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Novel bis(β-diketonato)diorganotin(IV) derivatives containing bulky 4-acyl-5-pyrazolonato ligands: Influence of the steric hindrance of the acyl moiety on the solid state structures of tin complexes and their behaviour in solution

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ABSTRACT

New $(Q)_2SnR_2$ derivatives (HQ in general; in detail: HQ^{CHPh_2} = 4-diphenylacetyl-3-methyl-1-phenyl-5-pyrazolone; HQ^{Bn} = 3-methyl-1-phenyl-4-phenylacetyl-5-pyrazolone; HQ^{naph} = 3-methyl-4-naphthoyl-1-phenyl-5-pyrazolone; R = CH_3, C_2H_5, C_6H_{11}, *n*- and *t*-C_4H_9, C_6H_5,) have been synthesised and characterised by analytical and spectral techniques. Variable temperature NMR studies of $(Q^{CHPh_2})_2SnR_2$ derivatives (R = CH_3 and C_2H_5) in chlorohydrocarbon solvents indicate a fluxional behaviour, with rapid interconversion between six- and five-coordinate species, the latter containing a bidentate acylpyrazolonate and a monodentate one. The X-ray crystal structures of the diorganotin(IV) derivatives $(Q^{CHPh_2})_2SnMe_2$, $(Q^{CHPh_2})_2SnEt_2$, $(Q^{Bn})_2SnMe_2$ and $(Q^{naph})_2SnBu^n_2$, inclusive of a representative of each Q^x family, show the metal centres in a skewed *trans* octahedral configuration. The 4-acyl moiety of the β-diketonate donor exerts a steric effect which is correlated to structural behaviour in the solid and solution state. A solid state ^{119}Sn CPMAS NMR study of the $(Q^{Bn})_2SnR_2$ (R = CH_3, C_2H_5, *t*-C_4H_9 and C_6H_5) complexes shows a marked deshielding effect and upfield movement of the ^{119}Sn isotropic chemical shift (δ_{iso}) through this series. The ^{119}Sn chemical shift spans (Ω) are the largest reported for directly oxo-coordinated Sn(IV) systems, although the markedly reduced Ω value for the $(Q^{Bn})_2SnPh_2$ complex may be indicative of a *cis* octahedral coordination, in contrast to the *trans* octahedral coordination characterising the other complexes of this suite.

1. Introduction

Six-coordinated tin(IV) and organotin(IV) complexes of *O,O′*-bidentate donors which can form six-membered chelate rings, with *cis* or *trans* octahedral configurations, are prominent in the literature [1]. Current interest arises from reports indicating tin(IV) complex activity against a wide variety of viruses, bacteria and tumours [2]. Much work has been done to correlate the geometries of organotin(IV) adducts of the type $[R_2SnX_2L_2]$ (R = alkyl or aryl group; X = halide; L = N- or O-donor ligand) with their effectiveness as antitumour agents [3]. Those with shorter Sn–L bond distances and *trans*-diethyl or *cis*-dichloro groups are the more active, the general mechanism involving pre-dissociation of the bidentate ligand as a crucial step in the formation of an Sn–DNA complex [4]. Several structural studies are available on diorgano- [5] and dihalotin(IV) [6] derivatives containing β-diketonates and monothio-β-diketonates showing that alkyl groups on the tin generally occupy *trans* positions [5] whereas the halides adopt *cis* positions [5c,6], the latter also exhibiting high *in vivo* activity against some tumours [6c]. We are currently interested in tin complexes of 4-acyl-5-pyrazolones, a family of asymmetric β-diketonates having the chelating moiety fused to a pyrazole ring; these are widely used as pigments for dyes [7], as metal extractants from acidic solutions [8], and for trace element spectrophotometric determinations [9]. Our strategy in this research has been to synthesise new donors with different substituents R^1, R^2 and R^3 (Scheme 1), so as to obtain variations in electronic and steric features of the ligands, and, consequently, in the properties of their metal derivatives. Structural and spectroscopic (IR, NMR and

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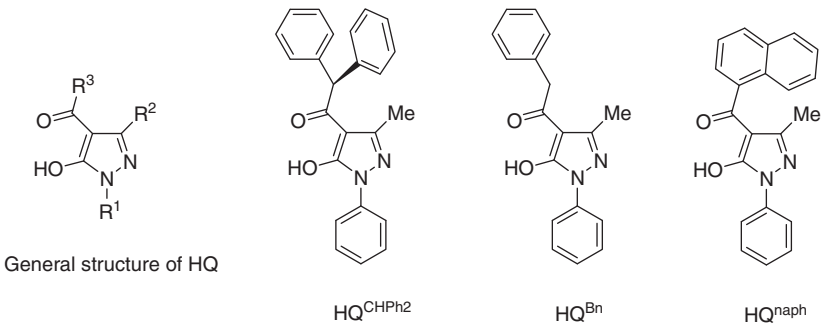


Scheme 1.

Mössbauer) data have shown that dialkyltin(IV) complexes generally adopt highly distorted *trans* octahedral geometries, with two sets of Sn–O bond distances, and C–Sn–C angles less than 160° [10]. By contrast, diaryltin(IV) complexes can exist in the solid and in solution states as mixtures of *cis* or *trans* isomers; for these, X-ray structures show less distorted C–Sn–C angles (in the range of 165–175°), and Mössbauer data also indicate the existence in the solid state of isomers for which those angles lie in the range of 110–120° [11]. The metal–ligand interactions are generally weaker than those found for analogous acetylacetonato/tin(IV) derivatives, an interesting feature in view of their potential bio-activity. In particular, the oxygen atom of the acyl moiety [O(acyl) = Oa] is always less tightly bound than that at the 5-position of the pyrazole [O(pyrazolonato) = Op]; this feature is observed also in the case of 4-acyl-5-pyrazolonato derivatives of lead [12], uranium [13], copper [14] and mercury [15]. In a previous paper, we showed that the use of R^3 = methyl considerably enhances the solubility in water of the metal derivatives, a useful property in view of possible biological applications [10g]. In this work, we report the synthesis and characterisation of a series of diorganotin(IV) complexes with new functionalized 4-acyl-5-pyrazolones (Scheme 1), having in the R^3 position a more sterically hindered group relative to the donors previously employed, with the goal of modifying the structural behaviour of the corresponding tin(IV) derivatives, both in the solid state and in solution. The crystal structures of four derivatives, representative of the R^3 = $CHPh_2$, Bn, and naphthyl families, are reported together with variable temperature NMR and solid state ^{119}Sn NMR studies.

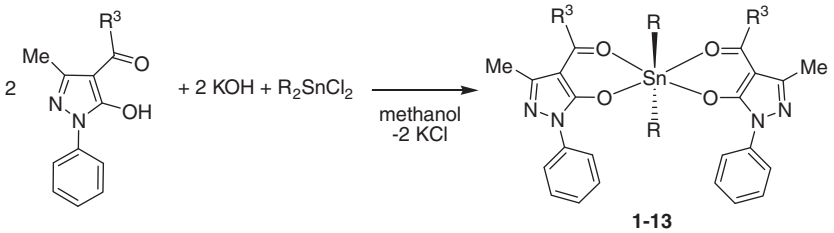
2. Results and discussion

Derivatives **1**–**13** have been synthesised from reaction between the donor HQ and the acceptor SnR_2Cl_2 in methanol in the presence of KOH base (Scheme 2).

All derivatives **1**–**13** are air and moisture stable solids, with sharp melting points, insoluble in water, alcohols, diethyl ether, and aliphatic hydrocarbons, sparingly soluble in aromatic solvents and soluble in acetone, DMSO and chlorohydrocarbon solvents, where they show a monomeric nature or, at least in dilute solutions, some limited partial dissociation, the ratio between experimental and theoretical molecular weight being in the range 0.70–0.90. They are non-electrolytes in the same solvents.

IR data show shifts to lower frequencies of ν(C=O) (from 1640 to 1600 cm^{-1}) and the disappearance of the broad band at 2700 cm^{-1} due to intramolecular ν(O–H···O) of the ligand upon coordination, thus indicating chelation of the donor through both carbonyl groups of the monoanionic deprotonated form. In the far-IR region the presence of both ν_s(Sn–C) and ν_{as}(Sn–C), and of several ν(Sn–O) bands (Fig. 1) is consistent with distortion from octahedral geometry about the tin atom, as in fact observed in the crystal structures of derivative $(Q^{CHPh_2})_2SnMe_2$, Et_2 and $(Q^{naph})_2SnBu^n{}_2$ (see below; structural section).

The broad signals at ca. 12.0 ppm due to enolic protons of the proligands in the ^{1}H NMR spectra disappear upon coordination, in accordance with coordination of the donor in monoanionic form. The integration of the signals due to the ligand and to the organotin moiety supports the 2:1 ligand to metal ratio proposed. At room temperature and in chlorohydrocarbon solution the dimethyltin(IV) derivative **1** shows unique sets of resonances for the hydrogen atoms in the Q^{CHPh_2} ligands and those of the organic groups on the tin atom, but on lowering the temperature the resonance for each chemically and magnetically equivalent group of H splits into two peaks (Fig. 2). The $^2J_{(Sn-H)}$ of the two different resonances for the $SnMe_2$ moiety (98.3 and 70.5 Hz) are consistent with the presence of two different isomers. From the Lockhart relationship [16], values of 159° and 120° for the C–Sn–C angle are obtained, typical of a *trans* skewed octahedral species and of a trigonal bipyramidal species, respectively. A variable temperature ^{1}H NMR study of the diethyltin(IV) derivative **2** shows a similar behaviour. Moreover,



1, R^3 = $CHPh_2$, R = Me
2, R^3 = $CHPh_2$, R = Et
3, R^3 = $CHPh_2$, R = Cy
4, R^3 = $CHPh_2$, R = Bu^t
5, R^3 = $CHPh_2$, R = Ph
6, R^3 = CH_2Ph, R = Me
7, R^3 = CH_2Ph, R = Et
8, R^3 = CH_2Ph, R = Cy
9, R^3 = CH_2Ph, R = Bu^t
10, R^3 = CH_2Ph, R = Ph
11, R^3 = 2-naphthyl, R = Me
12, R^3 = 2-naphthyl, R = Bu^n
13, R^3 = 2-naphthyl, R = Ph

Scheme 2.

