4-(*p*-bromobenzoyl)-3-methyl-1-phenylpyrazolon-5-ato]-diphenyltin,[17] [C−Sn−C′ bond angle of 173.0(7)°, Sn−O1 bond length of 2.143(7) Å, Sn−O1′ bond length of 2.12(1) Å, Sn−O2 bond length of 2.223(8) Å, Sn−O2′ bond length

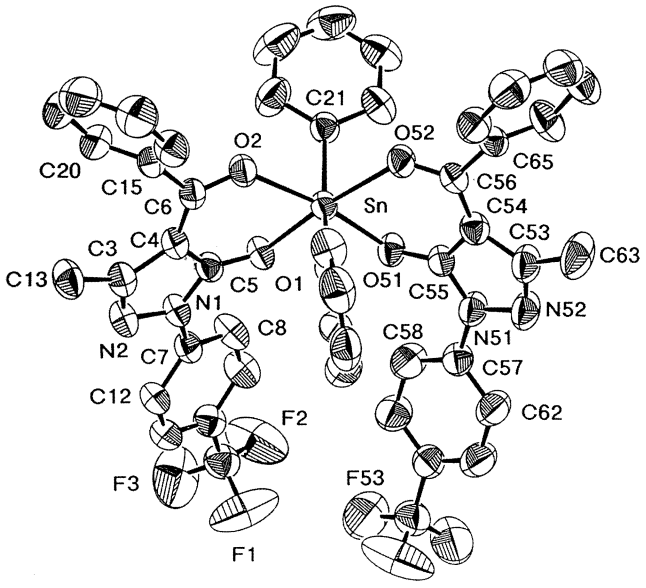


Figure 3. X-ray ORTEP drawing of bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]diphenyltin **6**

of 2.26(1) Å, O1−Sn−O2 bite angle of 84.5° and O1′−Sn−O2′ bite angle of 85.1(3)°].

The dihedral angles between the pyrazole ring and its attached *p*-CF_3-Ph ring are 16.6(7)° in one ligand, and −13.6(7)° in the other ligand, whereas in the above-mentioned bis(4-*p*-bromobenzoyl-3-methyl-1-phenyl)diphenyltin structure[17] the values are 13.9° and −11.7°, respectively. This quasi co-planarity between the rings is associated with the intramolecular distances O1···H1 [2.294(7) Å] and O51···H13 [2.265(8) Å], which are shorter than the van der Waals value of 2.60 Å[30] (H1 and H13 are bound to C8 and C58, respectively); this feature is also characteristic of these compounds. A specific feature of this structure is that the sum of the equatorial bond angles is equal to 360°: all other previously reported *syn* bis(4-acyl-5-pyrazolonato)-diorganotin complexes[10−14,17−21] show the tin somewhat shifted out of the equatorial plane, which makes this value smaller than 360°.

Theoretical Calculations

The molecular structures of bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin in both the *anti* and *syn* configurations were studied by theoretical methods. The starting coordinates for the *anti* compound were those obtained by X-ray diffraction[27] and were optimized by energy minimization with the Hartree−Fock (HF) and Density Functional Theory (DFT) methods (see Figures 4 and 5). Table 1 shows some geometrical features. There is excellent agreement with X-ray[27] data for the Sn polyhedron although HF calculates slightly shorter Sn−O bonds and slightly smaller bite angles, and, generally, DFT agrees better with the X-ray data than HF. A marked difference between HF and DFT is seen in the dihedral angle between the planar pyrazole and its attached phenyl. These values are 3.8 and −3.9° (DFT) and 24.2 and −24.3° (HF),

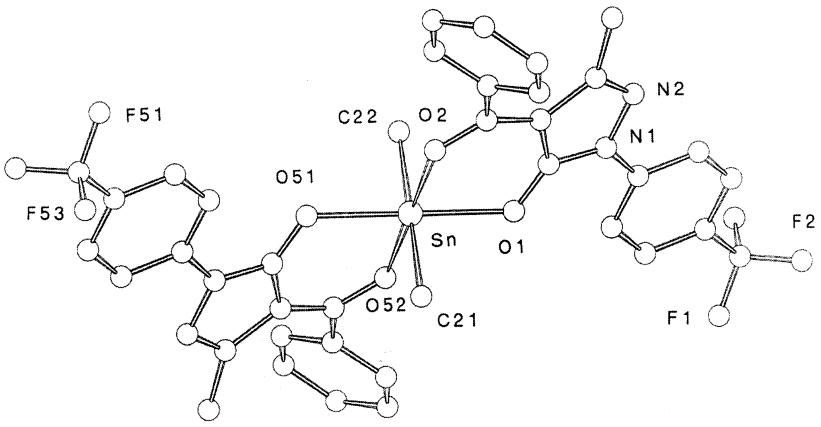


Figure 4. Bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin (*anti* configuration) obtained by the DFT method

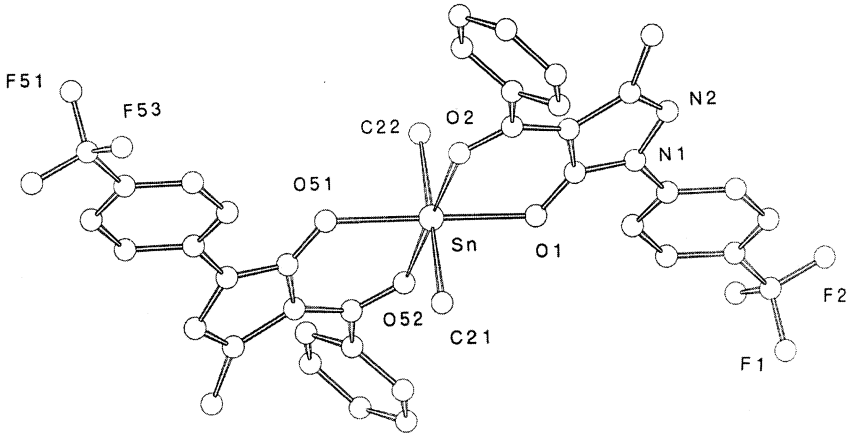


Figure 5. Bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin (*anti* configuration) obtained by the HF method

whereas the X-ray values are 16.6 and −16.6°. In the *syn* compounds there is a tendency for these two planes to be co-planar,[19] although this dihedral angle shows a large range of values, which suggests that the energy changes as a function of dihedral angle are small, and therefore can be affected by packing and/or intramolecular forces. Moreover, this angle can differ greatly even within the same molecule: for instance, in bis[4-(*p*-bromobenzoyl)-3-methyl-1-phenylpyrazolon-5-ato]dimethyltin it is 13.7° in one ligand and −39.8° in the second ligand.[13]

Since the theoretical results agree closely with the experimental values, we then proceeded to calculate the molecular structure of the *syn* configuration with the coordinates of bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)-pyrazolon-5-ato]diphenyltin **6** described above. The phenyl groups bound to tin were replaced by methyl groups and the structure was optimized as above. Selected structural parameters are also given in Table 1 and the calculated structures are shown in Figures 6 and 7.

The *syn* structures in Table 1 confirm that when methyl groups are replaced by phenyl groups a smaller octahedral distortion is induced. This was previously observed in bis(4-acylpyrazolon-5-ato)diorganotin complexes studied using X-ray diffraction methods.[17] The driving force is the electron-withdrawing effect of the Ph that attracts electron density from the tin atom and induces further ligand donation, which is provided by O2.[17] Consequently, in diphenyltin derivatives the Sn−O2 bond length is shorter than in dialkyltin derivatives. As a result, diphenyltin derivatives have similar Sn−O1 and Sn−O2 bond lengths and show less octahedral deformation, that is, the C−Sn−C′ bond angle is closer to 180°.

