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Organotin(IV) derivatives of novel β-diketones☆ Part V. Synthesis and characterization of di- and triorganotin(IV) derivatives of 4-acyl-5-pyrazolones modified in position 3 of the pyrazole. Crystal structure of (1,3-diphenyl-4-benzoyl-pyrazolon-5-ato)triphenyltin(IV)

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Abstract

The interaction between R_3SnCl, $(R_3Sn)_2O$, R_2SnO or R_2SnCl_2 acceptors (R = Me, ^{n}Bu or Ph) and the two novel β-diketone proligands (LH = 1,3-diphenyl-4-R^4(C=O)-pyrazol-5-one: L^1H, R^4 = Ph; L^2H, R^4 = Me) yields complexes $[SnR_3(L)(H_2O)]$ (R = Me or ^{n}Bu, L = L^1 or L^2), $[SnPh_3(L)]$ and $[SnR_2(L)_2]$ (L = L^1 or L^2). The phenyl substituent on position 3 induces instability of the triorganotin derivatives in solution with the formation of $SnR_2(L)_2$ and SnR_4 compounds. Moreover, diorganotin derivatives partially dissociate in solution yielding $[SnR_2(L)(solvent)]^{2+}$ species. When compared with the related 3-methyl species, the crystal structure of (1,3-diphenyl-4-benzoyl-pyrazolon-5-ato)triphenyltin(IV) is not modified by the 3-phenyl substitution. The chemical instability generated by the Ph in position 3 is greater than in positions 1 and 4. In addition, the Ph in position 3 of the pyrazole influences the solution behavior of the free neutral 4-acyl-5-pyrazolones stabilizing a novel amino-diketo tautomeric form.

Keywords: Triorganotin complexes; 4-Acyl-5-pyrazolones; Crystal structures; NMR; IR

1. Introduction

The understanding of the chemistry of di- and triorganotin derivatives is important because of their antitumoral [1] and biocide properties which make some of these species suitable for pharmaceutical, industrial and agricultural applications [2]. Several studies have appeared in the literature regarding structural and spectroscopic features of tin β-diketonates, including their catalytic properties in the formation of polyurethane in foams [3], their promising antineoplastic activity and, more recently, their use as molecular precursors in LAD (laser ablation and subsequent deposition) technology [4]. Triphenyltin compounds are widely used as biocides in agriculture whereas tributyltin species are the best additives for paints applied on the hull of vessels to avoid corrosion from marine microorganisms. Recently some triorganotin benzoates have also shown good antitumor activity [5]. There is much literature about triorganotin carboxylates [6] whereas analogous triorganotin β-diketonates has received less attention [7], probably due to their low stability, both in solution and in the solid state. In 1992, we initiated an investigation of the interaction between diorganotin acceptors and 4-acyl-5-pyrazolone proligands (LH) [8] which are asymmetric β-diketones (Fig. 1), synthesized first by

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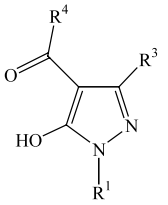


Fig. 1. 4-Acyl-pyrazol-5-one proligands LH.

Jensen [9], and then widely employed as dyes [10] and as metal extractants [11]. Recently some X-ray structures of their metal derivatives appeared in the literature showing that 4-acyl-5-pyrazolonates can display several modes of bonding [12].

We have synthesized several di- [8,13,14] and triorganotin(IV) acylpyrazolonates [15] earlier using ligands with different substituents near the carbonyl groups (positions 1 and 4 of the pyrazole), and studied their electronic and steric influence on their physicochemical and structural features, both in solution and in the solid state. The dialkyltin(IV)bis(acylpyrazolonato) derivatives generally possess either strongly deformed octahedral structures with both $(L)^-$ ligands pointing their equivalent arms in a *syn* configuration [8,13], or perfect octahedral tin coordination environments with centrosymmetrical (*anti*) configuration [14].

The trialkyltin(IV) derivatives are five-coordinate trigonal bipyramidal (TBP) aquo species with the acylpyrazolonato donor acting in the monodentate form through the O(pyrazolonato) (the oxygen closest to the pyrazole ring), while the O(acyl) participates in a network of H bonds. Instead, triphenyltin compounds adopt *cis*-trigonal bipyramidal geometry with the acylpyrazolonato coordinating the metal in a strongly asymmetric bidentate form. The *p*-CF_3–Ph group in position 1 of the pyrazole enhances the instability of these compounds in solution [15b]. This asymmetric binding is also observed in the diorganotin derivatives [13g].

Here we extend our investigation to include the synthesis of organotin(IV) compounds containing some novel acylpyrazolonates (L^1, $R^1 = R^3 = R^4 = Ph$; L^2, $R^1 = R^3 = Ph$, $R^4 = Me$) with a phenyl in position 3 of the pyrazole. Since thus far only a methyl group in such position had been known we demonstrate that all substitutions on the pyrazole (positions 1, 3 and 4) are chemically feasible.

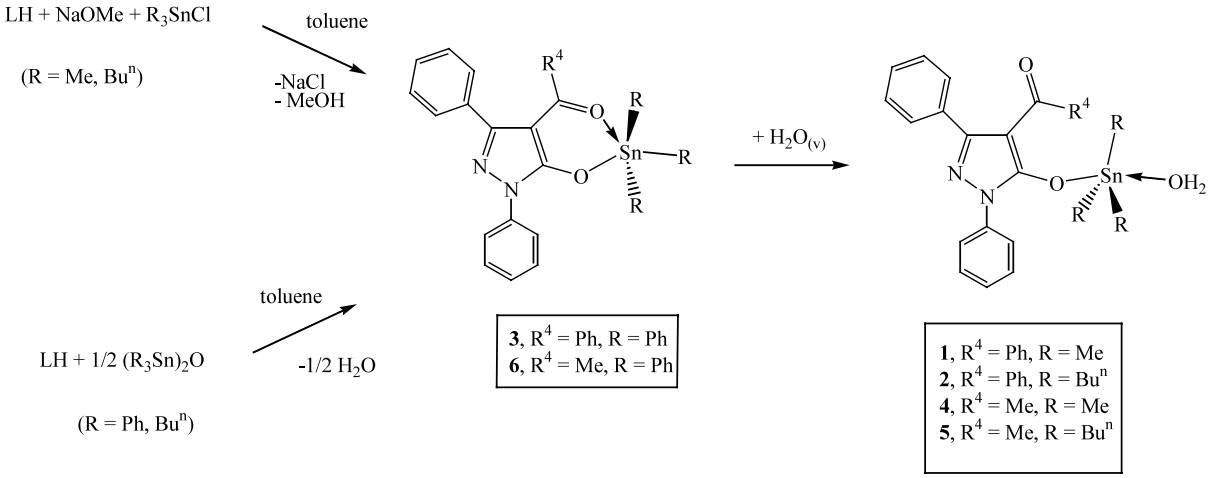
This research is performed using X-ray diffraction methods, solution multinuclear NMR and analytical techniques, and includes a systematic comparison of these derivatives with those synthesized earlier. It is our goal to tune the properties of these species through the appropriate choice of R^1, R^3 and R^4 substituents.