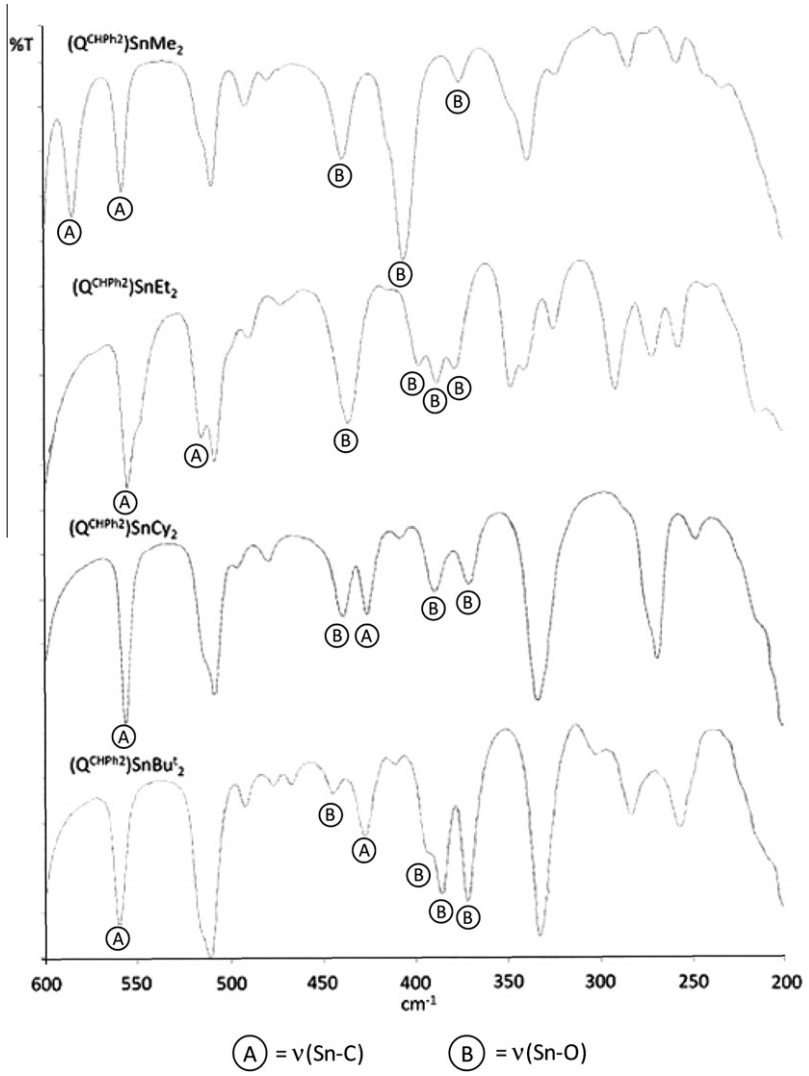


Fig. 1. Far-IR spectra of derivatives **1**–**4**.

room temperature studies of derivatives **3** and **4** display quite broad resonances. ^{119}Sn NMR spectra of **1** and **2** show a progressive broadening on cooling from 293 to 223 K.

This seems to support the view that the bis(β-diketonato)dialkyltin(IV) six-coordinate derivatives **1**–**4** of Q^{CHPh_2} exist as mixtures of isomers in chlorohydrocarbon solution (Scheme 3), this behaviour being observed here for the first time. In fact, for all previously studied acylpyrazolonates only one set of resonances (also at −90 °C) was found. This feature can be explained assuming (a) a very fast fluxionality about the tin, (b) the presence of only one *trans* isomer in solution (more likely), (c) formation of a neutral five-coordinate species, or (d) formation of an ionic four-coordinate tin complex from partial dissociation of one or both carbonyl arms of a Q ligand. The proton NMR spectra of the alkyltin(IV) derivatives **6**–**8** and **11**–**12** of Q^{Bn} and Q^{naph} display unique sets of sharp resonances both at room and low temperatures, thus indicating the presence in solution of only one isomeric species.

In ^{13}C NMR spectra of dialkyltin(IV) derivatives **1**–**3**, **6**–**8** and **10**–**11** the expected $^{n}J_{(Sn-C)}$ coupling constants have been observed, values being in the range of typical *trans*-octahedral compounds. In fact, by applying the empirical relation $\theta(C–Sn–C) = 0.178 \times |^{1}J(^{119}Sn–^{13}C)| + 14.74$, derived by Howard for octahedral dialkyltin complexes of type R_2SnCh_2 (R = alkyl, Ch = bidentate ligand) [17], the calculated C–Sn–C angle for **1**, **6** and **11** are 172°, 179° and 176° (angles calculated from this relationship have a standard error calculated as ±l2°). By contrast, ^{13}C NMR spectra of di-*tert*-butyltin(IV) derivatives **4** and **8**, and of diphenyltin(IV) derivatives **5**, **10** and **13** show broad resonances, in accordance with fluxionality between different geometrical isomers present in solution.

In our derivatives, the existence of a mixture of isomers in solution may be attributed to the effect of steric hindrance about the acyl moiety in the ligand Q^{CHPh_2}, which should destabilize one Sn–O bond. The increase of steric hindrance in the organic groups bonded to the tin atom generates an increase in the ^{119}Sn chemical shift toward lower frequencies. The effect is approximately additive, as shown in Fig. 3 [10b,c,f–h,11], presumably as consequence of increased electro-releasing properties on going from the methyl group to the *t*-butyl group, and also in accordance with crystallographic data, as seen in our previous work [10g,11].

The diphenyltin derivatives **5**, **10** and **13**, having bulky electron-releasing groups bound to the tin atom, show broad resonances in the ^{1}H NMR spectra and two sets of broad resonances in the ^{119}Sn NMR spectra, presumably due to *trans*-isomers (*syn*- and *anti*-configurations). In addition, derivative **13** also shows a resonance at −740 ppm, falling in a range typical of *cis*-dihalotin(IV) derivatives [10a,18]. We hypothesise that the large steric hindrance of the naphthyl groups in Q^{naph} ligands might require the phenyl groups

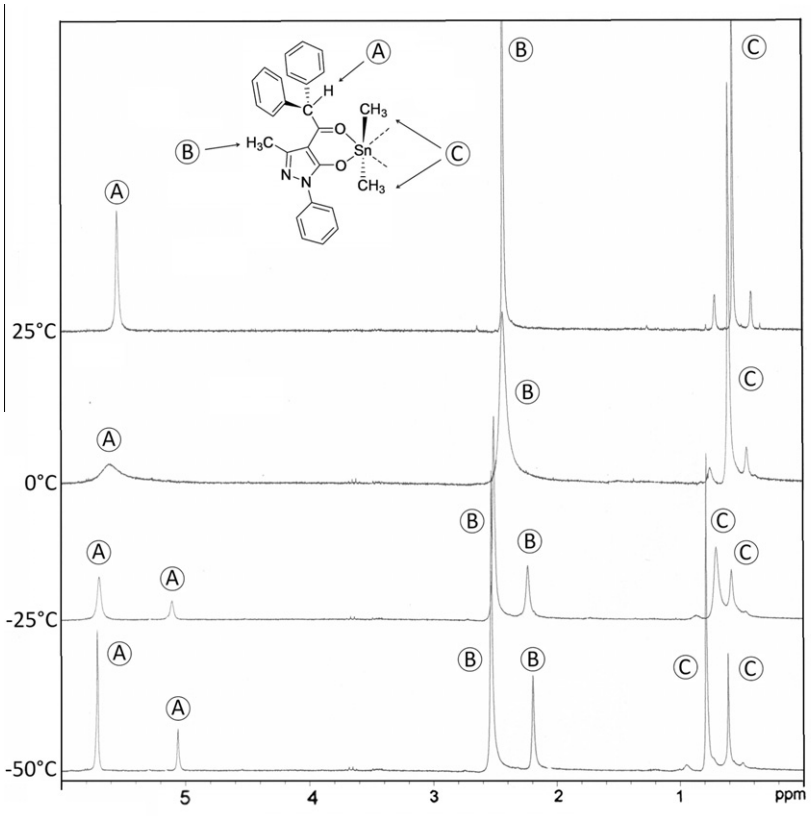
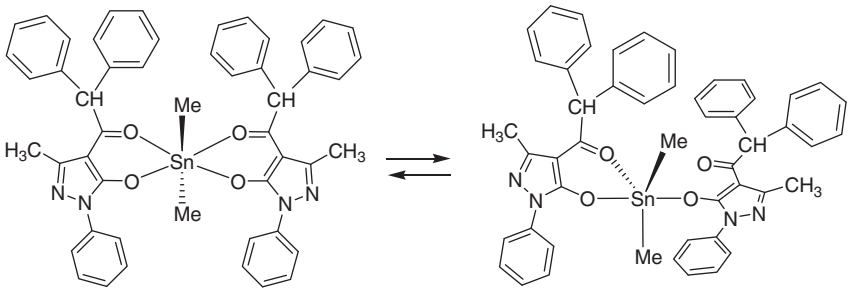


Fig. 2. Variable temperature ^{1}H NMR spectra for derivative **1**.



Scheme 3.

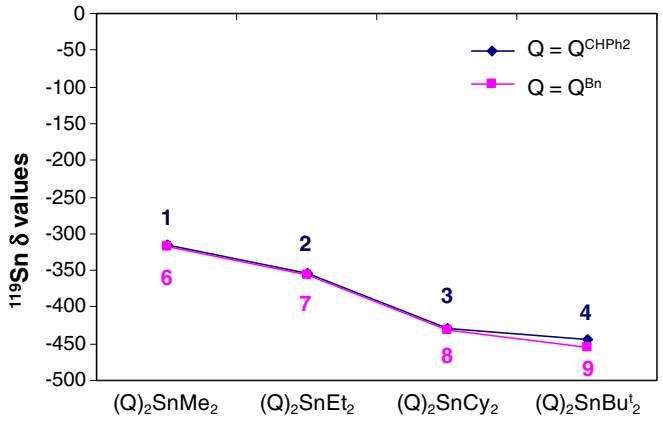
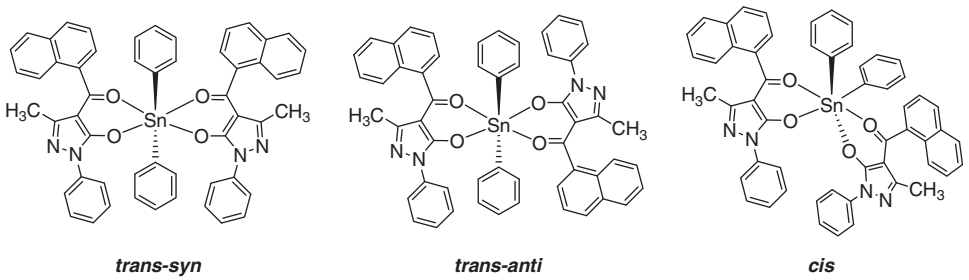


Fig. 3. Influence of steric bulk of the R groups on the ^{119}Sn NMR spectra of $(Q)_2SnR_2$ derivatives.

on the tin atom to assume a *cis*-configuration in order to reduce crowding around the metal (Scheme 4).

2.1. Structural studies

The results of the single crystal X-ray studies of $[(Q^{CHPh_2})_2SnR_2]$ (**1**: R = Me, **2**: R = Et), $[(Q^{Bn})_2SnMe_2]$ (**6**) and $[(Q^{naph})_2SnBu^n_2]$ (**12**), are consistent with a single molecule, devoid of crystallographic symmetry, comprising the asymmetric unit of each structure. The tin atoms are six-coordinate, the alkyl groups are *trans* and the organic ligands behave as *O*,*O*′-bidentates (Figs. 4–7 and Table 1). Coordination geometries are similar to those of other such *trans* $[Q_2SnR_2]$ complexes [10]. The present complexes are of particular interest, however, due to their bulky Q substituents: their impact on the molecular conformation, suggest (Figs. 4 and 5 and Table 1) the orientations of the pairs of the groups in each complex are such as to impose the adoption of approximated 2-fold symmetry for complexes **1** and **2**, having ligands Q^{CHPh_2}. This 2-fold axis is not



Scheme 4.