Table 1 shows that the polyhedron deformation in the *syn* structures (for the three methods, XR, HF, and DFT) is characterized by having Sn and its four linked O atoms in a plane [the sum of the four angles, O1−Sn−O2 (ligand 1 bite), O1′−Sn−O2′ (ligand 2 bite), O1−Sn−O1′ and O2−Sn−O2′, equals 360°]. As mentioned above, this is the first time that this feature (seen in compound **6**) has been observed for *syn*-bis(4-acyl-5-pyrazolonato)diorganotin complexes, and is confirmed theoretically.

All bis(4-acylpyrazolon-5-ato)diorganotin *syn* structures solved so far by X-ray diffraction display approximate mirror symmetry, with the mirror plane containing Sn and its two bonded C atoms. The calculated molecules are single and isolated (intermolecular forces do not exist) and, if mirror symmetry exists, should show equivalence in both bite angles, as well as the bond lengths Sn−O1 and Sn−O1′, Sn−O2 and Sn−O2′, and the angles O1−Sn−O2′ and O1′−Sn−O2. However, Table 1 shows that this is not the

Table 1. Selected geometrical parameters in bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]-di-R-tin compounds obtained with different structural methods (XR = X-ray diffraction, HF = Hartree−Fock, DFT = Density Functional Theory)

Compound	**4**	**4**	**4**
R	methyl	methyl	methyl
Method	XR	HF	DFT
Configuration	*anti*	*anti*	*anti*
Sn−O1	2.214(5)	2.179	2.216
Sn−O1′	2.214(5)	2.187	2.217
Sn−O2	2.220(6)	2.216	2.233
Sn−O2′	2.220(6)	2.205	2.233
O1−Sn−O2	85.9(2)	82.4	83.9
O1′−Sn−O2′	85.9(2)	82.6	84.0
C−Sn−C′	180	179.3	180
O1−Sn−O1′	180	179.5	180
O2−Sn−O2′	180	179.5	180
O1−Sn−O2′	94.1(2)	97.0	96.0
O1′−Sn−O2	94.1(2)	98.0	96.0
Compound	**6**	[a]	[a]
R	phenyl	methyl	methyl
Method	XR	HF	DFT
Configuration	*syn*	*syn*	*syn*
Sn−O1	2.140(4)	2.088	2.149
Sn−O1′	2.141(4)	2.084	2.145
Sn−O2	2.250(3)	2.385	2.338
Sn−O2′	2.273(5)	2.401	2.331
O1−Sn−O2	83.5(1)	79.1	81.5
O1′−Sn−O2′	84.1(1)	79.1	82.0
C−Sn−C′	165.2(2)	150.0	158.4
O1−Sn−O1′	87.2(1)	82.4	83.0
O2−Sn−O2′	105.2(1)	119.7	113.7
O1−Sn−O2′	171.3(1)	160.8	164.6
O1′−Sn−O2	170.4(2)	161.0	164.2

[a] Hypothetical compound. Labels in Figure 3 are related so that O51 is O1′, O52 is O2′, N51 is N1′, etc. Distances [Å], angles [°]. Energy values for calculated structures (a.u.): HF, −2573.72811 (*anti*), −2573.73406 (*syn*); DFT, −2587.11444 (*anti*), −2587.11749 (*syn*).

case. A peripheral structural feature confirms this: the dihedral angle between the pyrazole and its attached phenyl differs in each ligand (24.4° and 8.2° for DFT and 30.6° and 25.8° for HF). These results are in contrast with the *anti* species described above where both dihedral angles obtained from DFT, HF, and X-ray methods are equal.

Further analysis of the calculated *syn* structures for bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin in Table 1 shows good agreement with a characteristic feature observed by X-ray diffraction:[10−21] the Sn−O(pyrazolonato) bond lengths are shorter than the Sn−O(acyl) bond lengths. The variation between these sets of bond lengths using the DFT method is less than when using the HF method. This geometry was described as skewed trapezoidal bipyramidal (STB) by Kepert in a theoretical treatment.[31] The short side of the trapezoid links the two O(pyrazolonato) atoms that form the short Sn−O bonds, whereas the long side links the two O(acyl) atoms that form the long Sn−O bonds (see Figure 8).

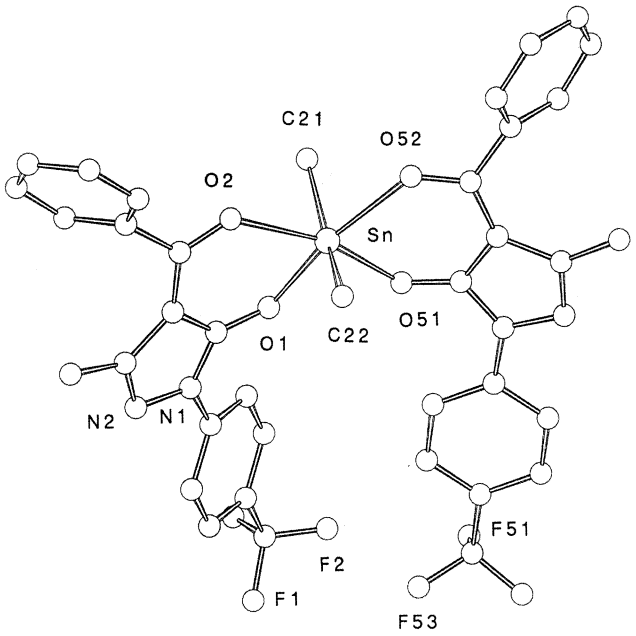


Figure 6. Bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin (*syn* configuration) obtained by the DFT method

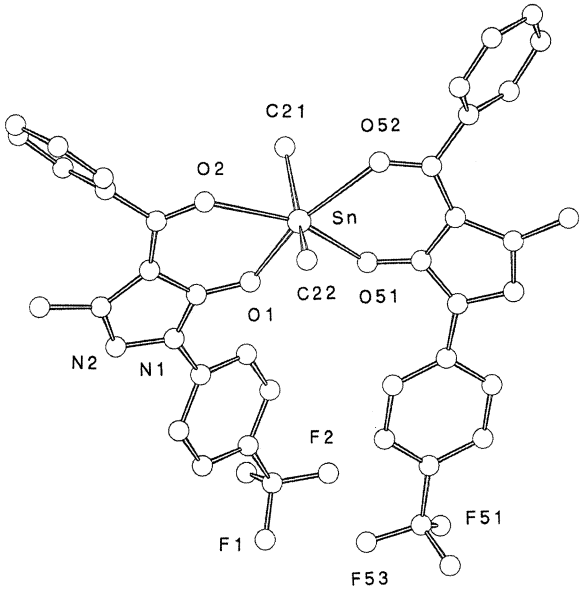


Figure 7. Bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin (*syn* configuration) obtained by the HF method

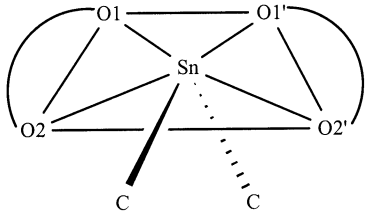


Figure 8. Skewed trapezoidal bipyramidal configuration

In the experimental *syn*-bis(4-acyl-5-pyrazolonato)-di-R-tin complexes studied so far, it is the R = alkyl substituents that induce the strongest octahedral deformation[10−14,17−21] on the geometry of these complexes. This is described by:[19]

(a) a small *trans* C−Sn−C′ angle
(b) a small O1−Sn−O1′ angle
(c) a large O2−Sn−O2′ angle.