2. Results and discussion

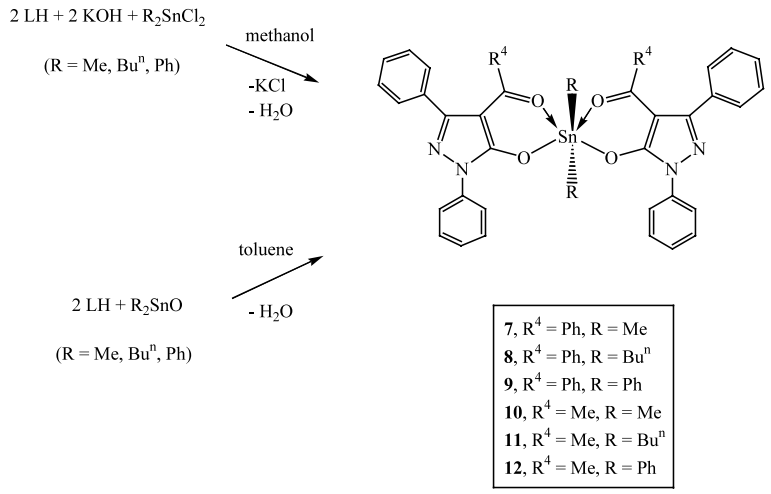
2.1. Synthesis of triorganotin(IV) derivatives **1**–**6**

The triorganotin(IV) derivatives $[SnR_3(L)(H_2O)_x]$ **1**–**6** ($x = 0$ or 1, $L = L^1$ or L^2) have been obtained from the metathesis reaction of the sodium salt of the acylpyrazolonate (NaL) with R_3SnCl (R = Me, ^{n}Bu or Ph) in 1:1 molar ratio in toluene (Scheme 1). The $[Sn^nBu_3(L)(H_2O)]$ and $[SnPh_3(L)]$ compounds can also be obtained in higher yields by reacting the corresponding $(R_3Sn)_2O$ with the neutral ligands LH in refluxing toluene (Scheme 1).

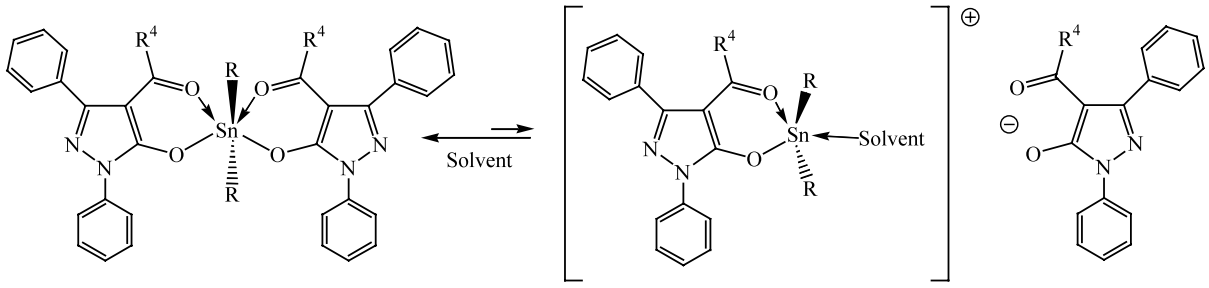
As observed earlier for similar species containing pyrazolonate ligands having a methyl in position 3, the tri-*n*-butyl- and trimethyl-tin(IV) derivatives rapidly absorb water on exposure to air, whereas the triphenyltin(IV) complexes are air and moisture stable. These species are generally low melting solids, with the exception of compound **5** that is a dense liquid at room



Scheme 1.



Scheme 2.



Scheme 3.

temperature. Derivatives **1**–**6** are highly soluble in acetone, acetonitrile, DMSO, alcohols and chlorohydrocarbons, sparingly soluble in diethyl ether and insoluble in hydrocarbons and water.

Conductivity values in dichloromethane indicate the existence of neutral species in solution. All these compounds undergo a partial dissociation in DMSO, a behavior also observed for diorganotin(IV) derivatives of 1-phenyl-3-methyl-4-trichloroacetyl-pyrazolon-5-ato ligand [13c,f] and triorganotin(IV) derivatives of 1-(4-trifluoromethyl)-phenyl-3-methyl-4-R^4(C=O)-pyrazolon-5-ato ligands (R^4 = Me, CF_3 or Ph) [15a].

The molecular weight determinations carried out in chloroform solution on selected triorganotin(IV) compounds indicate a partial dissociation in solution, especially in the case of aquo-triorganotin(IV) derivatives: the experimental molecular weight values are generally less than expected and the ratio r (r = MW/FW) is of the order of 0.7–0.9, generally increasing with concentration. This seems to indicate the partial dissociation of the anionic L^- donor and/or of H_2O. However, a decomposition process (1) that takes place in solution very slowly at room temperature (see Sections 2.4, 2.5 and 2.6), cannot be excluded:

$$2SnR_3(L)(H_2O) \xrightarrow[CHCl_3]{-2H_2O} 2SnR_3(L) \rightarrow SnR_2(L)_2 + SnR_4 \quad (1)$$

This process is accelerated at the experimental temperature of 40 °C. Only a negligible dissociation is shown by the triphenyltin(IV) derivative **3** whose ratio, r, is 0.91.

2.2. Synthesis of diorganotin(IV) derivatives 7–12

The diorganotin(IV) derivatives [$SnR_2(L)_2$] (**7**–**12**) were obtained from the reaction of 2 mmol of acylpyrazolones LH with 1 mmol of R_2SnCl_2 (R = Me, ^{n}Bu or Ph) and 2 mmol of potassium hydroxide in methanol (Scheme 2).

All complexes are air and moisture stable. They are highly soluble in acetone, acetonitrile, DMSO, and chlorohydrocarbon solvents, insoluble in diethyl ether, alcohols, hydrocarbons and water.

Compounds **7**–**12** undergo a partial dissociation in DMSO, as evidenced from the conductivity values in this solvent. In dichloromethane, however, values typical of non-electrolyte species have been found always. Molecular weight determinations, carried out in chloroform solution, also indicate a partial dissociation. Therefore, the formation of ionic pairs and the

occurrence of an equilibrium as that proposed in Scheme 3 is likely.

The dissociation is a function of the concentration of the solutions, the ratio r between the experimental and calculated molecular weight ranging from 0.71 to 0.96 at concentrations between 0.7 and 1.9×10^{-2} m.

2.3. IR data

In the solid state, the donors L^1H and L^2H exist in the keto-enolic tautomeric form and show a broad absorption at 2600 cm^{-1} due to intramolecular (O–H···O) bond. Upon coordination, these absorptions disappear and, for derivatives **2**, **3** and **6**–**12** the ν(C=O) at ca. 1620 cm^{-1} shifts to lower frequencies (ca. 1600 cm^{-1}), in accordance with the loss of the acidic proton and binding of both carbonyls to the metal. For derivatives **1**, **4** and **5** this band remains essentially unchanged, most likely indicating weak interactions with a neighboring H atom of tin-coordinated water, as observed earlier [15]. In the aquo derivatives the band at 3100–3200 cm^{-1} is attributed to the intermolecularly H-bonded water. The absorption bands of the azomethine and phenyl groups are found between 1500 and 1600 cm^{-1}. Bands due to ν(Sn–O) have been assigned in the 400–500 cm^{-1} range, based on previous reports [16]. Some bands of methyl- (**1**, **4**, **7**, **10**) and butyl-tin(IV) (**2**, **5**, **8**, **11**) derivatives, in the 500–620 cm^{-1} range, are likely due to ν_{as}(Sn–C) and ν_s(Sn–C) [17] whereas the corresponding absorptions for phenyltin(IV) complexes (**3**, **6**, **9**, **12**) have been observed in the 200–300 cm^{-1} region [18]. By comparing these bands with those observed in the known organotin(IV) acylpyrazolonates no correlation is found between the Sn–O bond strength and the instability of these compounds in solution.

2.4. ^1H-NMR data

Since the acidic proton signal is found between 2.50 and 4.50 ppm, a chemical shift typical for N–*H* groups, L^1H and L^2H exist in chloroform in the amino-diketo tautomeric form. Instead, the earlier 4-acylpyrazolones showed a resonance up to 10.0 ppm due to (O–*H*···O) systems [9,12]. Therefore, electron-withdrawing groups such as Ph, in position 3 of the pyrazole ring, influence the solution behavior of the free neutral acylpyrazolones.

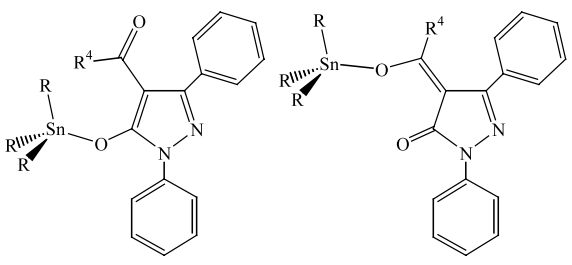


Fig. 2. Two tetrahedral possible isomers for trimethyl- and tributyltin(IV) species.