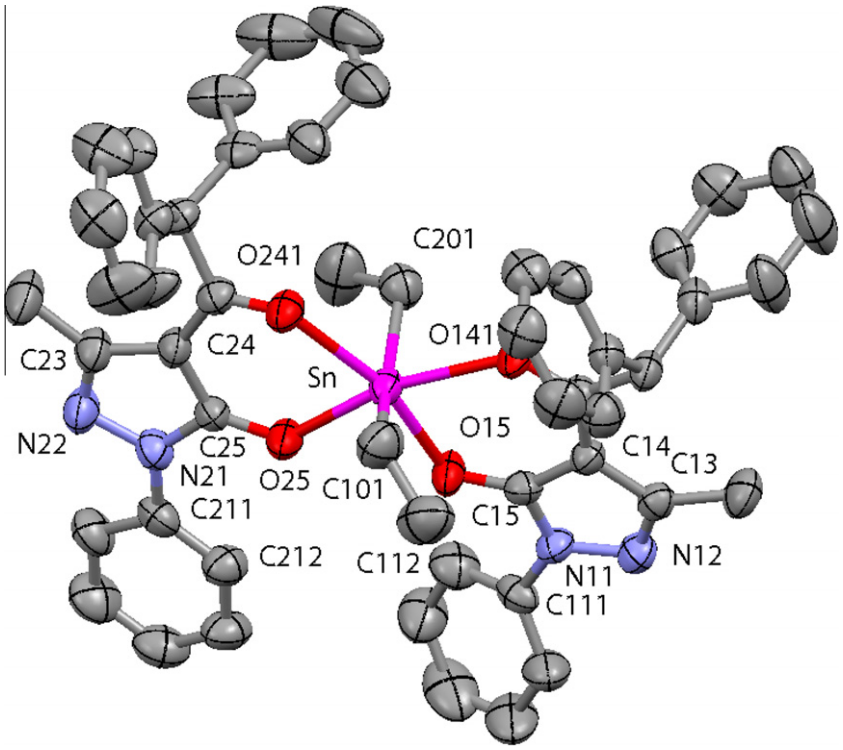


Fig. 4. Molecular projection of bis(4-diphenylacetyl-3-methyl-1-phenyl-pyrazolon-5-ato)diethyltin(IV) (2) showing coordination sphere labels (H atoms omitted). The torsion angles between Ph and the attached pyrazole rings are 10.6° (C15–N11–C111–C112) and 32.7° (C25–N21–C211–C212). Labelling is consistent with those in Figs. 5–7.

retained at the periphery of the benzyl and naphthyl complexes **6** and **12** (Fig. 7).

The crystal structures of **1**, **2**, **6**, and **12**, Figs. 4–7, show a skewed trapezoidal bipyramidal arrangement about the metal atom. This is characterised by short Sn–O(pyrazolonato) and long Sn–O(acyl) bond lengths; e.g. in the ethyl complex (**2**) they are [2.122(6) and 2.148(5) Å] and [2.324(5), 2.311(6) Å], respectively. The trend is similar for the other derivatives as seen in Table 1. In addition, the longer Sn–O(acyl) bonds form a *O*(acyl)–Sn–*O*′(acyl) bond angle much wider than *O*(pyrazolonate)–Sn–*O*′(pyrazolonate)– 116.5(2)° and 82.3(2)°, respectively, in the ethyl complex. Both carbon atoms bound to the tin tend to occupy the space left by the two *O*(acyl) moieties so that a wider *O*(acyl)–Sn–*O*′(acyl) bond angle corresponds to a smaller C–Sn–C′ bond angle. This trend is generally seen in the literature of 4-acyl-5-pyrazolonato-diorganotin compounds, the only exceptions being bis(4-benzoyl-3-methyl-1-(4-(trifluoromethyl)phenyl)-pyrazolon-5-ato)-dimethyl-tin(IV) [19] and *cis*-bis((μ_2-1,4-bis(3-methyl-5-oxy-1-phenyl-1*H*-pyrazol-4-yl)butane-1,4-dione)-di-*n*-butyl-tin(IV)) [20], which display regular octahedral arrangements with the ligand *anti*, in contrast to those of the previous compounds that are *syn*. The dihedral angles between the phenyl rings and their attached pyrazole rings are given in Table 1, as their associated torsion angles. These differ widely between ligands, ranging from 3.6(8)° to −47.4(7)° in complex **12**, susceptible to packing forces as seen in related compounds [11]. The ligand bite angle in Table 1 is within the range 80.4–82.5° similar to related compounds [11]. As mentioned earlier the complex with R^1 = p-CF_3–Ph shows the dramatic influence of the repulsion between both R^1 ligands resulting from the fluorine atoms on its structure by stabilizing an anomalous centrosymmetric arrangement. This is due to the small *O*(pyrazolonate)–Sn–*O*′(pyrazolonate) bond angle that makes both R^1 groups close enough for repulsion. In the present case, the large R^3 groups may establish a similar hindrance, although, the large space available to the acyl groups, because of a wide *O*(acyl)–Sn–*O*′(acyl) angle, may still accommodate groups as large as the Ph_2C and naphthyl in the present compounds. The crystal structures show no unexpected geometrical features. Thus, for instance, the C–Sn–C′ bond angles in the four derivatives range from 153.0(2)° to 160.00(9)° about the median value of 156° for the corresponding range 150–173° found in the literature and so we conclude that the presence of the large acyl moieties

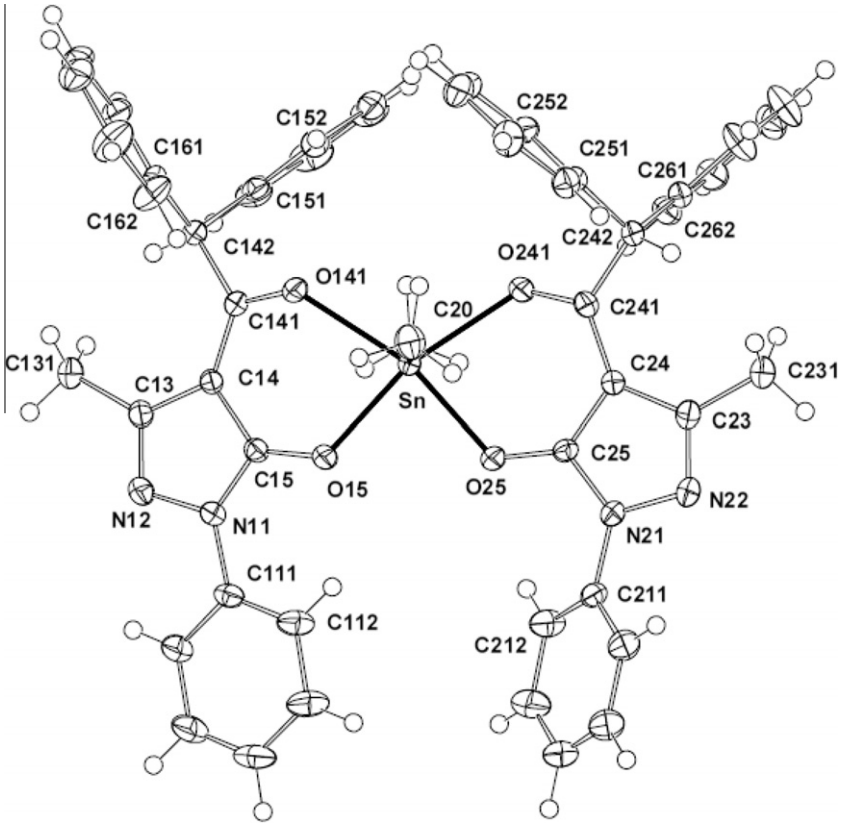


Fig. 5. Molecular projection of bis(4-diphenylacetyl-3-methyl-1-phenyl-pyrazolon-5-ato)dimethyltin(IV) (**1**) down the C–Sn–C 'line', showing the approximate 2-fold axis through the metal in the plane of the page.

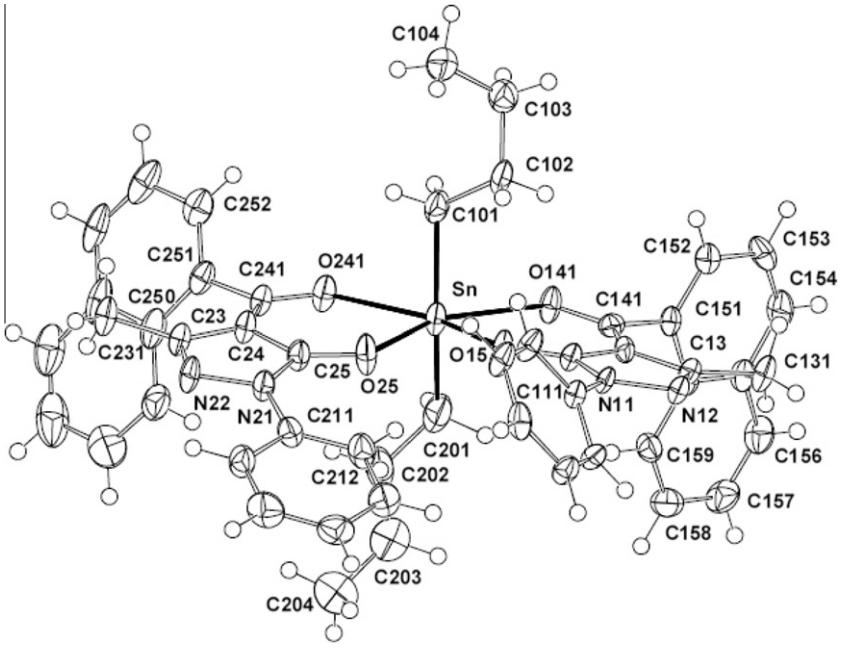


Fig. 6. Molecular projection of bis(3-methyl-4-naphthoyl-1-phenyl-pyrazolon-5-ato)di-*n*-butyltin(IV) (**12**).

does not modify substantially the coordination sphere in the solid state.

2.2. ^{119}Sn solid state NMR section

The ^{119}Sn CPMAS NMR data for the *bis*(3-methyl-1-phenyl-4-phenylacetylpyrazolon-5-ato) series $[(Q^{Bn})_2SnMe_2]$ (**6**), $[(Q^{Bn})_2Sn\text{-}Et_2]$ (**7**), $[(Q^{Bn})_2SnBu^t_2]$ (**9**) and $[(Q^{Bn})_2SnPh_2]$ (**10**) are shown in Fig. 8, and the associated ^{119}Sn chemical shift tensor parameters elucidated from these data are summarised in Table 2. For each system ^{119}Sn MAS NMR data have been acquired at MAS frequencies of 4 and 11 kHz to facilitate an accurate determination of the fundamental shift parameters $\delta_{iso,mas}$, δ_{11}, δ_{22} and δ_{33}, and subsequently the chemical shift tensor descriptors such as span Ω, skew κ, anisotropy $\Delta\delta$, and asymmetry η.

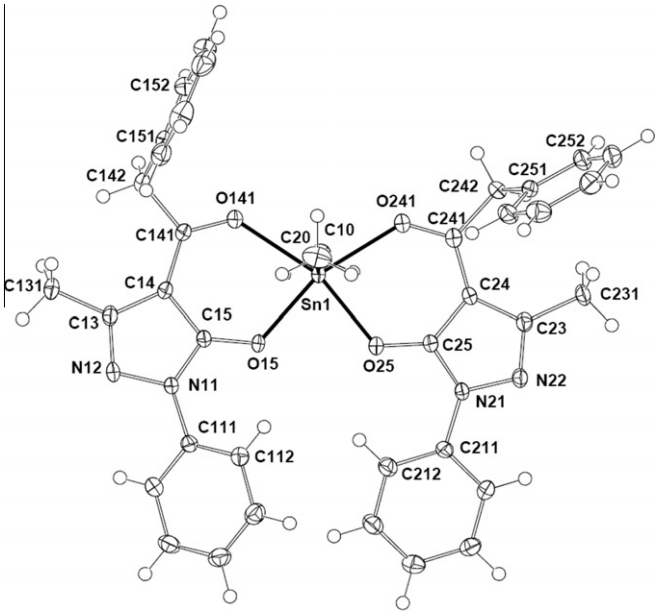


Fig. 7. Molecular projection of bis(3-methyl-1-phenyl-4-phenylacetyl-5-pyrazolon-5-ato)di-methyltin(IV) (**6**).