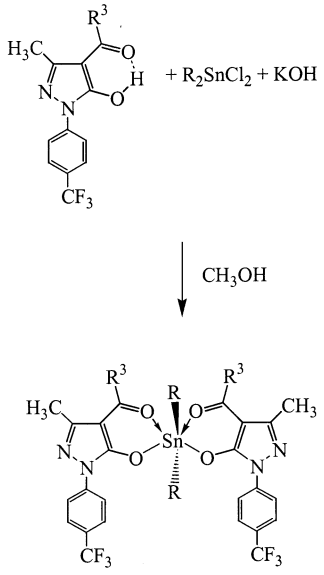
Experimentally, when R^1 = Ph, R^2 = methyl, R^3 = Ph and R = methyl, a *syn* species is obtained,[12] whereas when R^1 = *p*-CF_3-Ph, an unexpected *anti* species results.[27] Therefore, the CF_3 group causes a "perturbation". DFT and HF methods react differently to the CF_3 "perturbation": DFT predicts a large C−Sn−C′ angle while, in contrast, HF calculates a smaller C−Sn−C′ angle. Table 1 shows markedly different (a) and (c) values for HF and DFT calculations on the hypothetical *syn*-bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin. However, the value of O1−Sn−O1′ is similar for both DFT (83.0°) and HF (82.4°); in general, the value of O1−Sn−O1′ in bis(4-acyl-5-pyrazolonato)dialkyltin complexes (containing R^1 = Ph) is smaller. The O1−Sn−O1′ angle for both DFT and HF theoretical methods corresponds to the closest approach of the F atoms (the shortest separations are F1···F53 = 3.09 Å and F2···F53 = 3.05 Å, for HF, and F2···F53 = 2.88 Å and F2···F51 = 3.00 Å, for DFT; these distances are close to the F···F van der Waals value of 2.94 Å).[30] We see that the limiting *syn* octahedral deformation predicted by theory corresponds to an O1−Sn−O1′ angle that differs from those previously observed[19] (as mentioned above, X-ray values are smaller). We conclude that the CF_3 "perturbation" is associated with greater intramolecular R^1···R^1 steric hindrance; it is therefore not surprising that an *anti* species (that avoids such strain) is obtained. It is worthwhile to note that diorganotin STB deformation can be greatly enhanced; for instance, in the less crowded bis(*N*-benzoyl-*N*-phenylhydroxylamino)di-*n*-butyltin complex, the C−Sn−C′ bond angle is 133(9)°.[32] This also suggests that repulsion factors are responsible for the extent of deformation in the STB configuration. Moreover, Kepert's theoretical treatment is based on repulsion features[31] (in other words increasing deformation may imply stronger repulsion on the short side of the trapezoid).

The strength of repulsive F···F interactions is demonstrated by the existence of WF_6 as a gas at room temperature. The large polarization of F−W bonds makes the F atoms highly negatively charged; the WF_6 octahedrons therefore repel each other inducing an unusual gaseous state. In our case, the alternative to the sterically hindered R^1···R^1 *syn* structure is the *anti* structure. We have calculated the energy for bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin to be slightly lower for the *syn* structure than for the *anti* structure (3.7 kcal/mol, for HF, and 1.9 kcal/mol for DFT); this feature will be addressed later.

Solution Study

Since the crystals of *anti*-bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin **4** were obtained directly from the alcoholic reaction mixture,[27] while all the previous bis(4-acylpyrazolon-5-ato)diorganotin derivatives precipitated in such a medium (they were later recrystallized from other solvents to obtain crystals suitable for diffraction),[11−13,16−21] we decided to study the behavior of **4** and related complexes containing ligands with the same R^1 substituent, in solution.

The proligands 4-acetyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazol-5-one (L^1H), 4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazol-5-one (L^2H), and 3-methyl-4-(trifluoroacetyl)-1-(4-trifluoromethylphenyl)pyrazol-5-one (L^3H) react with dichlorodiorganotin(IV) acceptors in basic methanol solution by substitution of the two chlorine atoms and yield the six-coordinate tin(IV) derivatives L_2SnR_2 **1−9** (see Scheme 1).

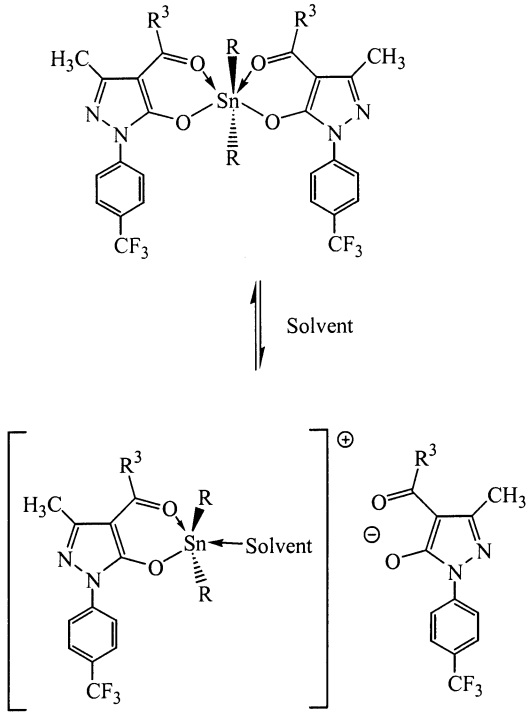


Compound	L	R^3	R
1	L^1	CH_3	CH_3
2	L^1	CH_3	Bu^n
3	L^1	CH_3	Ph
4	L^2	Ph	CH_3
5	L^2	Ph	Bu^n
6	L^2	Ph	Ph
7	L^3	CF_3	CH_3
8	L^3	CF_3	Bu^n
9	L^3	CF_3	Ph

Note: R^1 = *p*-CF_3-Ph and R^2 = CH_3 in all compounds.

Scheme 1

They are air- and moisture-stable solids, very soluble in aromatic and chlorohydrocarbons, acetone and dimethylsulfoxide (DMSO). They are partially dissociated in all these solvents with the exception of the aromatic hydrocarbons: In fact, vapor pressure osmometric molecular mass determinations of derivatives **1** and **3−5** in chloroform indicate a partial dissociation, the ratio *r* (molecular mass/formula mass) being generally in the range 0.60−0.90. Conductivity data carried out in dichloromethane seem to indicate the presence of non-ionic species. This could be due to ion-pairing effects, which result in a much lower conductivity value than that observed in DMSO. The molecular mass study on derivative $(L^2)_2SnMe_2$ **4**, shown in Figure S1 (Supporting Information, see also footnote on the first page of this article), indicates that dissociation increases with dilution. In fact, the experimental molecular mass values increase with concentration of the solution, approaching the theoretical formula mass when the concentration is higher than 0.02 m (m = mol of solute/kg of solvent). This behavior in solution is unexpected since previous studies[11−13,16−21] show an absence of conductivity for bis(4-acyl-5-pyrazolonato)diorganotin complexes, and the experimental molecular mass values in solution are typical of mononuclear non-ionic species. These results demonstrate that the CF_3 substituent in the *para* position of R^1 phenyl can influence the stability of the L_2SnR_2 species in solution.