In the ^1H spectrum of derivatives **1**–**3** and **7**–**9** the acylpyrazolonato aromatic signals undergo a more complex pattern upon chelation, whereas the CH_3(C=O) group shows only a negligible shift in **4**–**6** and three signals or one very broad high-field shifted in **10**–**12**.

The trimethyl- and tri-*n*-butyl-tin(IV) derivatives show at least two different sets of signals for the alkyl groups bonded to tin, with the coupling constant $^2J(^{119}Sn–^1H)$ falling in the 55–58 Hz range, typical values of four- to five-coordinate species [19]. On the basis of conductivity and osmometric molecular weight values reported above, we conclude that these compounds lose the molecule of coordinated water in solution, forming isomeric tetrahedral non-fluxional forms as those shown in Fig. 2, or five-coordinate tin(IV) species containing a bidentate acylpyrazolonato.

This suggests equivalence, at least in solution, of the donating ability of the two carbonyls, similarly to triorganotin(IV) derivatives containing an electron-withdrawing *p*-CF_3–Ph group in position 1 of the pyrazole ring [15b]. This differs from the triorganotin(IV) derivatives of 1-phenyl-3-methyl-4-acylpyrazolonates reported earlier [15a].

For triphenyltin(IV) complexes it is not possible to distinguish between signals due to aromatic ligand protons and those linked to tin, but integration takes their presence into account.

The dimethyl-tin(IV) (**7**, **10**) and di-*n*-butyl-tin(IV) (**8**, **11**) derivatives show at least two different sets of signals for the alkyl groups bonded to tin, with the coupling constant $^2J(^{119}Sn–^1H)$ of the more intense signal falling in the 96–102 Hz range, typical values for six-coordinate species having skewed trapezoidal bipyramidal geometry [19]. The less intense signal is likely due to the five-coordinate organotin(IV) species originating from the partial dissociation of the complex in chloroform solution (see Section 2.6). The proton spectra of the diphenyltin(IV) complexes **9** and **12** show broad signals suggesting fluxionality in solution between different geometrical isomers and/or dissociation equilibria as (1) also in accordance with ^{13}C and ^{119}Sn data (see below).

2.5. ^{13}C-NMR data

In the ^{13}C-NMR spectra of the proligands L^1H and L^2H the pyrazole C_3 resonance, bonded to Ph (R^3 group), falls at ca. 151 ppm, deshielded by about 5 ppm with respect to that of the same C atom in all previous acylpyrazolones containing a Me group in position 3. This signal is slightly shifted upon coordination, be-

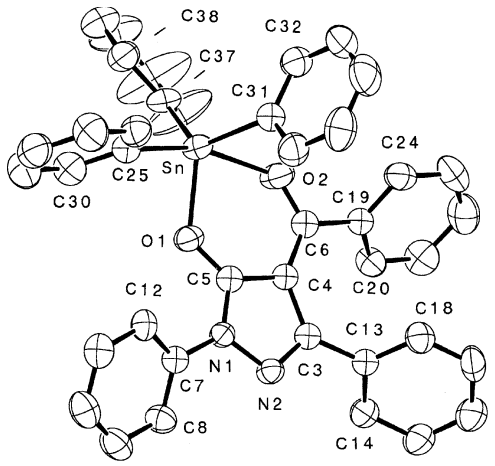


Fig. 3. X-ray molecular structure of (1,3-diphenyl-4-benzoyl-pyrazolon-5-ato)triphenyltin(IV) with H atoms omitted.

cause of reduced shielding due to electron density flow toward tin.

The tributyltin derivatives **2** and **5** show at least two sets of resonances and those of triphenyltin **3** and **6** broad signals, due to the presence of the forms hypothesized in Fig. 2. It was not possible to obtain ^{13}C-NMR spectra of the trimethyltin derivatives **1** and **4** which disproportionate in solution yielding the corresponding diorganotin derivatives **7** and **10** and Me_4Sn during the time necessary to acquire a sufficient number of transients.

The ^{13}C-NMR spectra of the species resemble those of the previously reported ones [8,13,14]. The values of $^1J(^{13}C–^{119}Sn)$ for dimethyltin derivatives **7** and **10** and dibutyltin **8** and **11** are in the 870–950 Hz range, thus indicating six-coordinated tin atoms. On the basis of the empirical relation derived by Lockhart [19a] the C–Sn–C angles for derivatives **7**, **8**, **10** and **11** were found in the 153–160° range typical of skewed *trans*-octahedral species. In the case of **8**, **9** and **12** more than one set of resonance or broad signals has been observed for each magnetically equivalent carbon atom, in accordance with the ^{1}H- and ^{119}Sn-NMR spectra likely due to different geometrical isomers or to the presence of species arising from dissociation of one acylpyrazolone donor, as hypothesized in Scheme 1.

2.6. ^{119}Sn-NMR data

The trialkyltin(IV) acylpyrazolonates show two signals in the + 80 to + 155 ppm range typical of tetrahedral species $SnOR_3$ [20], corresponding to Sn–OH_2 bond cleavage and formation of isomers as of those in Fig. 2.

Instead, the triphenyltin(IV) derivatives give a unique resonance between − 132 and − 181 ppm due to a five-coordinate TBP geometry [21]. In the ^{119}Sn spectrum of **3** a small absorption at − 47 ppm has been observed, likely due to a tetrahedral $[SnPh_3(L)]$ species in which the donor is probably monodentate. This shows that the Sn–O binding is weaker than in the previous triphenyltin(IV) derivatives containing a methyl group in position 3 of the pyrazole [15], and indicates the possibility of tuning the donor ability of this class of β-diketones also by using this peripheral position.

Derivatives **1**–**6** slowly decompose in chloro-hydrocarbon solvents giving SnR_4 and $SnR_2(L)_2$ species within 2 days. It is worth noting that 3-methyl related species showed such a reaction for trialkyltin but not for triphenyltin derivatives [15]. From ^{119}Sn-NMR spectroscopy we find that $[SnPh_3(L)]$ are always more stable than the $[SnMe_3(L)(H_2O)]$ and $[Sn^nBu_3(L)(H_2O)]$ derivatives, however, they are less stable than all the previously reported triphenyltin(IV) acylpyrazolonates [15].

The dialkyltin(IV)pyrazolonato derivatives **7**, **8**, **10** and **11** show two different signals, one in the range typical of a four- to five-coordinate tin center, the other typical of SnO_4C_2 cores [19], in accordance with the molecular weight measurements and ^{1}H-NMR data from which a partial dissociation of these complexes in solution has been hypothesized.

In the case of the diphenyltin(IV) derivative **9** one signal for a five-coordinate tin center and two different signals for the six-coordinate species have been found, the latter due to different isomers that are non-fluxional at room temperature, as previously reported [8,13]. The two signals collapse at 328 K in a single resonance at − 486 ppm.

2.7. X-ray crystal structure of $[SnPh_3(L^1)]$ (3)

The crystal structure of the title compound shows little intermolecular interaction. The molecular structure is depicted in Fig. 3 and selected geometrical parameters are shown in Table 1.

The metal is five-coordinate in a TBP arrangement, made up of three C from the phenyls and two O from the chelating ligand. The apical positions are occupied by one oxygen and one carbon, O2 and C25, respectively. The intrinsically asymmetric ligand 4-acyl-pyrazolonato generally displays a covalent Sn–O1 (pyrazolonato) bond and a weaker, longer, Sn–O2 (acyl) bond: these values are 2.053(5) and 2.409(5) Å, respectively, in this structure. In the TBP geometry, the axial lengths are longer than those equatorial and O2 occupies the expected position. For 'O_2SnC_3' TBP cores, the literature shows the two apical positions occupied by either two oxygens or one oxygen and one carbon. The former type is electronically preferred by the metal (because of the greater electronegativity of O) and is generally found in polymeric structures. Instead,

the chelating nature of our ligand induces the latter form, although the bite generates distortion from a regular TBP geometry. Thus, the ideal *trans* axial angle of 180° differs from the found C25–Sn–O2 bond angle of 163.6(3)°. The metal is 0.33 Å out of the equatorial plane (defined by O1, C31 and C37) towards C25 and the sum of the equatorial angles (O1–Sn–C31, O1–Sn–C37, C31–Sn–C37) is 352.6° which differs from 360°. The torsion angle C8–C7–N1–C5 of 32.0(9)° is greater than that of [1-(4-trifluoromethylphenyl)-3-methyl-4-acetylpyrazolon-5-ato]triphenyltin(IV) (22°) and indicates no extended conjugation between the C7–C12 phenyl and the pyrazole rings. In contrast, such co-planarity is seen in bis(4-acyl-5-pyrazolonato)diorganotin compounds [13e]. Fig. 3 shows that the Ph ring C36···C41 is affected by disorder.