From Table 2 it can be observed that an excellent agreement exists between the measured isotropic chemical shift ($\delta_{iso,mas}$) and the calculated isotropic chemical shift ($\delta_{iso,calc}$), thus suggesting that the nominated positions of δ_{11}, δ_{22} and δ_{33} from each ^{119}Sn CPMAS spectrum have been determined accurately. These data are consistent with the crystallographic description of **6** above where the structural disposition of the six-coordinate tin environment (skewed trapezoidal bipyramidal arrangement) provides no apparent formal point symmetry, although the quasi-planar *O,O′*-bidentate environment and the alkyl/aromatic *trans*-substitution invokes an approximate 2-fold symmetry. This is reflected by the moderately high κ values (or moderately low η values) suggesting approximate axial symmetry. From Table 2 the measured isotropic chemical shifts $\delta_{iso,mas}$ for the series **6**, **7**, **9** and **10** exhibit a monotonic decrease from δ −316 ppm (for **6**) to δ −474 ppm (for **10**), commensurate with the decreasing electron donation (or increased deshielding) capability of the *trans*-organic substituents, considering that the ^{119}Sn nucleus possesses a negative gyromagnetic ratio ($\gamma = -10.0138 \times 10^7$ rad T^{-1} s^{-1}). Similar trends have been previously reported for Sn-*tris*(tropolonato) [21] and Sn-oxydiacetate [22] suites of complexes. The spans for complexes **6**, **7** and **9** from Table 2 of up to ~1430 ppm represent the largest Ω values for directly oxo-coordinated Sn(IV) systems [21–25], but are much smaller than reported values for 2-coordinate Sn(II) systems such as [SnC$_6$H$_3$-2,6-Trip$_2$] where Ω can exceed 4000 ppm [26]. For **10** a much reduced Ω value of 605 ppm is reported (see Table 2), which is less than half the magnitude of that measured in complexes **6**, **7** and **9**. This observation could be attributed to (i) fast phenyl rotation (on the timescale of the NMR experiment) where tensor elements δ_{11} and δ_{33} can become partially averaged, or (ii) the phenyl derivative may adopt a *cis* octahedral environment in contrast to the *trans* octahedral arrangement that characterises the other complexes of this suite.

3. Conclusions

Several diorganotin(IV) derivatives containing sterically hindered 4-acyl-5-pyrazolonate ligands have been reported and fully characterised by a combination of solid state and solutions techniques. Solution NMR data indicate that bulky substituents on the acyl moiety of chelating ligands, in conjunction with *tert*-butyl or phenyl groups on tin, play a key role in the formation of isomeric species. In the case of very bulky Q^{CHPh_2} ligand, six-coordinate tin species also have been observed to exist in equilibrium with five-coordinate species, likely arising from the

Table 1
Metal atom coordination geometries [(Q^{CHPh_2})$_2$SnMe$_2$, Et$_2$] (**1**, **2**), [(Q^{Bn})$_2$SnMe$_2$] (**6**) and [(Q^{naph})$_2$SnBu$^n_2$] (**12**) (Counterpart values for (**2**, **6**, **12**) follow those for (**1**).)

Atoms	Parameter	Atoms	Parameter
Distance (*Å*)			
Sn–C(10)	2.106(2), 2.11(1), 2.095(2), 2.117(5)	Sn–C(20)	2.099(2), 2.111(9), 2.097(2), 2.115(6)
Sn–O(15)	2.129(1), 2.122(6), 2.121(2), 2.133(3)	Sn–O(25)	2.135(1), 2.148(5), 2.126(2), 2.097(3)
Sn–O(141)	2.306(1), 2.324(5), 2.325(2), 2.398(3)	Sn–O(241)	2.278(1), 2.311(6), 2.276(2), 2.383(3)
Angles (°)			
C(10)–Sn–C(20)	160.00(9), 154.1(1), 157.68(10) 153.0(2)		
O(15)–Sn–O(25)	83.96(5), 82.3(2), 80.03(6), 74.9(2)	O(141)–Sn–O(241)	113.66(5), 116.5(2), 114.74(6), 125.4(1)
O(15)–Sn–O(141)	80.58(2), 80.5(2), 82.51(6), 80.4(1)	O(25)–Sn–O(241)	81.84(2), 80.7(2), 82.81(6), 79.8(1)
O(15)–Sn–O(241)	165.71(5), 162.9(2), 162.56(6), 154.1(1)	O(25)–Sn–O(141)	164.42(5), 162.8(2), 162.40(6), 154.5(1)
C(10)–Sn–O(15)	96.64(7), 99.3(3), 99.86(9), 98.8(2)	C(10)–Sn–O(25)	97.74(7), 101.4(3), 98.09(8), 103.4(2)
C(20)–Sn–O(15)	98.46(7), 99.4(3), 96.11(9), 102.1(2)	C(20)–Sn–O(25)	96.82(7), 98.7(3), 99.96(9), 98.1(2)
C(10)–Sn–O(141)	85.97(7), 81.0(3), 82.66(8), 86.2(2)	C(10)–Sn–O(241)	83.72(7), 84.6(3), 85.58(9), 82.0(2)
C(20)–Sn–O(141)	83.66(7), 84.6(3), 84.07(9), 80.8(2)	C(20)–Sn–O(241)	84.86(7), 82.8(3), 83.78(9), 86.5(2)
Interplanar dihedral angles (°)			
$C_3O_2(1)/C_3O_2(2)$	11.40(6), 7.5(3), 8.57(6), 7.8(3)		
$C_3O_2(1)/C_3N_2(1)$	5.84(7), 5.0 (3), 2.25(7), 2.0(2)	$C_3O_2(2)/C_3N_2(2)$	6.17(7), 4.9(3), 1.99(7), 5.8(2)
$C_6(11)/C_3N_2(1)$	5.96(8), 6.8(3), 39.91(8), 46.7(2)	$C_6(21)/C_3N_2(2)$	39.42(8), 33.0(3), 5.02(8), 2.4(2)
$C_6(15)/C_3O_2(1)$	79.84(7), 82.8(4), 86.78(8), –	$C_6(25)/C_3O_2(2)$	84.44(6), 89.0(3), 85.97(8), –
$C_6(16)/C_3O_2(1)$	69.06(8), 77.4(4), –	$C_6(26)/C_3O_2(2)$	76.40(7), 79.4(3), –
Ph-pyrazole and CHPh$_2$ torsion angles (°) (*carbon atoms denoted by number only*)			
15–N(11)–111–112	5.9(3), 11(1), 39.7(3), −47.4(7)	25–N(21)–211–212	41.7(3), 33(1), −2.8(3), 3.6(8)
O(141)–141–142–151	57.5(2), 50.6(9), −54.7(2)	O(241)–241–242–251	44.2(2), 40.1(9), 101.3(2)
141–142–151–152	−73.3(2), −71.6(9), −70.4(2)	241–242–251–252	−77.6(2), −80.4(9), −21.4(3)
O(141)–141–142–161	−66.6(2), −74.6(9)	O(241)–241–242–261	−82.0(2), −85.6(9)
141–142–161–162	−2.8(3), −12.9(11)	241–242–261–262	14.3(3), 13.6(11)

The Sn atom lies 0.844(2), 0.609(2) Å out of the C_3O_2 planes in (**1**), 0.386(9), 0.188(7) in (**2**), 0.289(3), 0.333(3) in (**6**), 0.238(7), 0.085(7) Å in (**12**). In (**12**), the naphthyl planes lie at 88.5(2), 65.5(2)° to their associated C_3O_2 planes.

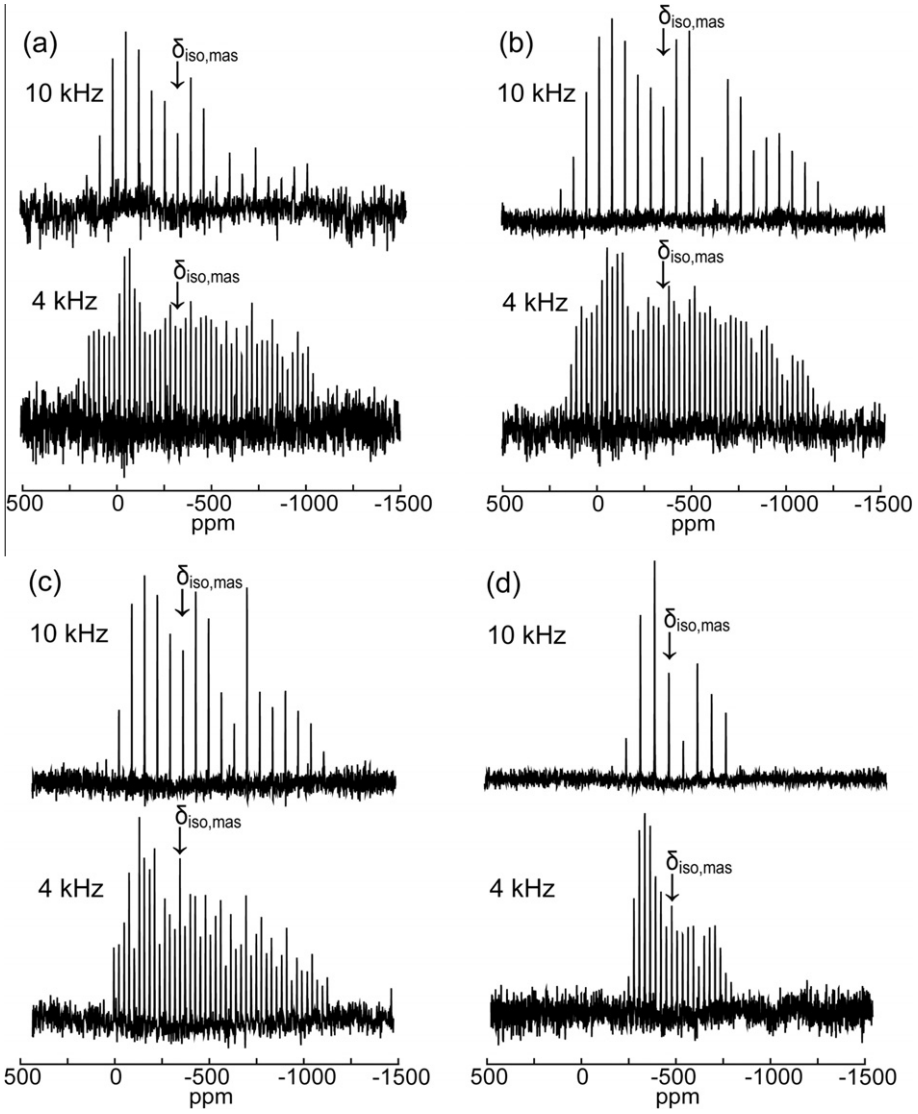


Fig. 8. ^{119}Sn CPMAS NMR spectra of the bis(3-methyl-1-phenyl-4-phenylacetylpyrazolon-5-ato) complexes $[(Q^{Bn})_2SnMe_2]$ **6**, (a), $[(Q^{Bn})_2SnEt_2]$ **7**, (**b**), $[(Q^{Bn})_2SnBu^t_2]$ **9**, (c) and $[(Q^{Bn})_2SnPh_2]$ **10**, (d).

Table 2
^{119}Sn isotropic chemical shifts and chemical shift tensor parameters measured from the ^{119}Sn CPMAS NMR data of Fig. 8.