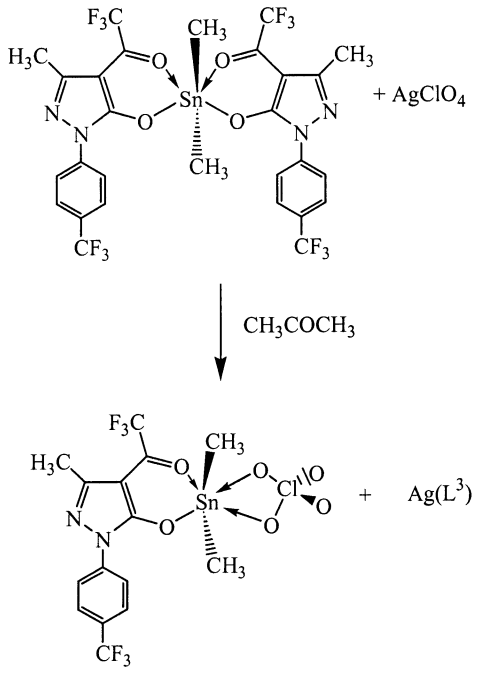
Scheme 2

Dissociation is confirmed by multinuclear NMR spectroscopic experiments. Broad resonances (compounds **1** and **2**) or three sets of signals (compounds **4** and **5**) for the ligand moiety in the ^1H NMR spectra, and two sets of signals for the $(alkyl)_2Sn$ moiety in the ^1H and ^{119}Sn NMR spectra are observed. This is in agreement with Scheme 2. We observed the same multiplicity in the ^{13}C NMR spectra. The assignments of the ^{13}C resonances of the groups bonded to tin are straightforward from the $^nJ(^{13}C\text{-}^{119/117}Sn)$ coupling constants, whereas the L carbon resonance assignments are based on the $^{13}C\text{-}^{19}F$ coupling constants. Holecek[33] and Lockhart[34] reported that $^1J(^{13}C\text{-}^{119}Sn)$ can be used to indicate the tin coordination number in diorganotin(IV) compounds. Six-coordinate dialkyl- and diaryltin(IV) complexes exhibit couplings in the range 800−1000 Hz, whereas five-coordinate complexes are in the range 500−700 Hz.[33−35] Most of the diorganotin(β-diketonates) in this work exhibit at least one signal with characteristic coupling satellites. The $^1J(^{13}C\text{-}^{119}Sn)$ coupling constants vary in the range 700−900 Hz, in accordance with a coordination number halfway between 5 and 6. These values can also be related to the size of the C−Sn−C angle, according to the equations derived by Holecek[33] and Lockhart.[34] The θ values of the studied compounds range from 145 to 157°. They are greater for L^1 and L^2 than for L^3 diorganotin(IV) derivatives. This suggests that the solid state six-coordinate structure is lost in solution in the case of L^3 complexes to generate a five-coordinate species, as also indicated by the values of the $^2J(^1H\text{-}^{119}Sn)$ coupling constants in the spectra of the dimethyl- and diphenyltin derivatives **7** and **9**, which correspond to typical five-coordinate diorganotin(IV) complexes.[33−35] However, it should be noted that the coupling constants values are determined by the metal coordination number as well as by electronic and steric factors, and we cannot exclude the occurrence of strong deformations from the octahedral structure in solution.

^{119}Sn NMR spectroscopic data further confirm the presence of different species in solution for dimethyl, di-*n*-butyl and diphenyltin(IV) derivatives of L^1 and L^2 as at least two resonances are found. The more intense is in the typical range for six-coordinate species [δ = −300 to −500 from $Sn(CH_3)_4$],[17] whereas the other is in the typical range for five-coordinate species δ = −80 to −250 from $Sn(CH_3)_4$].[33,35] The existence of species such as $[L(solvent)_xSn(CH_3)_2]^+$ (deduced from the equilibrium in Scheme 2) was confirmed by treating an acetone solution of $(L^3)_2Sn(CH_3)_2$ **7** with $AgClO_4$, yielding $[(L^3)Sn(CH_3)_2ClO_4]$ (**10**) according to Scheme 3 (see Exp. Sect.). Upon addition of a large excess of HL^1 and NEt_3 (1:1 relative molar ratio) to a $CDCl_3$ solution of **1**, the signal at δ = −100.6 disappeared, whereas that at δ = −323.9 remained unchanged.

The ^{19}F NMR spectra of the L^1 derivatives **1** and **3** have one resonance at room temperature that splits into four or five resonances at −50 °C (Figure S2), whereas the ^{19}F NMR spectra of derivatives **4−9** recorded at room temperature show several signals, in accordance with dissociation (Scheme 2).

Therefore, dissociation of a pyrazolonato anion in Scheme 2 generates ionic species, increasing the solubility in the moist alcoholic reaction mixture and allowing slow crystallization of the *anti* species **4**.



Scheme 3

Conclusion

Theoretical methods (HF and DFT) give calculated energies for the *syn* and *anti* configurations of bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin that are almost equivalent: the energy needed for the existence of the *anti* species could easily be provided by crystallization. In addition, such an arrangement for bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin, experimentally obtained in the solid state after crystallization from the reaction mixture, is favored by partial complex dissociation with the formation of the ionic species $[(solvent)(L)Sn(CH_3)_2]^+$ and the pyrazolonato anion (in contrast to ligands containing R^1 = Ph or methyl). Furthermore, the calculated O1−Sn−O1′ angle of the hypothetical *syn*-bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin is wider than those of other bis(4-acyl-5-pyrazolonato)dialkyltin complexes and this is due to repulsive F···F interactions. Therefore, the *anti* species arises from the synergistic action of: a) increased solubility in the reaction mixture due to ionic separation; b) repulsion between CF_3 groups for the *syn* configuration that is avoided in the *anti* species; and c) the small energy difference between the *syn* and *anti* configurations, which can be accounted for by the crystallization process.

The *syn* configuration [clearly preferred in bis(4-acyl-5-pyrazolonato)diorganotin complexes] is observed experimentally for bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]diphenyltin (**6**) The intramolecular repulsion between $R^1\cdots R^1$ groups in this less-distorted octahedral species is avoided because of the wider O1−Sn−O1′ angle than that of the calculated dimethyltin analogue.

Experimental Section

General: The organotin(IV) halides were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. − The samples for microanalysis were dried in vacuum to constant mass (20 °C, about 0.1 Torr). − Elemental analyses (C,H,N) were performed in house with Fisons Instruments 1108 CHNS-O Elemental Analyzer. − Molecular mass determinations (molecular mass) were performed at 40 °C with a Knauer KNA0280 vapor pressure osmometer calibrated with benzil. The solvent was Baker Analyzed Spectrophotometric grade chloroform. The results were reproducible to ±2%. − IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin−Elmer System 2000 FT-IR instrument. − ^1H, ^{19}F, ^{13}C, and ^{119}Sn NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^1H, 75 MHz for ^{13}C, 282.2 MHz for ^{19}F, and 111.9 MHz for ^{119}Sn), referred to TMS (^1H and ^{13}C), $CFCl_3$ (^{19}F), and $(CH_3)_4Sn$ (^{119}Sn). The ^{119}Sn NMR experiments were carried out with a spectral width of 900 ppm. − Melting points were taken on an IA 8100 Electrothermal Instrument. − The electrical conductances (reported as Ω^{-1} cm^2 mol^{-1}) of dichloromethane, DMSO, and acetone solutions (M = mol/L) were measured with a Crison CDTM 522 conductimeter at room temperature.