This structure is similar to the related species [1-(4-trifluoromethylphenyl)-3-methyl-4-acetylpyrazolon-5-ato]triphenyltin [15b]. On the other hand, it is interesting to compare the title compound with the aquo related species [$LSnR_3(H_2O)$], L = 1-phenyl-3-methyl-4-benzoyl-pyrazolon-5-ato, R = ^{n}Bu [22], L = 1-phenyl-3-methyl-4-*p*-methoxybenzoyl-pyrazolon-5-ato, R = Me [15a], where the *O*-acyl is out of the coordination sphere and involved in intermolecular H bonding, and the molecule of water is weakly coordinated to the metal (Sn–O 2.34 Å [22] or 2.41Å [15a]). The different structural behavior may be explained using an electronic basis. Phenyls are electron-withdrawing groups and alkyls are electron releasing, therefore in triphenyltin species the electron density is shifted from the metal to the phenyls. It is likely that a weakly coordinated molecule of water, such as in the alkyl structure, could not provide enough electron donation to balance the Ph electronic request (the water molecule is also involved in a supramolecular H bonding arrangement). Thus, the unstable TBP axial system ···H···O(aquo)···Sn–O(pyrazolonato)C=O(acyl)···H··· cannot form while a contribution from the acyl carbonyl to the coordination sphere results in the formation of a stable chelate. Support for this explanation is observed experimentally as the aquo derivatives react more easily than the chelate triphenyltin derivatives. In addition, if the 4-acyl-5-pyrazolonato ligand itself contains electron-withdrawing groups, then the additional competition may develop instability. As shown in ^{119}Sn-NMR spectra, the triphenyltin derivative **3** is more unstable than the previous 3-methyl-4-acyl-5-pyrazolonato-triphenyltin species. We conclude that the electron-withdrawing effect of Ph in position 3 is more destabilizing than in positions 1 and 4 as the Ph in these positions is not able to induce reaction (1).

Instead, reaction (1) was increased when *p*-CF_3–Ph was the substituent in position 1 [15b]. It is a more potent electron-withdrawing group than Ph and its behavior concurs with the competitive effect mentioned above. Further, when position 4 is occupied by the electron-withdrawing group CCl_3, the haloformic reaction takes place in alcohol (R′OH) changing the CCl_3 substituent to a COR′ group [13c,f]. This reaction, although different than reaction (1), is nevertheless an expression of instability.

Such a feature may be important in explaining the antitumor activity of some triphenyltin-benzoates [5] since benzoates containing F (an electron-withdrawing atom) show increased antitumor activity. It is likely that these triorganotins evolve or metabolize to diorganotins in a reaction like (1), for instance, since not only tri- [5] but also diorganotins are a systematic class of antitumor species [5e,23]. Therefore, the F containing benzoate may augment destabilizing its triorganotin derivatives as the Ph, in position 3 of pyrazole, does for reaction (1) in this study.

Table 1
Selected bond lengths (Å) and bond angles (°)

Bond lengths	
Sn–O1	2.053(5)
Sn–O2	2.409(5)
Sn–C25	2.139(7)
Sn–C31	2.12(1)
Sn–C37	2.12(1)
O1–C5	1.304(9)
O2–C6	1.251(9)
Bond angles	
C31–Sn–O1	115.5(3)
O2–Sn–O1	77.0(2)
O2–Sn–C31	80.7(3)
C37–Sn–O1	114.3(3)
C37–Sn–C31	122.8(3)
C37–Sn–O2	84.7(3)
C25–Sn–O1	87.0(2)
C25–Sn–C31	103.3(3)
C25–Sn–O2	163.6(2)
C25–Sn–C37	105.6(3)
Sn–O1–C5	129.1(5)
Sn–O2–C6	130.8(5)
C6–C4–C5	121.5(6)
O1–C5–C4	131.5(6)
O2–C6–C4	121.3(6)

3. Conclusions

Since 1959, 4-acyl-5-pyrazolones have had exclusively a methyl group in position 3 of the pyrazole and this work reports the synthesis and characterization of novel 3-phenyl substituted compounds. The uncoordinated ligand is in the keto-enolic tautomeric form in solution, which was not found for other 4-acyl-5-pyrazolonates. A disproportion reaction not observed earlier in solution for related 3-methyl-triphenyltins is

found for 3-phenyl-triphenyltin derivatives. However, the metal coordination of 3-methyl- and 3-phenyl-triphenyltin compounds is similar in the solid state. It is also found that the Ph in position 3 acts as a stronger destabilizer than in positions 1 and 4. To generate chemical instability from positions 1 and 4 more powerful electron-withdrawing groups are needed: these are *p*-CF_3–Ph [15] and CCl_3 [13c,f], respectively.

Thus far, only substitution on position 4 of the 1-R^1-3-R^3-4-C=O–R^4-5-pyrazolone was widely applied, mainly for dyes and extraction purposes, and until recently R^1 and R^3 were exclusively Ph and Me, respectively. Recently, we obtained 1-methyl [13e] and 1-(*p*-CF_3–Ph) [14,15b] derivatives. The present study shows that a Ph substituent in position 3 induces novel features making this area worth exploring further.

4. Experimental

The reactions were carried out under N_2 stream using Schlenk techniques. Solvents were dried by standard techniques. The samples were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr). Elemental analyses (C, H, N) were performed in-house with a Carlo–Erba Strumentazione 1106 instrument. Melting points (m.p.) were measured with an IA 8100 Electrothermal instrument. The electrical resistances of solutions were measured with a Crison CDTM 522 Conductimeter at room temperature (r.t.). Molecular weight determinations were performed with a Knauer A0280 Vapour Pressure Osmometer. Mass Spectra were obtained in a HP 5971A Mass Spectrometer. IR spectra from 4000 to 100 cm^{-1} were recorded with a Perkin–Elmer 2000 FT-IR instrument. ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectra were recorded in a VXR-300 Varian spectrometer operating at r.t. (300 MHz for ^{1}H, 75 MHz for ^{13}C and 111.9 MHz for ^{119}Sn). H and C chemical shifts are reported in ppm versus $SiMe_4$ whereas Sn chemical shifts are reported in ppm versus $SnMe_4$. Relative intensity of signals is given in square brackets. The C spectra were run in samples with high concentrations ($> 4 \times 10^{-2}$ m), to avoid complications due to dissociative and/or degradative processes in dilute solutions. The Sn spectra were run with a spectral width of 1000 ppm. Each tin spectrum was acquired in ca. 1/2 h (ca. 300 transients). All the chemicals were analytical reagent grade from Aldrich.

4.1. Syntheses of proligands

4.1.1. 1,3-Diphenylpyrazol-5-one

Ethyl benzoylacetate (0.052 mol, 10.0 g) was added dropwise to a solution (30 ml) of phenylhydrazine (0.052 mol, 5.63 g). The mixture was stirred to refluxing 1 h, then the solvent was removed in a rotary evaporator and the crude product washed with Et_2O (50 ml) and light petroleum (50 ml). After filtration, the brown powder was dried in vacuo and shown to be 1,3-diphenylpyrazol-5-one. Yield: 78%. M.p. 138–139 °C. MS; *m*/*z*: 236 [M^+]. Anal. Found: C, 76.46; H, 5.18; N, 11.65. Calc. for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86%; IR (cm^{-1}): *v* 1699s br, 1655sh, 1632m, 1592s, 1561m, 1495s, 651s, 616m, 600s, 595sh, 526m. ^{1}H-NMR ($CDCl_3$): δ 3.85s (2H, 4CH_2), 7.25t, 7.45m, 7.70m, 8.02dd (10H, N(1)–C_6H_5, C(3)–C_6H_5).