Sn complex	$\delta_{iso,mas}$[a] (ppm) (±2)	$\Delta\delta_{iso,calc}$[b] (ppm) (±20)	δ_{11} (ppm) (±20)	δ_{22} (ppm) (±20)	δ_{33} (ppm) (±20)	Ω[c] (ppm) (±20)	κ[c] (±0.005)	$\Delta\delta$[d] (ppm) (±20)	η[d] (±0.005)
$[(Q^{Bn})_2SnMe_2]$ (**6**)	−316	−314	220	48	−1209	1429	0.77	−1343	0.19
$[(Q^{Bn})_2SnEt_2]$ (**7**)	−346	−345	195	−47	−1184	1379	0.65	−1258	0.23
$[(Q^{Bn})_2SnBu^t_2]$ (**9**)	−450	−434	34	−156	−1181	1215	0.69	−1120	0.25
$[(Q^{Bn})_2SnPh_2]$ (**10**)	−474	−474	−205	−407	−810	605	0.33	−504	0.60

[a] Measured directly from ^{119}Sn MAS data.
[b] Determined from the tensorial positions via the relationship $\delta_{iso,calc} = (\delta_{11} + \delta_{22} + \delta_{33})/3$.
[c] Herzfeld–Berger shift convention: $\delta_{11} \geqslant \delta_{22} \geqslant \delta_{33}$ (tensorial representation not shown above), $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, $\Omega = (\delta_{11} - \delta_{33})$, $\kappa = 3(\delta_{22} - \delta_{iso})/(\delta_{11} - \delta_{33})$ $(1 \geqslant \kappa \geqslant -1)$.
[d] Haeberlen shift convention: $|\delta_{33} - \delta_{iso}| \geqslant |\delta_{11} - \delta_{iso}| \geqslant |\delta_{22} - \delta_{iso}|$ (tensorial representation shown above), $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, $\Delta\delta = \delta_{33} - 1/2(\delta_{11} + \delta_{22}) = 3/2(\delta_{33} - \delta_{iso})$, $\eta_\delta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso})$ $(1 \geqslant \eta_\delta \geqslant 0)$.

breaking of one Sn–O bond. Moreover, the diphenyltin(IV) derivative of Q^{naph} is likely to exist in solution as a mixture of *trans* and *cis* isomers. Solid state ^{119}Sn NMR data are in accordance with a general *trans*-arrangement of the organyl groups on tin, as also confirmed by the X-ray structural determination of two dimethyltin(IV), one diethyltin(IV) and one di-*n*-butyltin(IV) derivative. However in the case of the diphenyltin(IV) derivative of Q^{Bn} a much reduced Ω value seems to indicate fast phenyl rotation or even a *cis*-arrangement of the phenyl groups.

4. Experimental section

4.1. General comments

The tin(IV) and organotin(IV) halides were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. The samples for microanalyses were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr). Elemental analyses (C, H, N) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental Analyzer. Molecular weight determinations were performed with a Knauer membrane osmometer. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin Elmer System 2000 FT-IR instrument. ^{1}H, ^{19}F and ^{119}Sn NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^{1}H, 282.2 MHz for ^{19}F and 111.9 MHz for ^{119}Sn). ^{119}Sn NMR experiments were carried out aliasing by varying the centre of the window, to avoid falling-out resonances, with a spectral width of 900 ppm. Melting points were taken on an IA 8100 Electrothermal Instrument. The electrical conductances of the dichloromethane and DMSO solutions were measured with a Crison CDTM 522 conductimeter at room temperature.

4.2. Syntheses of the proligands

4.2.1. 4-Diphenylacetyl-3-methyl-1-phenyl-pyrazol-5-one HQ^{CHPh_2}

3-Methyl-1-phenyl-pyrazol-5-one (15.0 g, 0.088 mol) was placed in a flask equipped with a stirrer, separating funnel and a reflux condenser. Dry dioxane (80 ml) was added by warming and to the clear solution calcium hydroxide (12.0 g, 0.162 mol) and then diphenylacetyl chloride (19.9 g, 0.087 mol) were added, the latter dropwise for 10 min. The mixture was heated to reflux for 4 h and then poured into HCl 2 N (300 ml) to decompose the calcium complex. A red oily precipitate immediately formed, which was separated from the solution and dried under reduced pressure at 50 °C. Recrystallization was performed by treating the solid with hot diethyl ether: slow cooling of the solution afforded a brown-red crystalline powder. Yield 56%. Mp 113–115 °C. Elemental analyses Calc. for $C_{24}H_{20}N_2O_2$: C, 73.4; H, 5.2; N, 10.1. Found: C, 73.6; H, 5.2; N, 10.1%. IR (nujol) data: 2700–3200br, ν(O–H···O); 1620vs, ν(C=O). ^{1}H ($CDCl_3$) NMR: δ 2.42s, (3 H, C3–CH_3); 5.64s, (1 H, $(C_6H_5)_2CHC$=O); 7.15–7.59m, 7.82d, (15 H, $(C_6H_5)_2$CHC=O and N–C_6H_5); 11.3br, (1 H, O*H*···O).

4.2.2. 3-Methyl-1-phenyl-4-phenylacetylpyrazol-5-one HQ^{Bn}

It was synthesised by a similar method of HQ^{CHPh_2}. Yield 82%. Mp 104–106 °C. Elemental analyses Calc for $C_{18}H_{16}N_2O_2$: C, 74.0; H, 5.5; N, 9.6. Found: C, 73.9; H, 5.6; N, 9.6%. IR (nujol) data: 2400–2800br, ν(O–H···O); 1619vs, ν(C=O). ^{1}H ($CDCl_3$) NMR: δ 2.53s, (3H, C3–CH_3); 4.09s, (2H, $C_6H_5CH_2$C=O); 7.12–7.48m, 7.82d, (10H, $C_6H_5CH_2$C=O and N–C_6H_5); 10.6br, (1H, O*H*···O).

4.2.3. 3-Methyl-4-naphthoyl-1-phenyl-pyrazol-5-one HQ^{naph}

It was synthesised by a similar method of HQ^{CHPh_2}. Yield 88%. Mp 177–183 °C. Elemental analyses Calc for $C_{21}H_{16}N_2O_2$: C, 76.81; H, 4.91; N, 8.53. Found: C, 76.32; H, 5.11; N, 8.50%. IR (nujol) data: 2400–2800br, ν(O–H···O); 1616vs, ν(C=O). ^{1}H ($CDCl_3$) NMR: δ 1.63s, (3H, C3–CH_3); 7.30t, 7.60m, 7.92dd, 8.03m (12H, C–H_{naph} and N–C_6H_5); 4.8br, (1H, O*H*···O).

4.3. Syntheses of the metal derivatives

4.3.1. Bis(4-diphenylacetyl-3-methyl-1-phenyl-pyrazolon-5-ato)-dimethyltin(IV) $(Q^{CHPh_2})_2SnMe_2$ (**1**)

To a methanol solution (30 ml) of HQ^{CHPh_2} (2 mmol) were added KOH (2 mmol) and $(CH_3)_2SnCl_2$ (1 mmol). A precipitate formed immediately. The mixture was stirred overnight and the precipitate was then filtered off, washed with methanol (ca. 10 ml) and dried under reduced pressure at room temperature. This was recrystallised from chloroform/methanol. Yield 57%. Mp 177–180 °C. Elemental analyses Calc for $C_{50}H_{44}N_4O_4Sn$: C, 68.0; H, 5.0; N, 6.3. Found: C, 67.7; H, 5.2; N, 6.4%. F.w. = 884; M.w. = 633 (0.9×10^{-2} m) (r = M.w./F.w. = 0.72), 671 (1.6×10^{-2} m) (r = 0.76). IR (nujol) data: 1603vs, ν(C=O), 585m, 558s, ν(Sn–C), 439m, 406s, 376w ν(Sn–O). ^{1}H ($CDCl_3$) NMR (293 K): δ, 0.59s [$^{2}J(^{119}Sn–^{1}H)$: 93.4 Hz, $^{2}J(^{117}Sn–^{13}C)$: 88.9 Hz] (6H, Sn–CH_3), 2.45s (6H, C3–CH_3), 5.57s (2H, $(C_6H_5)_2CHC$=O), 7.18–7.26m, 7.80d (30H, $(C_6H_5)_2$CHC=O and N–C_6H_5). ^{1}H ($CDCl_3$) NMR (223 K): δ, 0.79s [$^{2}J(^{119/117}Sn–^{1}H)$: 98.3 Hz], 0.60s [$^{2}J(^{119/117}Sn–^{1}H)$: 70.5 Hz] (6H, Sn–$CH_3$), 2.52s, 2.30s, 2.22s (6H, C3–CH_3), 5.68s, 5.08s (2H, $(C_6H_5)_2CHC$=O), 7.03–7.38m, 7.45t, 7.68d, 7.72d (30H, $(C_6H_5)_2$CHC=O and N–C_6H_5). ^{13}C ($CDCl_3$) NMR (293 K): δ, 8.7s [$^{1}J(^{119}Sn–^{13}C)$: 895, $^{1}J(^{117}Sn–^{13}C)$: 854 Hz] (Sn–CH_3), 17.8s (C3–CH_3), 58.4s ($(C_6H_5)_2$CHC=O), 121.4s, 125.9s, 127.3s, 128.6s, 128.8s, 129.0s, 129.3s, 138.2s, 148.2s ($C_{aromatic}$ of Q^{CHPh_2}), 105.1s (*C*4), 139.2s (*C*3), 163.1s (*C*5), 193.3s (*C*O). ^{119}Sn ($CDCl_3$) NMR (293 K): δ, −314.4. ^{119}Sn ($CDCl_3$) NMR (223): δ, −307.3br. Derivatives **2**–**13** were synthesised and crystallised similarly.

4.3.2. Bis(4-diphenylacetyl-3-methyl-1-phenyl-pyrazolon-5-ato)-diethyltin(IV) $(Q^{CHPh_2})_2SnEt_2$ (**2**)

Yield 51%. Mp 188–190 °C. Elemental analyses Calc for $C_{52}H_{48}N_4O_4Sn$: C, 68.5; H, 5.3; N, 6.1. Found: C, 68.3; H, 5.4; N, 6.0%. F.w. = 912; M.w. = 632 (0.8×10^{-2} m) (r = M.w./F.w. = 0.69), 724 (1.9×10^{-2} m) (r = 0.79). IR (nujol) data: 1595s, ν(C=O), 554s, 515m, ν(Sn–C), 436s, 398s, 388s, 378s ν(Sn–O). ^{1}H ($CDCl_3$) NMR (293 K): δ, 0.89t [$^{3}J(^{119}Sn–^{1}H)$: 161.2 Hz, $^{2}J(^{117}Sn–^{13}C)$: 153.1 Hz], 1.26q [$^{2}J(^{119}Sn–^{1}H)$: 107.2 Hz, $^{2}J(^{117}Sn–^{13}C)$: 103.3 Hz], (10H, Sn–CH_2CH_3), 2.40s br (6H, C3–CH_3), 5.68s br (2H, $(C_6H_5)_2CHC$=O), 7.12–7.29m br, 7.83m br (30H, $(C_6H_5)_2$CHC=O and N–C_6H_5). ^{1}H ($CDCl_3$) NMR (223 K): δ, 0.78br, 0.89t br, 1.26br, 1.36q br, (10H, Sn–CH_2CH_3), 2.21s br, 2.52s br (6H, C3–CH_3), 5.05s br, 5.73s br (2H, $(C_6H_5)_2CHC$=O), 7.05–7.20m br, 7.22–7.50m, 7.78d br (30H, $(C_6H_5)_2$CHC=O and N–C_6H_5). ^{13}C ($CDCl_3$) NMR (293 K): δ, 9.2s [$^{1}J(^{119/117}Sn–^{13}C)$: 57 Hz] (Sn–$CH_2CH_3$), 17.9s (C3–$CH_3$), 21.6s [$^{1}J(^{119}Sn–^{13}C)$: 865, $^{1}J(^{117}Sn–^{13}C)$: 826 Hz] (Sn–CH_2CH_3), 58.5s ($(C_6H_5)_2$CHC=O), 121.2s, 125.7s, 127.3s, 128.5s, 128.6s, 128.8s, 129.1s, 129.3s, 138.3s, 148.2s ($C_{aromatic}$ of Q^{CHPh_2}), 105.5s (*C*4), 139.3s (*C*3), 163.2s (*C*5), 194.2s (*C*O). ^{119}Sn ($CDCl_3$) NMR (293 K): δ, −354.9. ^{119}Sn ($CDCl_3$) NMR (223): δ, −345.1br.