Synthesis of the Donors: The donors L^1H, L^2H, and L^3H were synthesized by previously reported methods.[36]

Synthesis of the Metal Derivatives

Bis[4-acetyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]-dimethyltin(IV) $(L_1)_2SnMe_2$ (1): KOH (2 mmol) and Me_2SnCl_2 (1 mmol) were added to a methanol solution (30 mL) of L^1H (2 mmol). A precipitate formed immediately. The mixture was stirred overnight and the precipitate was then filtered, washed with methanol (ca. 10 mL) and dried under reduced pressure at room temperature. The product was then recrystallized from chloroform/*n*-hexane. Yield: 86%. M.p. 230−231 °C. − $C_{26}H_{26}F_6N_4O_4Sn$: calcd. C 47.02, H 3.66, N 7.83; found C 47.34, H 3.76, N 8.02; formula mass 715; molecular mass 486 ($0.9\cdot10^{-2}$ m; r = 0.68), 529 ($1.4\cdot10^{-2}$ m; r = 0.74). − Molar conductance: Λ_M ($0.8\cdot10^{-3}$ M in CH_2Cl_2) = 0.3; Λ_M [$0.9\cdot10^{-3}$ M in $(CH_3)_2SO$] = 17.7. − IR (nujol): $\tilde{\nu}$ = 1618 s ν(C=O), 593 s ν(Sn−C), 442 s, 401 s ν(Sn−O). − ^1H NMR ($CDCl_3$): δ = 0.86 [s, $^2J(^1H\text{-}Sn)$ = 103.6, 99.6 Hz, 3 H, Sn−CH_3], 1.12 [s, $^2J(^1H\text{-}Sn)$ = 79.3 Hz, 3 H, Sn−CH_3], 2.44, 2.46 (2 br. s, 12 H, CH_3C=O and C3−CH_3), 7.55, 7.70, 8.10, 8.16 (4 d, 8 H, AA′BB′ pattern for the four protons in C_6H_4-4-CF_3). − ^{13}C NMR ($CDCl_3$, 20 °C): δ = 9.18 (s, Sn−CH_3), 9.75 (s, Sn−CH_3), 16.14 (s, 3-CH_3), 17.89 (s, 3-CH_3), 26.10 (s, CH_3CO), 28.51 (s, CH_3CO), 105.20 (s, C3), 120.4 (s, CH_{arom}), 120.9 (s, CH_{arom}), 124.4 [q, CF_3, ^1J(C−F): 271.5 Hz], 126.4 (s, CH_{arom}), 127.1 (s, CH_{arom}), 141.4 (s, C4), 141.62 (s, C4), 150.22 (s, C−N), 150.35 ($C-CF_3$), 162.92 (C5), 193.7 (C=O). − ^{19}F NMR ($CDCl_3$, 20 °C): δ = −62.9; ($CDCl_3$, −50 °C): δ = −62.1, −62.2, −62.3, −62.6. − ^{119}Sn NMR ($CDCl_3$): δ = −100.6 [1], −323.9 [2]; ^{119}Sn NMR ([D_6]benzene): δ = −324.1. − Derivatives **2−3**, **5−6**, **9**, were synthesized in a similar way.

Bis[4-acetyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]di-*n*-butyltin(IV) $(L^1)_2Sn{n}Bu_2$ (2): Yield: 73%. M.p. 173−175 °C. − $C_{34}H_{38}F_6N_4O_4Sn$: calcd. C 51.02, H 4.79, N 7.01; found C 50.96, H 4.63, N 7.13; formula mass 799. Molar conductance: Λ_M ($0.3\cdot10^{-3}$ M in CH_2Cl_2) = 0.5; Λ_M [$0.6\cdot10^{-3}$ M in $(CH_3)_2SO$] = 16.3. − IR (nujol): $\tilde{\nu}$ = 1618 s ν(C=O), 604 s ν(Sn−C), 440 s, 425 s, 392 s ν(Sn−O). − ^1H NMR ($CDCl_3$): δ = 0.80 (t), 0.94 (t), 1.28 (m), 1.52 (m), 1.75 (m), (18 H, Sn−*n*Bu), 2.45, 2.48 (2 br. s, 12 H, CH_3C=O and C3−CH_3), 7.52, 7.70, 8.05, 8.17 (4 d), 8 H, AA′BB′

pattern for the four protons in C_6H_4-4-CF_3). – ^{13}C NMR ($CDCl_3$, 20 °C): δ = 13.56 (s, Sn−*n*Bu), 16.86 (s, 3-*C*H$_3$), 17.45 (s, 3-*C*H$_3$), 25.97 (s, Sn−*n*Bu) 26.36 (s, Sn−*n*Bu) 26.86 (s, Sn−*n*Bu), 27.66 (s, Sn−*n*Bu), 28.01 (s, Sn−*n*Bu) 28.03 (s, *C*H$_3$CO), 28.98 (s, Sn−*n*Bu), 29.70 [s, Sn−*n*Bu, ^1J(^{13}C-Sn) = 875 Hz], 104.87 (s, *C*3), 120.12 (s, *C*H$_{arom}$), 120.47 (s, *C*H$_{arom}$), 123.8 (q, *C*F$_3$), 125.98 (s, *C*H$_{arom}$), 126.90 (s, *C*H$_{arom}$), 141.25 (s, *C*4), 149.63 (s, C−N), 152.8 (s, C−CF$_3$), 161.9 (C5), 193.49 (C=O). – ^{19}F NMR ($CDCl_3$): δ = −62.8. – ^{119}Sn NMR ($CDCl_3$): δ = −126.1 [1], −358.2 [4].

Bis[4-acetyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]-diphenyltin(IV) (L^1)$_2$SnPh$_2$ (3): Yield: 80%. M.p. 205−207 °C. – $C_{38}H_{30}F_6N_4O_4Sn$: calcd. C 54.38, H 3.60, N 6.67; found C 54.30, H 3.42, N 6.38; formula mass 839; molecular mass 658 ($1.1\cdot10^{-2}$ m; *r* = 0.78), 709 ($2.9\cdot10^{-2}$ m; *r* = 0.84). – Molar conductance: Λ_M ($0.8\cdot10^{-3}$ M in CH_2Cl_2) = 0.1; Λ_M [$0.9\cdot10^{-3}$ M in $(CH_3)_2SO$] = 13.0. – IR (nujol): $\tilde{\nu}$ = 1617 s ν(C=O), 247 m, 215 s ν(Sn−C), 455 m, 439 vs, 404 m ν(Sn−O). – ^{1}H NMR ($CDCl_3$): δ = 2.27, 2.38 (2 br. s), 2.46, 2.63 (2 s, 12 H, CH_3C=O and C3−CH_3), 7.30−7.40, 7.50−7.70, 7.90−8.24 (3 m, 18 H, AA′BB′ pattern for the four protons in C_6H_4-4-CF_3 + Sn-Ph). – ^{13}C NMR ($CDCl_3$, 20 °C): δ = 16.72, 16.86, 17.45, 17.7 (4 s, 3-*C*H$_3$), 28.01, 28.05, 28.32, 28.53 (4 s, *C*H$_3$CO), 104.7, 104.92, 104.96 (3 s, *C*3), 120.8 (s, *C*H$_{arom}$), 120.9 (s, *C*H$_{arom}$), 121.2 (s, *C*H$_{arom}$), 123.8 (q, *C*F$_3$), 126.1 (s, *C*H$_{arom}$), 126.9 (s, *C*H$_{arom}$), 128.5 [s, Sn−Ph, ^3J(^{13}C-Sn) = 54 Hz], 128.6 (s, Sn−Ph), 129.6 [s, Sn−Ph, ^4J(^{13}C-Sn) = 19 Hz], 130.1 (s, Sn−Ph), 135.7 [s, Sn−Ph, ^2J(^{13}C-Sn) = 60 Hz], 135.82 (s, Sn−Ph), 135. 9 (s, Sn−Ph), 141.3 (s, *C*4), 149.8 (s, C−N), 153.4 (s, C−CF$_3$), 162.3 (C5), 193.0 (C=O). – ^{19}F NMR ($CDCl_3$, 20 °C): δ = −62.7, −62.8; ($CDCl_3$, −50 °C): δ = −62.0, −62.1, −62.2, −62.4, −62.5. – ^{119}Sn NMR ($CDCl_3$, 20 °C): δ = −275.2 [1], −483.2 [6].

Bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]-dimethyltin(IV) (L^2)$_2$SnMe$_2$ (4): This compound was reported previously;[27] additional data are: formula mass 839; molecular mass 562 ($0.6\cdot10^{-2}$ m; *r* = 0.67), 612 ($0.9\cdot10^{-2}$ m; *r* = 0.73), 647 ($1.3\cdot10^{-2}$ m; *r* = 0.77), 712 ($1.9\cdot10^{-2}$ m; *r* = 0.84), 787 ($2.5\cdot10^{-2}$ m; *r* = 0.94). – Molar conductance: Λ_M ($0.7\cdot10^{-3}$ M in CH_2Cl_2) = 0.2; Λ_M [$0.8\cdot10^{-3}$ M in $(CH_3)_2SO$] = 18.7; Λ_M [$0.9\cdot10^{-3}$ M in $(CH_3)_2CO$] = 1.3. – ^{13}C NMR ($CDCl_3$, 20 °C): δ = 9.62 [s, Sn−*C*H$_3$, ^1J(^{13}C-Sn): 900 Hz], 16.5 (s, 3-*C*H$_3$), 104.8 (s, *C*3), 120.4 (s, *C*H$_{arom}$), 120.3 (s, *C*H$_{arom}$), 124.1 [q, *C*F$_3$, ^1J(C-F): 288 Hz], 126.7 (s, *C*H$_{arom}$), 127.8 (s, *C*H$_{arom}$), 128.4 (s, *C*H$_{arom}$), 131.5 (s, *C*H$_{arom}$) 139.15(s, *C*H$_{arom}$), 141.0 (s, *C*4), 150.22 (s, C−N), 150.2 (*C*−CF$_3$), 163.49 (C5), 191.5, 193.0 (C=O). – ^{119}Sn NMR ($CDCl_3$, 20 °C): δ = −102.00 [1], −321.4 [5].

Bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]-di-*n*-butyltin(IV) (L^2)$_2$Sn*n*Bu$_2$ (5): Yield: 74%. M.p. 99−102 °C. – $C_{44}H_{42}F_6N_4O_4Sn$: calcd. C 57.23, H 4.58, N 6.07; found C 57.08, H 4.72, N 5.95; formula mass 923. Molar conductance: Λ_M ($0.7\cdot10^{-3}$ M in CH_2Cl_2) = 0.4; Λ_M [$0.5\cdot10^{-3}$ M in $(CH_3)_2SO$] = 12.9. – IR (nujol): $\tilde{\nu}$ = 1616 m ν(C=O), 592 s, 513 vs ν(Sn−C), 445 sh, 434 vs, 398 vs ν(Sn−O). – ^{1}H NMR ($CDCl_3$): δ = 1.83, 1.92, 2.14 (3 s, 6 H, C3−CH_3); 0.75 (t), 0.92 (t), 1.20−1.40 (m), 1.55−1.75 (m) [18 H, Sn−C_4H_9, ^2J(^{1}H-^{119}Sn) = 104.2, ^2J(^{1}H-^{117}Sn) = 99.8 Hz], 7.46 (d), 7.50−7.70 (m), 7.75 (m), 8.10 (m), 8.22 (d) (18 H, AA′BB′ pattern for the four protons in C_6H_4-4-CF_3 and aromatic protons in the benzoyl moiety). – ^{13}C NMR ($CDCl_3$, 20 °C): δ = 13.61 (s, Sn−*n*Bu), 16.57 (s, 3-*C*H$_3$), 25.98 [s, Sn−*n*Bu, J(^{13}C-Sn = 132 Hz)], 27.09 [s, Sn−*n*Bu, J(^{13}C-Sn) = 47 Hz], 29.69 [s, Sn−*n*Bu, ^1J(^{119}Sn-^{13}C) = 875 Hz, ^1J(^{117}Sn-^{13}C) = 820 Hz], 105.02 (s, *C*3), 120.1 (s, *C*H$_{arom}$), 124.0 [q, *C*F$_3$, ^1J(C-F): 280 Hz)], 126.0 (s, *C*H$_{arom}$), 127.7 (s, *C*H$_{arom}$), 128.4 (s, *C*H$_{arom}$), 131.4 (s, *C*H$_{arom}$) 139.4 (s, *C*H$_{arom}$), 141.2 (s, *C*4), 150.2 (*C*−CF$_3$), 163.71 (C5), 191.9 (C=O). – ^{19}F NMR ($CDCl_3$, 20 °C): δ = −62.7, −62.8, −62.9. – ^{119}Sn NMR ($CDCl_3$, 20 °C): δ = −127.7 [1], −359.5 [4].

Bis[4-benzoyl-3-methyl-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]-diphenyltin(IV) (L^2)$_2$SnPh$_2$ (6): Yield: 78%. M.p. 244−246 °C. – $C_{48}H_{34}F_6N_4O_4Sn$: calcd. C 59.80, H 3.56, N 5.81; found C 59.72, H 3.64, N 5.76; formula mass 963; molecular mass 732 ($0.8\cdot10^{-2}$ m; *r* = 0.76), 818 ($1.6\cdot10^{-2}$ m; *r* = 0.85). – Molar conductance: Λ_M ($0.9\cdot10^{-3}$ M in CH_2Cl_2) = 0.9; Λ_M [$0.5\cdot10^{-3}$ M in $(CH_3)_2SO$] = 12.3. – IR (nujol): $\tilde{\nu}$ = 1615 m ν(C=O), 252 vs, 249 sh ν(Sn−C), 451 vs, 417 vs, 404 s ν(Sn−O). – ^{1}H NMR ($CDCl_3$, 20 °C): δ = 1.63, 1.89 (2 br. s, 6 H, C3−CH_3), 7.30−7.60 (m), 7.75 (m), 7.98 (d), 8.08 (d), 8.27 (d) [28 H, AA′BB′ pattern for the four protons in C_6H_4-4-CF_3 + aromatic protons in the benzoyl moiety + Sn−C_6H_5, ^2J(^{1}H-Sn) = 102 Hz]. – ^{13}C NMR ($CDCl_3$, 20 °C): δ = 16.7 (s, 3-*C*H$_3$), 105.93 (s, *C*3), 120.49 (s, *C*H$_{arom}$), 120.6 (br., *C*H$_{arom}$), 124.7 [q, *C*F$_3$, ^1J(C-F): 290 Hz], 126.4 (s, *C*H$_{arom}$), 126.51 (s, *C*H$_{arom}$), 127.22 (s, *C*H$_{arom}$), 128.3 (s, *C*H$_{arom}$), 128.5 [s, Sn−Ph, ^3J(Sn-^{13}C) = 54 Hz], 128.86 (s, *C*H$_{arom}$), 129.58 [s, Sn−Ph, ^4J(Sn-^{13}C) = 18 Hz], 132.29 (s, *C*H$_{arom}$), 135.72 [s, Sn−Ph, ^2J(Sn-^{13}C) = 60 Hz], 136.33 (s, *C*H$_{arom}$), 138.69 (s, *C*H$_{arom}$), 141.00 (s, *C*4), 148.04 (s, C−N), 150.6 (*C*−CF$_3$), 165.19 (C5), 192.24 (C=O). – ^{19}F NMR ($CDCl_3$, 20 °C): δ = −62.7, −62.8. – ^{119}Sn NMR ($CDCl_3$, 20 °C): δ = −274.0 [1], −480.9 [1], −486.6 [2].