The donors L^1H and L^2H were then synthesized following the procedure reported by Jensen [9].

4.1.2. 1,3-Diphenyl-4-benzoylpyrazol-5-one (L^1H)

Yield: 84%. M.p. 114–116 °C. MS; *m*/*z*: 340 [M^+]. Anal. Found: C, 77.48; H, 4.80; N, 8.05. Calc. for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23%. IR (Nujol, cm^{-1}): *v*(OH···O) 2700br; 1620vs (br). ^{1}H-NMR ($CDCl_3$): δ 2.50s (br, 1H, NH···O), 7.05m, 7.25m, 7.75m, 7.88d (15H, C_6H_5). ^{13}C-NMR ($CDCl_3$): δ 121.4, 121.8, 126.0, 126.3, 126.5, 126.8, 127.9, 128.0, 128.4, 128.8, 129.2, 129.7, 131.7 (s, C_{arom} of C_6H_5), 103.8 (s, C_3), 150.8 (s, C_4), 161.0 (s, C_5), 193.4 (s, CO).

4.1.3. 1,3-Diphenyl-4-acetylpyrazol-5-one (L^2H)

Yield: 72%. M.p. 145–147 °C. MS; *m*/*z*: 278 [M^+]. Anal. Found: C, 73.16; H, 5.16; N, 10.12. Calc. for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07%. IR (Nujol, cm^{-1}): *v*(OH···O) 2800br; 1622vs (br). ^{1}H-NMR ($CDCl_3$): δ 2.18s (3H, CH_3(C=O)), 3.20s (br, 1H, NH···O), 7.25m, 7.33d, 7.60m, 7.92d (10H, C_6H_5). ^{13}C-NMR ($CDCl_3$): δ 26.8 (s, CH$_3$(C=O)), 120.9, 126.8, 128.5, 128.7, 129.1, 129.3, 129.4, 132.9, 137.3 (s, C_{arom} of C_6H_5), 104.0 (s, C_3), 151.3 (s, C_4), 160.5 (s, C_5), 195.3 (s, CO).

4.2. Syntheses of the complexes

4.2.1. [$SnMe_3(L^1)(H_2O)$] (1)

A toluene solution (30 ml) of the proligand L^1H (1.0 mmol, 340 mg) was added to a methanolic solution (10 ml) of CH_3Ona (1.0 mmol, 54 mg) and refluxed for 1 h. A toluene solution (20 ml) of Me_3SnCl (1.0 mmol, 200 mg) was then added to the above solution drop-wise and the reaction mixture was stirred at r.t. for about 3 h. Sodium chloride was filtered and the solvent removed under reduced pressure on a rotary evaporator until a thick oil was obtained. This was treated with Et_2O and light petroleum, and a brown solid afforded. This was recrystallized from toluene–petroleum ether mixture and shown to be compound **1**. Yield: 56%, m.p. 212–214 °C. Anal. Found: C, 57.35; H, 5.23; N, 5.28. Calc. for $C_{25}H_{26}N_2O_3Sn$: C, 57.61; H, 5.03; N, 5.37%. FW 521. Molecular weight ($CHCl_3$, 40 °C, *c* (mol kg^{-1} solvent) = 1.2×10^{-2} M), MW 385 (*r* = MW/FW = 0.74). Conductivity (CH_2Cl_2, *c* (mol l^{-1}) =

0.610^{-2} M), Λ_M (Ω^{-1} cm^2 mol^{-1}) = 0.3; (DMSO, $c = 0.8 \times 10^{-3}$ M), Λ_M = 10.0. IR (Nujol, cm^{-1}): ν(H_2O) 3250br; ν(H_2O) 1655m; ν(C=O) 1620vs (br); ν(Sn–O) 448m, 416s, 410m; ν(Sn–C) 552s, 548sh. ^{1}H-NMR ($CDCl_3$): δ 0.62s ($^2J(^{119}Sn–^1H) = 57.6$ Hz, $^2J(^{117}Sn–^1H) = 55.4$ Hz), 0.67s ($^2J(^{119/117}Sn–^1H) = 56.3$) (9H, Sn–C$H_3$), 2.50s (br) (2H, H_2O), 7.15m, 7.45m, 7.85m, 7.98d, 8.15d (15H, C_6H_5(L^1)). ^{1}H-NMR (DMSO-d_6): δ 0.25s (br), 0.45s (br), 1.00s ($^2J(^{117/119}Sn–^1H) = 100.8$ Hz) (9H, Sn–CH_3), 2.35s (br) (2H, H_2O), 7.20m, 7.35m, 7.55m, 7.98m (15H, C_6H_5 (L^1)). ^{13}C-NMR ($CDCl_3$): After acquiring 1000 cycles, the spectrum exhibits the same signals found in the spectrum of **7**. ^{119}Sn-NMR ($CDCl_3$): δ +146.6, +151.7.

Compounds **2**–**6** were obtained similarly.

4.2.2. [Sn^{n}Bu$_3$(L^1)(H$_2$O)] (2)

Yield: 97%, m.p. 69–70 °C. Anal. Found: C, 62.85; H, 7.02; N, 4.36. Calc. for $C_{34}H_{44}N_2O_3Sn$: C, 63.08; H, 6.85; N, 4.33%. FW 647. Molecular weight ($CHCl_3$, 40 °C, c (mol kg^{-1} solvent) = 0.9×10^{-2} M), MW = 500 (r = MW/FW = 0.77); ($CHCl_3$, 40 °C, $c = 2.4 \times 10^{-2}$ M), MW = 531 (r = 0.82). Conductivity (CH_2Cl_2, c (mol l^{-1}) = 1.0×10^{-3} M), Λ_M (Ω^{-1} cm^2 mol^{-1}) = 0.2; (DMSO, $c = 0.6 \times 10^{-3}$ M), Λ_M = 14.5. IR (Nujol, cm^{-1}): ν(H_2O) 3240br; ν(H_2O) 1648m; ν(C=O) 1598vs (br); ν(Sn–O) 460m, 412m, 390vs; ν(Sn–C) 627m, 509vs. ^{1}H-NMR ($CDCl_3$): δ 0.90t, 0.95t, 1.35m, 1.65m (27H, Sn-n–C_4H_9), 2.25s (br) (2H, H_2O), 7.10m, 7.20d, 7.35d, 7.45m, 7.95d (15H, C_6H_5 (L^1)). ^{13}C-NMR ($CDCl_3$): δ 13.7, 19.5br (^1J(Sn–^{13}C) = 256 Hz, Sn–^{n}*Bu*), 26.1 (J(Sn–^{13}C) = 86 Hz, s, Sn–^{n}*Bu*), 27.1 (J(Sn–^{13}C) = 45 Hz, s, Sn–^{n}*Bu*), 27.3, 27.8 (^2J(Sn–^{13}C) = 12.9 Hz, s, Sn–^{n}*Bu*), 29.3 (^1J(Sn–^{13}C) = 555 Hz, s, Sn–^{n}*Bu*), 103.3 (s, C_4), 121.2, 122.4, 125.7, 126.2, 127.4, 127.5, 127.6, 128.0, 128.6, 128.9, 129.0, 129.3, 130.1, 130.9, 131.3, 133.6, 133.8, 138.1, 138.4, 138.6, 139.3 (s, C_{arom} of C_6H_5 (L^1)), 151.9, 152.9 (s, C_3), 161.2, 163.5 (s, C_5), 191.5 (s, *C*O). ^{119}Sn-NMR ($CDCl_3$): δ +124.7.