4.3.3. Bis(4-diphenylacetyl-3-methyl-1-phenyl-pyrazolon-5-ato)-dicyclohexyltin(IV) $(Q^{CHPh_2})_2SnCy_2$ (**3**)

Yield 65%. Mp 223–227 °C. Elemental analyses Calc for $C_{60}H_{60}N_4O_4Sn$: C, 70.7; H, 6.0; N, 5.5. Found: C, 70.5; H, 6.2; N, 5.3%. IR (nujol) data: 1604s, ν(C=O), 556s, 426s, ν(Sn–C), 439m, 390m, 371m ν(Sn–O). ^{1}H ($CDCl_3$) NMR (293 K): δ, 0.94–1.79m br (22H, Sn–C_6H_{11}), 2.45s, 248s (6H, C3–CH_3), 5.73s br (2H, $(C_6H_5)_2CHC$=O), 7.07m br, 7.26m br, 7.82m br (30H, $(C_6H_5)_2$CHC=O and N–C_6H_5). ^{13}C ($CDCl_3$) NMR (293 K): δ, 17.8s (C3–CH_3), 26.6s, 28.4s [$^{2}J(^{119/117}Sn–^{13}C)$: 32 Hz], 29.0s, 47.5s [$^{1}J(^{119}Sn–^{13}C)$: 842, $^{1}J(^{117}Sn–^{13}C)$: 804 Hz] (Sn–C_6H_{11}), 59.1s ($(C_6H_5)_2$CHC=O), 121.1s, 125.5s, 127.2s, 128.5s, 128.6s, 128.8s, 129.0s, 129.1s, 129.4s, 129.5s, 138.5s, 148.2s ($C_{aromatic}$ of Q^{CHPh_2}), 105.3s (*C*4), 139.5s (*C*3), 163.1s (*C*5), 193.6s (*C*O). ^{119}Sn ($CDCl_3$) NMR (293 K): δ, −430.1.

4.3.4. Bis(4-diphenylacetyl-3-methyl-1-phenyl-pyrazolon-5-ato)-ditert-butyltin(IV) $(Q^{CHPh_2})_2SnBu^{t}_2$ (**4**)

Yield 50%. Mp 168–170 °C. Elemental analyses Calc for $C_{56}H_{56}N_4O_4Sn$: C, 69.5; H, 5.8; N, 5.8. Found: C, 69.2; H, 5.9; N, 5.7%. IR (nujol) data: 1596vs, ν(C=O), 559s, 427m, ν(Sn–C),

442m, 390sh, 386s, 372s ν(Sn–O). ^{1}H ($CDCl_3$) NMR (293 K): δ, 0.80s br, [$^2J_{(^{119/117}Sn-^1H)}$: 87.4 Hz] (18H, Sn–C(CH_3)$_3$), 2.41s br (6H, C3–CH_3), 5.69s br (2H, (C_6H_5)$_2CHC$=O), 7.09–7.40m br, 7.79d br (30H, (C_6H_5)$_2$CHC=O and N–C_6H_5). ^{13}C ($CDCl_3$) NMR (293 K): δ, 17.9br (C3–CH_3), 29.0br (Sn–C(CH_3)$_3$), 46.2br (Sn–C(CH_3)$_3$), 59.4br ((C_6H_5)$_2$CHC=O), 121.2br, 125.6br, 127.3br, 128.6br, 128.8br, 129.1br, 129.5br, 129.6br, 138.4br, 148.1br ($C_{aromatic}$ of Q^{CHPh_2}), 106.6br ($C4$), 139.3br ($C3$), 164.1br ($C5$), 194.4br (CO). ^{119}Sn ($CDCl_3$) NMR (293 K): δ, −445.0br.

4.3.5. Bis(4-diphenylacetyl-3-methyl-1-phenyl-pyrazolon-5-ato)-diphenyltin(IV) (Q^{CHPh_2})$_2SnPh_2$ (**5**)

Yield 59%. Mp 142–144 °C. Elemental analyses Calc for $C_{60}H_{48}N_4O_4Sn$: C, 71.5; H, 4.8; N, 5.6. Found: C, 71.3; H, 4.7; N, 5.4%. IR (nujol) data: 1611s, ν(C=O), 268s, 243m, ν(Sn–C), 448s br, 416w, 348m ν(Sn–O). ^{1}H ($CDCl_3$) NMR (293 K): δ, 2.82s, 2.42s (6H, C3–CH_3), 5.20s, 5.56s (2H, (C_6H_5)$_2CHC$=O), 6.83–7.38m, 7.46t, 7.72m, 7.96d (40H, (C_6H_5)$_2$CHC=O, N–C_6H_5 and Sn–C_6H_5). ^{13}C ($CDCl_3$) NMR (293 K): δ, 17.9br (C3–CH_3), 58.6br ((C_6H_5)$_2CHC$=O), 121.4br, 126.1br, 127.3br, 127.8br, 128.7br, 128.9br, 129.4br, 138.1br, 148.2br ($C_{aromatic}$ of Q^{CHPh_2} and Sn–C_6H_5), 106.1br ($C4$), 139.3br ($C3$), 163.0br ($C5$), 194.4br (CO). ^{119}Sn ($CDCl_3$) NMR (293 K): δ, −493.2br.

4.3.6. Bis(3-methyl-1-phenyl-4-phenylacetylpyrazolon-5-ato)-dimethyltin(IV) (Q^{Bn})$_2SnMe_2$ (**6**)

Yield 62%. Mp 153–155 °C. Elemental analyses Calc for $C_{50}H_{44}N_4O_4Sn$: C, 62.4; H, 5.0; N, 7.7. Found: C, 62.3; H, 5.1; N, 7.8%. IR (nujol) data: 1593vs, ν(C=O), 593m, 575sh, 543w ν(Sn–C), 460s, 447s, 440m, 405w, 395m ν(Sn–O). ^{1}H ($CDCl_3$) NMR (293 K): δ, 0.75s [$^2J_{(^{119}Sn-^1H)}$: 99.7 Hz, $^2J_{(^{117}Sn-^{13}C)}$: 95.3 Hz] (6H, Sn–CH_3), 2.45s (6H, C3–CH_3), 3.97s (4H, $C_6H_5CH_2C$=O), 7.17–7.31m, 7.84dd (20H, $C_6H_5CH_2C$=O and N–C_6H_5). ^{13}C ($CDCl_3$) NMR (293 K): δ, 9.1s [$^1J_{(^{119}Sn-^{13}C)}$: 922, $^1J_{(^{117}Sn-^{13}C)}$: 880 Hz] (Sn–CH_3), 17.6s (C3–CH_3), 45.5s ($C_6H_5CH_2C$=O), 121.3s, 125.8s, 127.1s, 128.8s, 129.1s, 135.0s, 148.6s ($C_{aromatic}$ of Q^{Bn}), 104.8s ($C4$), 138.3s ($C3$), 162.6s ($C5$), 192.8s (CO). ^{119}Sn ($CDCl_3$) NMR (293 K): δ, −318.2.

4.3.7. Bis(3-methyl-1-phenyl-4-phenylacetylpyrazolon-5-ato)-diethyltin(IV) (Q^{Bn})$_2SnEt_2$ (**7**)

Yield 74%. Mp 141–143 °C. Elemental analyses Calc for $C_{42}H_{40}N_4O_4Sn$: C, 63.3; H, 5.3; N, 7.4. Found: C, 63.1; H, 5.4; N, 7.4%. IR (nujol) data: 1610s, ν(C=O), 556s, 521m ν(Sn–C), 461s, 440s, 427s, 403m br ν(Sn–O). ^{1}H ($CDCl_3$) NMR (293 K): δ, 1.43q [$^2J_{(^{119}Sn-^1H)}$: 86.6 Hz, $^2J_{(^{117}Sn-^{13}C)}$: 83.3 Hz], 1.04t [$^3J_{(Sn-H)}$: 161.8, 154.6 Hz] (10H, Sn–CH_2CH_3), 2.48s (6H, C3–CH_3), 4.00s (4H, $C_6H_5CH_2C$=O), 7.15–7.38m, 7.82–7.91m (20H, $C_6H_5CH_2C$=O and N–C_6H_5). ^{13}C ($CDCl_3$) NMR (293 K): δ, 9.4s [$^1J_{(^{119/117}Sn-^{13}C)}$: 54 Hz] (Sn–$CH_2CH_3$), 17.6s (C3–$CH_3$), 21.8s [$^1J_{(^{119}Sn-^{13}C)}$: 856, $^1J_{(^{117}Sn-^{13}C)}$: 818 Hz] (Sn–CH_2CH_3), 45.5s ($C_6H_5CH_2C$=O), 121.0s, 125.5s, 127.0s, 128.7s, 129.0s, 135.0s, 148.5s ($C_{aromatic}$ of Q^{Bn}), 104.9s ($C4$), 138.4s ($C3$), 162.7s ($C5$), 193.1s (CO). ^{119}Sn ($CDCl_3$) NMR (293 K): δ, −356.6.

4.3.8. Bis(3-methyl-1-phenyl-4-phenylacetylpyrazolon-5-ato)-dicyclohexyltin(IV) (Q^{Bn})$_2SnCy_2$ (**8**)

Yield 82%. Mp 164–165 °C. Elemental analyses Calc for $C_{48}H_{52}N_4O_4Sn$: C, 66.4; H, 6.0; N, 6.5. Found: C, 66.1; H, 6.2; N, 6.5%. IR (nujol) data: 1614s, ν(C=O), 534m, 520s, 497s ν(Sn–C), 461m, 444s, 421s, 404m, 391s ν(Sn–O). ^{1}H ($CDCl_3$) NMR (293 K): δ, 0.98–1.82m (22H, Sn–C_6H_{11}), 2.52s (6H, C3–CH_3), 4.02s (4H, $C_6H_5CH_2C$=O), 7.11–7.35m, 7.88dd (20H, $C_6H_5CH_2C$=O and N–C_6H_5). ^{13}C ($CDCl_3$) NMR (293 K): δ, 17.8s (C3–CH_3), 26.8s, 28.9s [$^2J_{(^{119/117}Sn-^{13}C)}$: 32 Hz], 29.5s, 45.7s [$^1J_{(^{119}Sn-^{13}C)}$: 837, $^1J_{(^{117}Sn-^{13}C)}$: 801 Hz] (Sn–C_6H_{11}), 47.3s ($C_6H_5CH_2C$=O), 120.9s, 125.4s, 127.0s, 128.7s, 129.1s, 129.4, 135.2s, 148.4s ($C_{aromatic}$ of Q^{Bn}), 105.1s ($C4$), 138.6s ($C3$), 162.9s ($C5$), 193.1s (CO). ^{119}Sn ($CDCl_3$) NMR (293 K): δ, −431.0.