Bis[3-methyl-4-(trifluoroacetyl)-1-(4-trifluoromethylphenyl)-pyrazolon-5-ato]dimethyltin(IV) (L^3)$_2$SnMe$_2$ (7): KOH (2 mmol) and Me_2SnCl_2 (1 mmol) were added to a methanol solution (30 mL) of L^1 (2 mmol). The clear solution was stirred overnight at room temperature, and the solvent was then removed under reduced pressure, chloroform (10 mL) was added to the crude product and the mixture was filtered to separate the KCl precipitate. Light petroleum (20 mL) was then added to the filtrate and a precipitate was formed, which was filtered, washed with light petroleum (about 10 mL) and dried under reduced pressure at room temperature. This was recrystallized from dichloromethane/*n*-hexane. Yield: 65%. M.p. 149−150 °C. – $C_{28}H_{20}F_{12}N_4O_4Sn$: calcd. C 40.86, H 2.45, N 6.81; found C 40.59, H 2.65, N 6.84; formula mass 823.2. – Molar conductance: Λ_M ($0.9\cdot10^{-3}$ M in CH_2Cl_2) = 0.5; Λ_M [$0.6\cdot10^{-3}$ M in $(CH_3)_2SO$] = 27.5. – IR (nujol): $\tilde{\nu}$ = 1628 s ν(C=O), 588 s ν(Sn−C), 463 s, 437 m ν(Sn−O). – ^{1}H NMR ($CDCl_3$, 20 °C): δ = 1.00 [s, ^2J(^{1}H-Sn) = 83.8 Hz, 6 H, Sn−CH_3], 2.23 (q, 6 H, C3−CH_3), 7.68 (d), 8.04 (d) (8 H, AA′BB′ pattern for the four protons in C_6H_4-4-CF_3). – ^{13}C NMR ($CDCl_3$, 20 °C): δ = 9.5 [s, Sn-*C*H$_3$, ^1J(Sn-C) = 780 Hz], 12.4 (s, Sn-*C*H$_3$), 13.7 (s, Sn-*C*H$_3$), 15.8 (q, 3-*C*H$_3$), 17.05 (s, 3-*C*H$_3$), 101.4 (s, *C*3), 117.06 [q, *C*F$_3$, ^1J(C-F) = 284 Hz], 118.07 (s, *C*H$_{arom}$), 120.7 (s, *C*H$_{arom}$), 122.7 (s, *C*H$_{arom}$), 123.67 [q, *C*F$_3$, ^1J(C-F) = 270 Hz], 126.01 (s, *C*H$_{arom}$), 127.1 (s, *C*H$_{arom}$), 129.01 (s, *C*H$_{arom}$), 131.1 (s, *C*H$_{arom}$), (s, *C*H$_{arom}$), 140.07 (s, *C*4), 140.8 (s, *C*4), 149.00 (s, C−N), 156.89 (*C*−CF$_3$), 165.02 (C5), 170.76 (C=O). – ^{19}F NMR ($CDCl_3$, 20 °C): δ = −62.6, −75.7. – ^{19}F NMR ($CDCl_3$, −50 °C): δ = −62.0, −75.3. – ^{119}Sn NMR ($CDCl_3$, 20 °C): δ = −139.2, −140.9.

Bis[3-methyl-4-(trifluoroacetyl)-1-(4-trifluoromethylphenyl)-pyrazolon-5-ato]di-*n*-butyltin(IV) (L^3)$_2$SnBu$^n_2$ (8): This compound was obtained using the same procedure as for **7**. Yield: 45%. M.p. 98−100 °C. – $C_{34}H_{32}F_{12}N_4O_4Sn$: calcd. C 45.01, H 3.55., N 6.17; found C 44.88, H 3.68, N 6.25; formula mass 907.3. – Molar conductance: Λ_M ($0.8\cdot10^{-3}$ M in CH_2Cl_2) = 0.4; Λ_M [$0.9\cdot10^{-3}$ M in $(CH_3)_2SO$] = 19.5. – IR (nujol): $\tilde{\nu}$ = 1628 s ν(C=O), 557 s ν(Sn−C), 462 s, 407 m ν(Sn−O). – ^{1}H NMR ($CDCl_3$, 20 °C): δ = 2.63 (q), 2.44 (q), 2.40 (q) (6 H, C3−CH_3). 7.40−7.60 (m),

7.92−8.20 (m) (8 H, AA′BB′ pattern for the four protons in C_6H_4-4-CF_3), 0.95 (br. t), 1.32−1.90 (br. m) (18 H, Sn−*n*Bu). − ^{13}C NMR ($CDCl_3$, 20 °C): δ = 13.85 (s, Sn−*n*Bu), 14.02 (s, Sn−*n*Bu), 14.09 (s, Sn−*n*Bu), 16.33 (s, 3-*C*H_3), 16.44 (s, 3-*C*H_3), 17.46 (s, 3-*C*H_3), 26.35 [s, Sn−*n*Bu, J(^{13}C-Sn) = 125 Hz], 26.73 (s, Sn−*n*Bu), 26.96 (s, Sn−*n*Bu), 27.16 [s, Sn−*n*Bu, J(^{13}C-Sn) = 43 Hz], 27.52 (s, Sn−*n*Bu), 27.79 (s, Sn−*n*Bu), 30.41 [s, Sn−*n*Bu, ^1J(^{13}C-^{119}Sn) = 775 Hz, ^1J(^{13}C-^{117}Sn) = 720 Hz], 32.63 (s, Sn−*n*Bu), 32.74 (s, Sn−*n*Bu), (s, Sn−*n*Bu, 33.34 (s, Sn−*n*Bu), 102.03 (s, *C*3), 117.06 [q, *C*F_3, ^1J(^{19}F-^{13}C) = 284 Hz], 118.55 (s, *C*H_{arom}), 121.0 (s, *C*H_{arom}), 121.6 (s, *C*H_{arom}), 123.67 [q, *C*F_3, ^1J(^{19}F-^{13}C) = 270 Hz], 126.01 (s, *C*H_{arom}), 126.62 (s, *C*H_{arom}), 128.66 [q, C−*C*F_3, ^2J(^{19}F-^{13}C) = 33.5 Hz], 132.3 (s, *C*H_{arom}), 132.8 (s, *C*H_{arom}), 140.7 (s, *C*4), 141.1 (s, *C*4), 149.38 (s, *C*H_{arom}) 157.41, (s, C−N), 165.78 (s, C5), 171.28 (s, C5) 174.25 [q, C=O, ^2J(^{19}F-^{13}C) = 37.5 Hz]. − ^{19}F ($CDCl_3$, 20 °C) NMR: δ = −63.1, −63.3, −63.7, −71.8, −75.6, −76.0, −82.2, −82.4. − ^{119}Sn NMR ($CDCl_3$, 20 °C): δ = −88.5 [2], −112.3 [1], −114.9 [1], −126.2 [3], −130.2 [2], −143.2 [2], −173.7 [1].