4.2.3. [SnPh$_3$(L^1)] (3)

Yield: 73%, m.p. 90–92 °C. Anal. Found: C, 69.40; H, 4.50; N, 3.86. Calc. for $C_{40}H_{30}N_2O_2Sn$: C, 69.69; H, 4.39; N, 4.06%. FW 689. Molecular weight ($CHCl_3$, 40 °C, c (mol kg^{-1} solvent) = 1.6×10^{-2} M), MW = 627 (r = MW/FW = 0.91). Conductivity (CH_2Cl_2, c (mol l^{-1}) = 0.6×10^{-3} M), Λ_M (Ω^{-1} cm^{-2} mol^{-1}) = 0.2; (DMSO, $c = 0.7 \times 10^{-3}$ M), Λ_M = 4.9. IR (Nujol, cm^{-1}): ν(C=O) 1595vs (br); ν(Sn–O) 449vs, 422sh, 407w; ν(Sn–C) 263s, 233s. ^{1}H-NMR ($CDCl_3$): δ 6.95m, 7.10m, 7.35m, 7.70m, 8.08d (15H, Sn–C_6H_5, 15H, C_6H_5 (L′)). ^{13}C-NMR ($CDCl_3$): δ 103.7 (s, C_4), 120.9br, 126.3, 127.4, 127.6, 127.8, 128.2, 128.8, 129.5, 131.6, 133.1, 135.4, 136.5, 137.2, 138.0, 148.1 (s, C_{arom} of Sn–*Ph* and C_6H_5 (L^1)), 153.0 (s, C_3), C_5 not observed, 191.5 (s, *C*O). ^{119}Sn-NMR ($CDCl_3$): δ −132.0, −47.7.

4.2.4. [SnMe$_3$(L^2)(H$_2$O)] (4)

Yield: 42%, m.p. 107–110 °C. Anal. Found: C, 52.56; H, 5.22; N, 6.23. Calc. for $C_{20}H_{24}N_2O_3Sn$: C, 52.32; H, 5.27; N, 6.10%. FW 459. Molecular weight ($CHCl_3$, 40 °C, c (mol kg^{-1} solvent) = 1.1×10^{-2} M), MW = 326 (r = MW/FW = 0.71). Conductivity (CH_2Cl_2, c (mol l^{-1}) = 0.9×10^{-3} M), Λ_M (Ω^{-1} cm^2 mol^{-1}) = 0.4; (DMSO, $c = 1.3 \times 10^{-3}$ M), Λ_M = 8.7. IR (Nujol, cm^{-1}): ν(H_2O) 3320br; ν(H_2O) 1650m; ν(C=O) 1619vs (br); ν(Sn–O) 444sh, 431s, 424sh; ν(Sn–C) 553m. ^{1}H-NMR ($CDCl_3$): δ 0.62s ($^2J(^{117/119}Sn–^1H) = 57.5$ Hz), 0.67s ($^2J(^{119/117}Sn–^1H) = 56.6$) (9H, Sn–C$H_3$), 2.02s, 2.10s (3H, C$H_3$(C=O)(L^2)), 2.20s (br) (2H, H_2O), 7.12m, 7.48m, 7.95m (10H, C_6H_5 (L^2)). ^{13}C-NMR ($CDCl_3$) after acquiring 1000 cycles the spectrum exhibits some signals found in the spectrum of **10** + small signals due to **4**: δ 8.9 ($^1J(^{119}Sn–^{13}C) = 947$ Hz, $^1J(^{117}Sn–^{13}C) = 906$ Hz) (s, Sn–*C*H$_3$), 28.1 [6], 26.8 [1] (s, *C*H$_3$(C=O)(L^2)), 104.6 (s, C_4), 121.3, 125.8, 126.8, 128.4, 128.9, 129.4, 134.5, 138.3 (s, C_{arom} of C_6H_5 (L^2)), 153.0 (s, C_3), 161.6 (s, C_5), 194.0 (s, *C*O). ^{119}Sn-NMR ($CDCl_3$): δ +131.2, +135.4.

4.2.5. 3.2.5. [Sn^{n}Bu$_3$(L^2)(H$_2$O)] (5)

Yield: 55%, oil at r.t. Anal. Found: C, 59.64; H, 7.36; N, 4.43. Calc. for $C_{29}H_{42}N_2O_3Sn$: C, 59.51; H, 7.23; N, 4.79%. FW 585. Molecular weight ($CHCl_3$, 40 °C, c (mol kg^{-1} solvent) = 0.8×10^{-2} M), MW = 480 (r = MW/FW = 0.82). Conductivity (CH_2Cl_2, c (mol l^{-1}) = 1.1×10^{-3} M), Λ_M (Ω^{-1} cm^2 mol^{-1}) = 0.3; (DMSO, $c = 1.9 \times 10^{-3}$ M), Λ_M = 11.9. IR (Nujol, cm^{-1}): ν(H_2O) 3260br; ν(H_2O) 1648m; ν(C=O) 1620vs (br); ν(Sn–O) 455s, 407s; ν(Sn–C) 615m. ^{1}H-NMR ($CDCl_3$): δ 0.92t, 0.98t, 1.32m, 1.62m (27H, Sn-n–C_4H_9), 1.95s, 2.00s (3H, CH_3(C=O)(L^2)), 2.22s (br) (2H, H_2O), 7.25t, 7.44m, 7.88d (10H, C_6H_5 (L^2)). ^{13}C-NMR ($CDCl_3$): δ 13.6, 26.2, 27.5, 27.7, 28.0, 29.1 (s, Sn–^{n}*Bu*), 27.2, 28.4 (s, *C*H$_3$(C=O)(L^2)), 103.4 (s, C_4), 121.5, 122.8, 126.2, 126.5, 127.2, 127.4, 127.8, 128.1, 128.5, 128.9, 129.1, 129.3, 130.4, 130.7, 131.2, 133.3, 133.6, 138.4, 138.5, 138.8, 139.5 (s, C_{arom} of C_6H_5 (L^2)), 152.4, 153.4 (s, C_3), 162.6, 163.8 (s, C_5), 192.3 (s, *C*O). ^{119}Sn-NMR ($CDCl_3$): δ +103.8.

4.2.6. [SnPh$_3$(L^2)] (6)

Yield: 58%, m.p. 170–173 °C. Anal. Found: C, 67.25; H, 4.64; N, 4.46. Calc. for $C_{35}H_{28}N_2O_2Sn$: C, 67.01; H, 4.50; N, 4.47%. FW 627. Molecular weight ($CHCl_3$, 40 °C, c (mol kg^{-1} solvent) = 0.9×10^{-2} M), MW = 459 (r = MW/FW = 0.73) ($CHCl_3$, 40 °C, $c = 2.3 \times 10^{-2}$ M), MW = 519 (r = 0.83). Conductivity (CH_2Cl_2, c (mol l^{-1}) = 0.9×10^{-3} M), Λ_M (Ω^{-1} cm^2 mol^{-1}) = 0.42; (DMSO, $c = 0.6 \times 10^{-3}$ M), Λ_M = 16.9. IR (Nujol, cm^{-1}): ν(C=O) 1606vs (br); ν(Sn–O) 466m, 451vs; ν(Sn–C) 256s, 237s. ^{1}H-NMR ($CDCl_3$): δ 2.20s (3H, CH_3(C=O)(L^2)), 7.22d, 7.38m,

7.55m, 7.68m, 7.85d (15H, Sn–C_6H_5, 10H, C_6H_5 (L^2)). ^{13}C-NMR ($CDCl_3$): δ 27.6, 28.3 (s, CH_3(C=O)(L^2)), 104.4 (s, C_4), 122.7, 126.2, 126.6, 128.4, 128.5, 128.7, 128.9, 129.3, 129.4, 129.5, 134.1, 137.0 (s, C_{arom} of Sn–*Ph* and C_6H_5 (L^2)), 152.1, 153.0 (s, C_3), 160.4, 161.2 (s, C_5), 195.3 (s, *C*O). ^{119}Sn-NMR ($CDCl_3$): δ −180.7.