4.3.9. Bis(3-methyl-1-phenyl-4-phenylacetylpyrazolon-5-ato)di-t-butyltin(IV) (Q^{Bn})$_2$SnBu$^t_2$ (**9**)

Yield 85%. Mp 161–162 °C. Elemental analyses Calc for $C_{44}H_{48}N_4O_4Sn$: C, 64.8; H, 5.9; N, 6.9. Found: C, 64.5; H, 6.0; N, 6.9%. IR (nujol) data: 1603s, ν(C=O), 572m, 545s, 478w, 433vs, ν(Sn–C), 460m, 433s, 408m, 390s, ν(Sn–O). ^{1}H ($CDCl_3$) NMR (293 K): δ, 0.98s [$^3J_{(Sn-H)}$: 133.4, 127.2 Hz] (18H, Sn–C_4H_9), 2.52s (6H, C3–CH_3), 3.99s (4H, $C_6H_5CH_2C$=O), 7.12–7.35m, 7.86dd (20H, $C_6H_5CH_2C$=O and N–C_6H_5). ^{13}C ($CDCl_3$) NMR (293 K): δ, 17.9br (C3–CH_3), 29.3br (Sn–C(CH_3)$_3$), 30.2br (Sn–C(CH_3)$_3$), 45.7br ($C_6H_5CH_2C$=O), 120.9br, 125.4br, 127.0br, 128.5br, 129.1br, 129.8br, 134.7br, 148.3br ($C_{aromatic}$ of Q^{Bn}), 105.8br ($C4$), 138.6br ($C3$), 163.4br ($C5$), 193.2br (CO). ^{119}Sn ($CDCl_3$) NMR (293 K): δ, −455.2br.

4.3.10. Bis(3-methyl-1-phenyl-4-phenylacetylpyrazolon-5-ato)-diphenyltin(IV) (Q^{Bn})$_2SnPh_2$ (**10**)

Yield 79%. Mp 165–167 °C. Elemental analyses Calc for $C_{48}H_{40}N_4O_4Sn$: C, 67.4; H, 4.7; N, 6.5. Found: C, 67.2; H, 4.8; N, 6.7%. F.w. = 856. IR (nujol) data: 1605s br, ν(C=O), 265s, 244s, ν(Sn–C), 445vs br, 404w, 385m br ν(Sn–O). ^{1}H ($CDCl_3$) NMR (293 K): δ, 2.35s br, 2.47s br (6H, C3–CH_3), 3.72s br, 3.87s br (4H, $C_6H_5CH_2C$=O), 6.94–7.53m br, 7.82d br (30H, $C_6H_5CH_2C$=O, N–C_6H_5 and Sn–C_6H_5). ^{13}C ($CDCl_3$) NMR (293 K): δ, 17.3br, 17.6br (C3–CH_3), 44.5br, 44.9br ($C_6H_5CH_2C$=O), 121.0br, 121.2br, 125.9br, 126.9br, 127.5br, 128.0br, 128.1br, 128.4br, 128.6br, 128.7br, 129.0br, 130.7br, 133.8br, 135.2br, 148.1br, 148.3br, 148.6br ($C_{aromatic}$ of Q^{Bn} and of Sn–C_6H_5), 104.5br, 105.3br ($C4$), 136.2br, 137.9br ($C3$), 163.5br ($C5$), CO not observed. ^{119}Sn ($CDCl_3$) NMR (293 K): δ, −487.2br, −490.5br.

4.3.11. Bis(3-methyl-4-naphthoyl-1-phenyl-pyrazolon-5-ato)-dimethyltin(IV) (Q^{naph})$_2SnMe_2$ (**11**)

Yield 75%. Mp 207–208 °C. Elemental analyses: Calc for $C_{44}H_{36}N_4O_4Sn$: C, 65.77; H, 4.52; N, 6.97. Found: C, 65.28; H, 4.64; N, 6.99%. IR (nujol, cm^{-1}): 1600vs ν(C=O), 568s, 528m ν(Sn–C), 463w, 448m, 433m, 400s, 389s, 372m ν(Sn–O). ^{1}H NMR ($CDCl_3$) (293 K): δ, 1.20s ($^2J_{(Sn-H)}$: 101.4, 96.8 Hz) (6H, Sn–CH_3), 1.40s (6H, C3–CH_3), 7.20m, 7.48m, 7.90dd, 7.96m (24H, C–H_{naph} and N1–C_6H_5). ^{13}C NMR ($CDCl_3$) (293 K): δ, 9.8s [$^1J_{(^{119}Sn-^{13}C)}$: 906 Hz, $^1J_{(^{117}Sn-^{13}C)}$: 865 Hz] (Sn–CH_3), 15.5s (C3–CH_3), 121.0, 124.7, 124.8, 125.0, 125.7, 126.6, 127.3, 128.4, 129.0, 129.8, 130.2, 133.5, 137.1, 150.2s (C_{naph} and N1–C_6H_5), 106.3s ($C4$), 138.2s ($C3$), 162.6s ($C5$), 191.2s (CO). ^{119}Sn NMR ($CDCl_3$) (293 K): δ, −319.8.

4.3.12. Bis(3-methyl-4-naphthoyl-1-phenyl-pyrazolon-5-ato)di-n-butyltin(IV) (Q^{naph})$_2$SnBu$^n_2$ (**12**)

Yield 72%. Mp 151–153 °C. Elemental analyses: Calc for $C_{48}H_{48}N_4O_4Sn$: C, 66.76; H, 5.60; N, 6.49. Found: C, 66.72; H, 5.78; N, 6.28%. IR (nujol, cm^{-1}): 1596s ν(C=O), 566s, 529s ν(Sn–C), 440m, 405w, 396w, 383m, 369s ν(Sn–O). ^{1}H NMR ($CDCl_3$) (293 K): δ, 0.87t, 1.45m, 1.85m (18H, Sn–C_4H_9), 1.61s (6H, C3–CH_3), 7.20m, 7.50m, 7.91dd, 8.00m (24H, C–H_{naph} and N1–C_6H_5). ^{13}C NMR ($CDCl_3$) (293 K): δ, 15.7s (C3–CH_3), 13.9s, 26.4s [$^3J_{(^{119/117}Sn-^{13}C)}$: 138 Hz], 27.5s [$^3J_{(^{119/117}Sn-^{13}C)}$: 45 Hz], 29.8s [$^1J_{(^{119}Sn-^{13}C)}$: 870 Hz, $^1J_{(^{117}Sn-^{13}C)}$: 831 Hz] (Sn–C_4H_9), 120.9, 124.8, 124.9, 125.2, 125.7, 126.7, 127.4, 128.7, 129.2, 130.0, 130.3, 150.3s (N1–C_6H_5), 106.6s ($C4$), 138.5s ($C3$), 162.9s ($C5$), 191.8s (CO). ^{119}Sn NMR ($CDCl_3$) (293 K): δ, −354.0br.

*4.3.13. Bis(3-methyl-4-naphthoyl-1-phenyl-pyrazolon-5-ato)diphenyltin(IV) (Q^{naph})$_2$SnPh$_2$ (**13**)*

Yield 77%. Mp 247–250 °C. Elemental analyses: Calc for $C_{54}H_{40}N_4O_4Sn$: C, 69.92; H, 4.35; N, 6.04. Found: C, 69.54; H, 3.58; N, 6.4%. IR (nujol, cm^{-1}): 1604vs ν(C=O), 448vs, 434m, 403m, 392m ν(Sn–O), 267m, 245m, 225m ν(Sn–C). ^{1}H NMR ($CDCl_3$) (293 K): δ, 1.21br, 1.69s (6H, C3–CH_3), 7.20–7.60m, 7.80–8.10m (34H, Sn–C$_6H_5$, C–H_{naph} and N1–C$_6H_5$). ^{13}C NMR ($CDCl_3$) (293 K): δ, 15.4br (C3–CH_3), 120.9br, 121.3br, 123.7br, 125.0br, 126.2br, 126.6br, 127.2br, 128.4br, 129.1br, 129.9br, 130.2br, 133.4br, 135.6br, 136.6br, 148.2br, 150.6br, (Sn–C_6H_5, C–H_{naph} and N1–C_6H_5), 107.3br (*C*4), 138.0br (*C*3), 163.9br (*C*5), 191.8br (*C*O). ^{119}Sn NMR ($CDCl_3$) (293 K): δ, −479.8br, −486.8br, −740.6.

4.4. Structure determinations

For complex (**2**), a unique data single counter diffractometer set (Syntex P2$_1$ modified by Crystallogic) was measured at 298 K; for the complexes (**1**) and (**12**), full spheres of CCD/area detector data were measured at ca. 153 K (monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å (all structures)); for (**6**) *T* was 100 K. All unique data were included in the full matrix least squares refinements, refining anisotropic displacement parameter forms for the non-hydrogen atoms, hydrogen atom treatment following a riding model. Neutral atom complex scattering factors were employed. Full cif depositions reside with the Cambridge Crystallographic Data Centre, CCDC 779497 (**1**), 783539 (**2**), 787995 (**6**), 779909 (**12**).

4.4.1. Crystal/refinement data

*4.4.1.1. [(Q^{CHPh_2})$_2$SnMe$_2$] (**1**).* ≡$C_{50}H_{44}N_4O_4Sn$, M_r = 883.6. Monoclinic, space group $P2_1/c$ (C_{2h}^5, *No.* 14), a = 11.102(2), b = 15.713(2), c = 24.098(3) Å, β = 98.235(3)°, V = 4160(1) Å^3. D_c (Z = 4) = 1.41$_1$ g cm^{-3}. μ_{Mo} = 0.67 mm^{-1}; specimen: = 0.36 × 0.32 × 0.22 mm; '$T'_{min/max}$ ('empirical'/multiscan correction) = 0.90. $2\theta_{max}$ = 70°; 78,052 total reflections, merging to 18,421 unique (R_{int} = 0.047), 12,907 with $I > 2\sigma(I)$. R_1 = 0.044, wR_2 = 0.110. Refinement on F^2 (reflection weights: $(\sigma^2(F_o^2) + (0.050P)^2 + 1.62P)^{-1}$ ($P = (F_o^2 + 2F_c^2)/3$)) (SHELXL 97 [27]).

*4.4.1.2. [(Q^{CHPh_2})$_2$SnEt$_2$] (**2**).* ≡$C_{52}H_{48}N_4O_4Sn$, M_r = 911.7. Monoclinic, space group $P2_1/c$, a = 11.135(8), b = 16.427(12), c = 24.72(2) Å, β = 98.29(2)°, V = 4474(6) Å^3. D_c (Z = 4) = 1.35$_4$ g cm^{-3}. μ_{Mo} = 0.62 mm^{-1}; specimen: = 0.30 × 0.30 × 0.07 mm; '$T'_{min/max}$ = 0.85 (semi-empirical correction [28]). $2\theta_{max}$ = 60°; 12,943 unique reflections, 6075 with $F > 6\sigma(F)$. Refinement on |*F*|, *Rf* = 0.057, *wR* = 0.085 (CAOS [29]).

*4.4.1.3. [(Q^{Bn})$_2$SnMe$_2$] (**6**).* ≡$C_{38}H_{36}N_4O_4Sn$, M_r = 731.4. Monoclinic, space group $P2_1/n$, a = 10.7778(14), b = 15.6439(14), c = 19.920(3) Å, β = 95.985(15)°, V = 3340.3(8) Å^3. D_c (Z = 4) = 1.45$_4$ g cm^{-3}. μ_{Mo} = 0.81 mm^{-1}; specimen: = 0.67 × 0.46 × 0.07 mm; '$T'_{min/max}$ (face-indexed 'analytical' correction) = 0.46. $2\theta_{max}$ = 70°; 48,223 total reflections, merging to 13,850 unique (R_{int} = 0.077), 9917 with $I > 2\sigma(I)$. R_1 = 0.047, wR_2 = 0.118. Refinement on F^2 (reflection weights: $(\sigma^2(F_o^2) + (0.072P)^2)^{-1}$) (SHELXL 97 [27]).