Bis[3-methyl-4-(trifluoroacetyl)-1-(4-trifluoromethylphenyl)-pyrazolon-5-ato]diphenyltin(IV) (L^3)$_2$SnPh$_2$ (9): Yield: 72%. M.p. 254−256 °C. − $C_{38}H_{24}F_{12}N_4O_4Sn$: calcd. C 48.18, H 2.55, N 5.91; found C 47.95, H 2.70, N 5.68; formula mass 947.3. Molar conductance: Λ_M ($1.0\cdot10^{-3}$ M in CH_2Cl_2) = 0.3; Λ_M [$1.1\cdot10^{-3}$ M in $(CH_3)_2SO$] = 4.5. − IR (nujol): $\tilde{\nu}$ = 1628 s ν(C=O), 266 s, 223 vs ν(Sn−C), 449 vs, 424 s ν(Sn−O). − ^{1}H NMR ($CDCl_3$, 20 °C): δ = 2.19, 2.21, 2.30, 2.38 (4 q, 6 H, C3−CH_3), 7.12−7.62, 7.78−7.94 (2 br. m, 18 H, AA′BB′ pattern for the four protons in C_6H_4-4-CF_3 and Sn−Ph). − ^{13}C NMR ($CDCl_3$, 20 °C): δ = 15.65 (br., 3-*C*H_3), 15.93 (s, 3-*C*H_3), 17.05 (s, 3-*C*H_3), 102.0 (br., *C*3), 118.1 (s, *C*H_{arom}), 120.5 (br., *C*H_{arom} + *C*F_3), 125.86, 126.02, 126.08, 126.1 (m, *C*H_{arom} + *C*F_3 + Sn−Ph), 127.5, 128.0, 128.3, 128.5, 128.7, 128.9, 129.1 (m, *C*H_{arom} + *C*F_3 + Sn−Ph), 130.0 [s, Sn−Ph, ^4J(^{13}C-Sn) = 16 Hz], 134.6 (s, *C*H_{arom}), 135.4 (br., *C*H_{arom} + *C*F_3 + Sn−Ph), 136.2 (s, *C*H_{arom}) 140.0 (br., *C*4), 149.0 (br., *C*H_{arom}) 157.2, (br., C−N), 164.0 (m, C5). − ^{19}F ($CDCl_3$, 20 °C) NMR: δ = −63.3, −63.6, −69.3, −71.6, −76.7, −82.1. − ^{119}Sn NMR ($CDCl_3$, 20 °C): δ = −278.7 [2], −301.4 [1], −319.2 [1], −320.2 [1].

[3-Methyl-4-(trifluoroacetyl)-1-(4-trifluoromethylphenyl)pyrazolon-5-ato]dimethyltin(IV) Perchlorate [(L^3)SnMe$_2$(ClO_4)] (10): Silver perchlorate (0.104 g, 0.5 mmol) was added to a stirred acetone solution (30 mL) of [(L^3)$_2$SnMe$_2$] (0.358 g, 0.5 mmol). A colorless precipitate formed within 6 hours which was filtered and identified as Ag(L^3) by elemental analysis and IR data. Yield: 40%. M.p. <300 °C. − $C_{13}H_{10}AgF_3N_2O_2$ (391.1): calcd. C 39.92, H 2.58, N 7.16; found C 40.12, H 2.70, N 7.34. − IR (nujol): $\tilde{\nu}$ = 1646 vs ν(C=O). The clear solution was then evaporated and the pale yellow residue was washed with diethyl ether/*n*-hexane (20 mL) and shown to be compound **10**. It was recrystallized from acetone/diethyl ether. Yield: 40%, M.p. 150 °C. − $C_{15}H_{16}ClF_3O_6N_2Sn$ (531.4): calcd. C 33.90, H 3.03, N 5.27; found C 34.03, H 3.16, N 5.45. − IR (nujol): $\tilde{\nu}$ = 1621 vs ν(C=O), 1099 vs. br., 1076 vs. br., 618 s ν(ClO_4), 586 m ν(Sn−C), 440 s, 422 m ν(Sn−O). − ^{1}H NMR ($CDCl_3$, 20 °C): δ = 1.26 [^2J(^{1}H-^{119}Sn) = 105 Hz; ^2J(^{1}H-^{117}Sn) = 100 Hz, 6 H, Sn−CH_3], 2.48 (s, 3 H, C_3−CH_3), 2.63 (s, 3 H, CH_3C=O), 7.40, 7.73 (2 d, 4 H, N−$C_6H_4$$CF_3$).

X-ray Crystallographic Study: A preliminary study was performed with a Weissenberg Camera to determine cell parameters and the triclinic space group. A $P2_1$ Syntex diffractometer was used for the measurements of the cell constants and for the data collection; a set of 25 reflections (with high theta angle) was used to obtain refined cell parameters. Decay correction was applied since monitoring of three reflections (taken every 100 reflections) indicated decay, average 14.8%. Slight absorption anisotropy was found after a psi-scan (transmission factor range 0.93−1.00), and so data were corrected for absorption, as well as for Lorentz and polarization effects.[37] The molecular structure was solved using the Patterson−Fourier method using CAOS.[38]

Subsequent calculations were performed as follows: refinement based on the minimization of the function $w(|F_o| - |F_c|)^2$ with the weighting scheme $w = 1/(a + F_o + cF_o^2)$, where a and c are of the order of $2F_o$(min) and $2/F_o$(max), respectively;[39] anisotropic displacement parameters were refined for non-H atoms. After refinement convergence, H atoms were introduced at fixed positions with a C−H distance of 0.96 Å, and H isotropic displacement parameters were kept fixed until final refinement convergence was reached. Atomic scattering factors and anomalous dispersion terms were taken from the literature.[40] Chemical formula, $C_{48}H_{34}F_6N_4O_4Sn$; M_w = 963.50; crystal habitat, block; crystal size [mm], 0.40 × 0.25 × 0.15; crystal system, triclinic; space group, $P\bar{1}$ (no. 2); crystal color, colorless; a = 9.299(4), b = 16.004(7), c = 15.557(6) Å; α = 96.03(2)°, β = 95.69(2)°, γ = 112.80(2)°; V = 2098(3) Å^3; Z = 2; T = 298 K; $D_{calcd.}$ = 1.526 g/cm^3; $2\theta_{max}$ = 60°; μ = 0.698 mm^{-1} graphite monochromated wavelength, Mo-K_α; scan speed = 4 °/min; scan range = 1.3°; index range, *h*: 0/12, *k*: −22/20, *l*: −21/21; measured reflections, 12904; unique reflections, 12863; refined reflections [$F>6\sigma(F)$] = 8261; refined parameters, 568; R, R_w = 0.052, 0.068; S = 1.29; $R(F) = \Sigma||F_o| - |F_c||/\Sigma F_o$; $S = [\Sigma\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, n = no. of data and p = no. of refined parameters.

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149841. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax 44 123/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Theoretical Study: All computations were carried out with the MULLIKEN program[41] package on an IBM/SP2 supercomputer. Hartree−Fock and MB3LYPDFT (Density Functional Theory)[42] methods were used. The basis set used with both methods was 6-31G*. For the tin atom an ECP approximation[43−51] was applied, as implemented within MULLIKEN, using a double zeta basis. The MULLIKEN default convergence criteria were used in computations of energies and geometries.

Supporting Information Available: Figure S1 (molecular mass vs. concentration of **4**), Figure S2 (^{19}F NMR spectra of **1** and **3** at −50 °C); see footnote on the first page of this article.

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