In the case of derivatives **2**, **3**, **5** and **6** the following alternative synthesis can be used (the example applies to compound **3**):

A toluene solution (30 ml) of $(Ph_3Sn)_2O$ (1.0 mmol, 716 mg) was added to a toluene solution (30 ml) of the proligand L^1H (2.0 mmol, 680 mg), and the reaction mixture was refluxed for about 2 h. After removing the solvent under reduced pressure in a rotary evaporator, thick oil was obtained. This was treated with Et_2O and petroleum ether, and a pale yellow solid was formed. This was recrystallized from a toluene/petroleum ether mixture and shown to be compound **3**.

*4.2.7. [$SnMe_2(L^1)_2$] (**7**)*

To a MeOH solution (30 ml) of L^1H (2 mmol) KOH (2 mmol) and Me_2SnCl_2 (1 mmol) was added and a precipitate was formed immediately. The mixture was stirred overnight and the precipitate was then filtered, washed with MeOH (ca. 10 ml) and dried under reduced pressure at r.t. This was recrystallized from chloroform–MeOH. Yield: 81%, m.p. 215–218 °C. Anal. Found: C, 66.45; H, 4.51; N, 6.83. Calc. for $C_{46}H_{36}N_4O_4Sn$: C, 66.77; H, 4.39; N, 6.77%. FW 827. Conductivity (CH_2Cl_2, c (mol l^{-1}) = 0.6×10^{-3} M), Λ_M (Ω^{-1} cm^2 mol^{-1}) = 0.2; (DMSO, $c = 0.9 \times 10^{-3}$ M), Λ_M = 7.7. IR (Nujol, cm^{-1}): ν(C=O) 1600vs (br); ν(Sn–O) 455s, 409sbr; ν(Sn–C) 590m, 544s. ^{1}H-NMR ($CDCl_3$): δ 1.12s [5] ($^2J(^{119}Sn–^1H)$ = 101.5 Hz, $^2J(^{119}Sn–^1H)$ = 98.5 Hz), 1.24s [1] (6H, Sn–CH_3), 6.95–7.20m, 7.30–7.40m, 8.05d (30H, C_6H_5 (L^1)). ^{13}C-NMR ($CDCl_3$): δ 9.1 ($^1J(^{119}Sn–^{13}C)$ = 928 Hz, $^1J(^{117}Sn–^{13}C)$ = 885 Hz) (s, Sn–*Me*), 103.0 (s, C_4), 121.4, 125.9, 126.2, 127.5, 127.6, 127.7, 129.0, 129.4, 131.4, 133.5, 138.0, 138.4 (s, C_{arom} of Sn–C_6H_5 and C_6H_5 (L^1)), 153.0 (s, C_3), 163.2 (s, C_5), 191.2 (s, *C*O). ^{119}Sn-NMR ($CDCl_3$): δ −99.5, −319.7.

Compounds **8**–**12** were obtained similarly.

*4.2.8. [Sn^n$Bu_2(L^1)_2$] (**8**)*

Yield: 75%, m.p. 65–66 °C. Anal. Found: C, 68.73; H, 5.57; N, 6.21. Calc. for $C_{52}H_{48}N_4O_4Sn$: C, 68.51; H, 5.31; N, 6.15%. FW 912. Molecular weight ($CHCl_3$, 40 °C, c (mol kg^{-1} solvent) = 0.9×10^{-2} m), MW = 784 (r = MW/FW = 0.86) ($CHCl_3$, 40 °C, $c = 1.5 \times 10^{-2}$ m), MW = 839 (r = 0.92). Conductivity (CH_2Cl_2, c (mol l^{-1}) = 0.8×10^{-3} M), Λ_M (Ω^{-1} cm^2 mol^{-1}) = 0.3; (DMSO, $c = 0.6 \times 10^{-3}$ M), Λ_M = 5.3. IR (Nujol, cm^{-1}): ν(C=O) 1594vs (br); ν(Sn–O) 450m, 420sh, 408s; ν(Sn–C) 617m, 516s. ^{1}H-NMR ($CDCl_3$): δ 0.75m, 0.90m, 1.25–1.50m, 1.65–1.90m (18H, Sn-n-C_4H_9), 6.95–7.20m, 7.30–7.50m, 7.60m, 7.90dbr, 8.10dbr (30H, C_6H_5 (L^1)). ^{13}C-NMR ($CDCl_3$): δ 13.7, 26.2, 27.3 (^2J(Sn–^{13}C) = 24 Hz, Sn–^{n}*Bu*), 29.2 (^1J(Sn–^{13}C) = 650 Hz, Sn–^{n}*Bu*), 103.1 (s, C_4), 121.2, 126.0, 127.5, 127.7, 127.9, 129.0, 129.4, 131.5 (s, C_{arom} of C_6H_5 (L^1)), 152.7, 153.1 (s, C_3), 163.1 (s, C_5), 187.9br, 189.6br, 191.8 (s, *C*O). ^{119}Sn-NMR ($CDCl_3$): δ −133.9, −355.8.

*4.2.9. [$SnPh_2(L^1)_2$] (**9**)*

Yield: 78%, m.p. 152–155 °C. Anal. Found: C, 70.55; H, 4.38; N, 5.53. Calc. for $C_{56}H_{40}N_4O_4Sn$: C, 70.68; H, 4.24; N, 5.89%. FW 952. Molecular weight ($CHCl_3$, 40 °C, c (mol kg^{-1} solvent) = 0.8×10^{-2} m), MW = 738 (r = MW/FW = 0.77) ($CHCl_3$, 40 °C, $c = 2.0 \times 10^{-2}$ m), MW = 794 (r = 0.83). Conductivity (CH_2Cl_2, c (mol l^{-1}) = 0.7×10^{-3} M), Λ_M (Ω^{-1} cm^2 mol^{-1}) = 0.1; (DMSO, $c = 0.4 \times 10^{-3}$ M), Λ_M = 5.6. IR (Nujol, cm^{-1}): ν(C=O) 1595vs (br); ν(Sn–O) 448sbr; ν(Sn–C) 267m, 246m. ^{1}H-NMR ($CDCl_3$): δ 6.80–6.90m, 6.95–7.20m, 7.30–7.50m, 7.70mbr, 8.00mbr (40H, Sn–C_6H_5 and C_6H_5 (L^1)). ^{13}C-NMR ($CDCl_3$): δ 103.9 (s br, C_4), 120.4, 121.3, 121.9, 126.5, 127.2, 127.6, 127.6, 128.0, 128.2, 128.4, 128.6, 128.9, 129.1, 129.7, 129.9, 130.1, 130.2, 131.8, 132.6, 132.7, 132.9, 135.7, 136.2, 136.5, 137.3, 137.7, 138.2, 148.3 (s, C_{arom} of Sn–*Ph* and C_6H_5 (L^2)), 153.2 (s, C_3), 164.8 (s, C_5), 191.8 (s, *C*O). ^{119}Sn-NMR ($CDCl_3$, 295 K): δ −276.5, −482.5, −490.0. ^{119}Sn-NMR ($CDCl_3$, 328 K): δ −276.5, −486br.