*4.4.1.4. [(Q^{naph})$_2$SnBu$^n_2$] (**12**).* ≡$C_{50}H_{48}N_4O_4Sn$, M_r = 887.6. Monoclinic, space group $P2_1/n$, a = 11.462(2), b = 21.069(4), c = 18.333(3) Å, β = 105.280(6)°, V = 4271(1) Å^3. D_c (Z = 4) = 1.380 g cm^{-3}. μ_{Mo} = 0.65 mm^{-1}; specimen: 0.18 × 0.16 × 0.08 mm; '$T'_{min/max}$ = 0.71. $2\theta_{max}$ = 52°; 29,386 total reflections, merging to 8359 unique (R_{int} = 0.075), 5552 with $I > 2\sigma(I)$. R_1 = 0.056, wR_2 = 0.15. Refinement on F^2 (reflection weights: $(\sigma^2(F_o^2) + 2.1P)^{-1}$ (SHELXL 97 [27]).

4.5. ^{119}Sn solid state NMR

High-resolution solid-state ^{119}Sn magic-angle-spinning (MAS) NMR spectra were acquired at ambient temperatures using a Bruker DSX-400 NMR spectrometer (B_0 = 9.4 T) operating at a ^{119}Sn Larmor frequency of 149.20 MHz. These experiments were conducted using a Bruker 3.2 mm double-air-bearing MAS probe from which rotational frequencies of 4 and 10 kHz were implemented. All experimental data were acquired under ^{1}H–^{119}Sn cross-polarisation conditions which used recycle delays of 5–10 s, Hartmann–Hahn contact periods of 5 ms, and an initial ^{1}H $\pi/2$ pulse width of 3.5 μs. A nominal ^{1}H decoupling field strength of ~80 kHz was employed during acquisition. Each spectrum was externally referenced to the Sn primary reference Me_4Sn (δ 0.0 ppm) via a secondary reference Cy_4Sn located upfield at δ −97.35 ppm [30]. This sample of Cy_4Sn was also used to establish the Hartmann–Hahn contact condition required for cross-polarisation data acquisition. The ^{119}Sn CPMAS spectrum of each complex was acquired at two different MAS frequencies to allow an unambiguous assignment of the isotropic chemical shift (δ_{iso}), and to clearly identify the chemical shift tensor elements δ_{11}, δ_{22} and δ_{33}. The MAS NMR spectra acquired at 4 kHz were more selectively utilised to identify δ_{11}, δ_{22} and δ_{33} since increased MAS rates invoked the appearance of biasing the downfield tensorial positions to lower ppm values and the upfield tensorial positions to higher ppm values. Parameters defining the chemical shift interaction were calculated from these measured chemical shift tensorial elements (δ_{11}, δ_{22}, δ_{33}) according to IUPAC-recognised conventions as discussed by Mason [31] and Mackenzie et al. [32]. The Herzfeld–Berger convention is described by using the isotropic chemical shift $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$ ($\delta_{11} > \delta_{22} > \delta_{33}$), span $\Omega = (\delta_{11} - \delta_{33})$, and skew $\kappa = 3(\delta_{22} - \delta_{iso})/(\delta_{11} - \delta_{33})$ (where $1 \geqslant \kappa \geqslant -1$). An alternative representation such as the Haeberlen convention uses the anisotropy ($\Delta\delta$) and asymmetry (η) if a different frequency convention $|\delta_{33} - \delta_{iso}| \geqslant |\delta_{11} - \delta_{iso}| \geqslant |\delta_{22} - \delta_{iso}|$ is invoked; in this case the anisotropy $\Delta\delta = \delta_{33} - (\delta_{11} + \delta_{22})/2) = 3(\delta_{33} - \delta_{iso})/2$ and asymmetry $\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso})$, where η is restricted within the range $1 \geqslant \eta \geqslant 0$.

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References

[1] P.G. Harrison, Chemistry of Tin, Blackie, Glasgow, 1989.
[2] (a) M. Gielen, E.R.T. Tiekink, Metallotherapeutic Drugs and Metal-Based Diagnostic Agents: The Use of Metals in Medicine, John Wiley & Sons, United Kingdom, 2005;
(b) A.G. Davies, M. Gielen, K.H. Pannell, E.R.T. Tiekink, Tin Chemistry: Fundamentals, Frontiers, and Applications, John Wiley & Sons, United Kingdom, 2008.
[3] A.J. Crowe, P.J. Smith, C.J. Cardin, H.E. Parge, F.E. Smith, Cancer Lett. 24 (1984) 45.
[4] G. Han, P. Yang, J. Inorg. Biochem. 91 (2002) 230. and references therein.
[5] (a) G.A. Miller, E.O. Schlemper, Inorg. Chem. 12 (1977) 677;
(b) G. Poli, C.J. Cheerand, W.H. Nelson, J. Organomet. Chem. 306 (1986) 347;

(c) C. Sreelatha, D.K. Srivastava, V.D. Gupta, H. Nöth, J. Chem. Soc., Dalton Trans. (1988) 407.
[6] (a) G.A. Miller, E.O. Schlemper, Inorg. Chim. Acta 30 (1978) 131;
(b) J. Angenault, C. Mondi, A. Rimsky, Inorg. Chim. Acta 37 (1979) 145;
(c) D. Searle, P.J. Smith, N.A. Bell, L.A. March, I.W. Nowell, J.D. Donaldson, Inorg. Chim. Acta 162 (1989) 143.
[7] K. Venkataraman, The Chemistry of Dyes, vol.1, Academic Press, New York, 1952.
[8] (a) Y.A. Zolotov, N.M. Kuzmin, in: Metal Extraction with Acylpyrazolones, Izdat Nauka, Moscow, 1977;
(b) E.C. Okafor, Z. Naturforsch. Teil B 36 (1981) 213;
(c) S. Umetani, H. Freiser, Inorg. Chem. 26 (1987) 3179;
(d) E.C. Okafor, B.A. Uzoukwu, Radiochim. Acta 51 (1990) 167.
[9] (a) E.C. Okafor, Spectrochim. Acta, Part A 37 (1987) 939;
(b) R. Morales, H. Nekimken, C.S. Bartholdi, P.T. Cunningham, Spectrochim. Acta, Part A 44 (1988) 165. and references therein.
[10] (a) S. Saxena, R. Bhora, A.K. Ray, Inorg. Chim. Acta 173 (1990) 191;
(b) C. Pettinari, G. Rafaiani, G. Gioia Lobbia, A. Lorenzotti, B. Bovio, J. Organomet. Chem. 458 (1991) 75;
(c) B. Bovio, A. Cingolani, F. Marchetti, C. Pettinari, J. Organomet. Chem. 458 (1993) 39;
(d) C. Pettinari, F. Marchetti, D. Leonesi, M. Rossi, F. Caruso, J. Organomet. Chem. 483 (1994) 123;
(e) A. Jain, S. Saxena, R. Bohra, A.K. Ray, Main Group Met. Chem. 18 (1995) 139;
(f) C. Pettinari, F. Marchetti, A. Gregori, A. Cingolani, J. Tanski, M. Rossi, F. Caruso, Inorg. Chim. Acta 257 (1997) 37;
(g) C. Pettinari, F. Marchetti, A. Cingolani, D. Leonesi, E. Mundorff, M. Rossi, F. Caruso, J. Organomet. Chem. 557 (1998) 187;
(h) F. Marchetti, C. Pettinari, M. Rossi, F. Caruso, Main Group Met. Chem. 21 (1998) 255.
[11] (a) F. Caruso, D. Leonesi, F. Marchetti, E. Rivarola, M. Rossi, V. Tomov, C. Pettinari, J. Organomet. Chem. 519 (1996) 29;
(b) C. Pettinari, F. Marchetti, A. Cingolani, A. Lorenzotti, E. Mundorff, M. Rossi, F. Caruso, Inorg. Chim. Acta 262 (1997) 33.
[12] B.A. Uzoukwu, P.U. Adiukwu, S.S. Al-Juaid, P.B. Hitchcock, J.D. Smith, Inorg. Chim. Acta 250 (1996) 173.
[13] (a) R.R. Ryan, G.D. Jarvinen, Acta Crystallogr., Part C 43 (1987) 1295;
(b) E.C. Okafor, A.B. Uzoukwu, P.B. Hitchcock, J.D. Smith, Inorg. Chim. Acta 172 (1990) 97.
[14] F. Marchetti, C. Pettinari, A. Cingolani, D. Leonesi, M. Camalli, A. Pifferi, Polyhedron 15 (1996) 3835.
[15] M.F. Mahon, K.C. Molloy, B.A. Omotowa, M.A. Mesubi, J. Organomet. Chem. 525 (1996) 239.
[16] (a) T.P. Lockhart, W.F. Manders, Inorg. Chem. 25 (1986) 892;
(b) B. Wrackmeyer, Ann. Rep. NMR Spectrosc. 16 (1985) 73;
(c) W.F. Howard Jr., R.W. Crecely, W.H. Nelson, Inorg. Chem. 24 (1985) 2204.
[17] W.F. Howard, R.W. Crecely, W.H. Nelson, Inorg. Chem. 24 (1985) 2204.
[18] C. Pettinari, F. Caruso, N. Zaffaroni, R. Villa, F. Marchetti, R. Pettinari, C. Phillips, J. Tanski, M. Rossi, J. Inorg. Biochem. 100 (2006) 58.
[19] F. Caruso, M. Rossi, F. Marchetti, C. Pettinari, Organometallics 18 (1999) 2398.
[20] C. Pettinari, F. Marchetti, R. Pettinari, A. Cingolani, A. Drozdov, S. Troyanov, J. Chem. Soc., Dalton Trans. (2002) 188.
[21] C. Camacho-Camacho, R. Contreras, H. Noth, M. Bechmann, A. Sebald, W. Milius, B. Wrackmeyer, Magn. Reson. Chem. 40 (2002) 31.
[22] C. Di Nicola, A. Galindo, J.V. Hanna, F. Marchetti, C. Pettinari, R. Pettinari, E. Rivarola, B.W. Skelton, A.H. White, Inorg. Chem. 44 (2005) 3094.
[23] A. Sebald, Advanced applications of NMR to organometallic chemistry, in: Solid State NMR Applications in Organotin and Organolead Chemistry, John Wiley & Sons, Chichester, UK, 1996, pp. 123–155 (Chapter 5).
[24] R.K. Harris, A. Sebald, J. Organomet. Chem. 331 (1987) C9.
[25] S.W. Ng, J.M. Hook, M. Gielen, Appl. Organomet. Chem. 14 (2000) 1.
[26] B.E. Eichler, B.L. Phillips, P.P. Power, M.P. Augustine, Inorg. Chem. 39 (2000) 5450.
[27] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
[28] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr., Sect. A 24 (1968) 351.
[29] M. Camalli, R. Spagna, J. Appl. Crystallogr. 27 (1994) 861.
[30] J. Kümmerlen, A. Sebald, H. Reuter, J. Organomet. Chem. 427 (1992) 309.
[31] J. Mason, Solid State Nucl. Magn. Reson. 2 (1993) 285.
[32] J.K.D. Mackenzie, M.E. Smith, Multinuclear Solid State NMR of Inorganic Materials, Pergamon, Oxford, UK, 2002.