*4.2.10. [$SnMe_2(L^2)_2$] (**10**)*

Yield: 67%, m.p. 244–247 °C. Anal. Found: C, 61.23; H, 4.73; N, 8.07. Calc. for $C_{36}H_{32}N_4O_4Sn$: C, 61.48; H, 4.59; N, 7.97%. FW 703. Molecular weight ($CHCl_3$, 40 °C, c (mol kg^{-1} solvent) = 0.7×10^{-2} m), MW = 537 (r = MW/FW = 0.76) ($CHCl_3$, 40 °C, $c = 1.3 \times 10^{-2}$ m), MW = 556 (r = 0.79) ($CHCl_3$, 40 °C, $c = 1.6 \times 10^{-2}$ m), MW = 571 (r = 0.81) ($CHCl_3$, 40 °C, $c = 1.7 \times 10^{-2}$ m), MW = 600 (r = 0.85) ($CHCl_3$, 40 °C, $c = 1.9 \times 10^{-2}$ m), MW = 685 (r = 0.97). Conductivity (CH_2Cl_2, c (mol l^{-1}) = 0.7×10^{-3} M), Λ_M (Ω^{-1} cm^2 mol^{-1}) = 0.1; (DMSO, $c = 0.6 \times 10^{-3}$ M), Λ_M = 12.5. IR (Nujol, cm^{-1}): ν(C=O) 1613vs (br); ν(Sn–O) 444w, 413m; ν(Sn–C) 587s. UV–vis: λ (nm) (ε, mol l^{-1} cm^{-1}) ($CHCl_3$): 242 (55 900). ^{1}H-NMR ($CDCl_3$): δ 0.95s [6] ($^2J(^{119}Sn–^1H)$ = 102.7 Hz, $^2J(^{119}Sn–^1H)$ = 98.2 Hz), 1.15s [1] (6H, Sn–CH_3), 1.98s [6], 2.05s [1], 2.22s [1] (6H, CH_3(C=O)(L^2)), 7.15–7.30m, 7.40–7.52m, 7.95d (20H, C_6H_5 (L^2)). ^{13}C-NMR ($CDCl_3$): δ 9.0 ($^1J(^{119}Sn–^{13}C)$ = 948 Hz, $^1J(^{117}Sn–^{13}C)$ = 906 Hz) (s, Sn–*Me*), 28.3 (s, C_3–*Me*), 104.8 (s, C_4), 121.5, 125.9, 128.6, 129.1, 129.6, 134.7, 138.5 (s, C_{arom} of C_6H_5 (L^2)), 153.2 (s, C_3), 161.8 (s, C_5), 194.2 (s, *C*O). ^{119}Sn-NMR ($CDCl_3$): δ −100.7, −321.0.

Table 2
Crystal data and structure refinement parameters for (1,3-diiphenyl-4-benzoyl-pyrazolon-5-ato)triphenyltin(IV)

Empirical formula	$C_{40}H_{30}N_2O_2Sn$
Formula weight	689.38
Temperature (K)	298
Wavelength (Å) (graph monochr)	Mo–K_α
Crystal habit	Bloc
Crystal size (mm)	$0.35 \times 0.20 \times 0.20$
Crystal system	Monoclinic
Space group	$P2_1/c$
Crystal color	Pale-yellow
Unit cell dimensions	
a (Å)	10.674(5)
b (Å)	29.452(14)
c (Å)	11.054(5)
β (°)	109.31(1)
V (Å^3)	3279(3)
Z	4
D_{calc} (g cm^{-3})	1.397
$2\theta_{max}$ (°)	56
μ (mm$_)^{-1}$	0.82
Scan speed (° min^{-1})	2.3
Transmission factors	0.90/1.00
Scan range (°)	1.0
Scan mode	ω
Reflections collected	7147
Unique reflections	5725
Refined reflections [$F > 5\sigma(F)$)]	3559
Refined parameters	361
R, [a] R_w	0.050, 0.056
S [b]	0.90

[a] $R(F) = \Sigma\|(F_o - F_c)\|/\Sigma F_o$.
[b] $S = [\Sigma\{w(F_o^2 - F_c^2)^2\}/(n-p)]^{0.5}$, n = no. of data and p = no. of refined parameters.

4.2.11. [Sn^{n}Bu$_2$(L^2)$_2$] (**11**)

Yield: 70%, m.p. 168–171 °C. Anal. Found: C, 63.84; H, 5.72; N, 7.10. Calc. for $C_{42}H_{44}N_4O_4Sn$: C, 64.06; H, 5.63; N, 7.11%. FW 787. Conductivity (CH_2Cl_2, c (mol l^{-1}) = 0.9×10^{-3} M), Λ_M (Ω^{-1} cm^2 mol^{-1}) = 0.3; (DMSO, $c = 0.6 \times 10^{-3}$ M), Λ_M = 9.2. IR (Nujol, cm^{-1}): ν(C=O) 1610vs (br); ν(Sn–O) 459m, 446sh, 428s; ν(Sn–C) 593m. UV–vis: λ (nm) (ε, mol l^{-1} cm^{-1}) ($CHCl_3$): 236 (57 000). ^{1}H-NMR ($CDCl_3$): δ 0.82t [6], 0.95t [1], 1.35mbr, 1.60m [6], 1.78m [1] (18H, Sn-*n*–C_4H_9), 1.98s [6], 2.05s [1], 2.22s [1] (6H, CH_3(C=O)(L^2)), 7.15–7.30m, 7.40–7.55m, 7.96dd (30H, C_6H_5 (L^2)). ^{13}C-NMR ($CDCl_3$): δ 28.3 (s, CH$_3$(C=O)(L^2)), 13.9, 26.3 ($^2J(^{119/117}Sn–^{13}C) = 44$ Hz), 27.2 ($^3J(^{119}Sn–^{13}C) = 127$ Hz, $^3J(^{117}Sn–^{13}C) = 121$ Hz), 28.9 ($^1J(^{119}Sn–^{13}C) = 870$ Hz, $^1J(^{117}Sn–^{13}C) = 830$ Hz) (s, Sn–^{n}*Bu*), 105.0 (s, C_4), 121.3, 125.8, 128.6, 129.1, 129.6, 134.9, 138.7 (s, C_{arom}), 153.1 (s, C_3), 162.0 (s, C_5), 191.5 (s, CO). ^{119}Sn-NMR ($CDCl_3$): δ −132.1, −355.9.

4.2.12. [SnPh$_2$(L^2)$_2$] (**12**)

Yield: 65%, m.p. 180–183 °C. Anal. Found: C, 66.40; H, 4.53; N, 6.85. Calc. for $C_{42}H_{36}N_4O_4Sn$: C, 66.77; H, 4.39; N, 6.77%. FW 827. Conductivity (CH_2Cl_2, c (mol l^{-1}) = $1.0 \cdot 10^{-3}$ M), Λ_M (Ω^{-1} cm^2 mol^{-1}) = 0.1; (DMSO, $c = 0.7 \times 10^{-3}$ M), Λ_M = 5.4. IR (Nujol, cm^{-1}): ν(C=O) 1614vs (br); ν(Sn–O) 455m, 447s, 426s; ν(Sn–C) 243s. UV–vis: λ (nm) (ε, mol l^{-1}cm^{-1}) ($CHCl_3$): 232 (36 200), 250 (29 650), 282 (20 100). ^{1}H-NMR ($CDCl_3$): δ 1.95sbr (6H, CH_3(C=O)(L^2)), 7.15–7.55mbr, 7.75mbr, 7.90–8.10mbr (30H, Sn–C_6H_5 and C_6H_5 (L^2)). ^{13}C-NMR ($CDCl_3$): δ 27.6 (s, CH$_3$(C=O) (L^2)), 105.6 (s, C_4), 120.7, 121.2br, 126.2, 127.6, 128.4, 128.8, 128.9, 129.1, 129.3, 133.9, 135.4, 138,0, 147.9 (s, C_{arom} of Sn–C_6H$_5$ and C_6H$_5$ (L^2)), 153.0 (s, C_3), 162.9 (s, C_5), 195.3 (s, CO). ^{119}Sn-NMR ($CDCl_3$): δ −280.1, −484.3.

4.3. Crystallographic study of [SnPh$_3$(L^1)] (**3**)

A preliminary study was performed with a Weissenberg Camera to determine the cell parameters and the monoclinic space group. A P2$_1$ Syntex diffractometer was used for measuring the cell constants and for data collection; a set of 25 reflections (with high theta angle) was used to obtain refined cell parameters. A summary of crystal data together with details of data collection and structure solution is given in Table 2.

No decay was observed after monitoring the three reflections (taken every 100 reflections). Slight absorption effect was found after a psi-scan and so data were corrected for absorption as well as for Lorentz and polarization effects [24]. The molecular structure was solved using the Patterson–Fourier method using the CAOS program [25].

Subsequent calculations were performed as follows: refinement based on the minimization of the function $\Sigma w(|F_o| - |F_c|)^2$ 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 [26]. 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 the final refinement convergence was reached. Atomic scattering factors and anomalous dispersion terms were taken from the literature [27].

5. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 169093 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Atomic coordinates; anisotropic displacement parameters; full list of bond distances and angles; and F_o/F_c listing is available from F. Caruso on request.

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