Tin(II) and Lead(II) 4-Acyl-5-pyrazolonates: Synthesis, Spectroscopic and X-ray Structural Characterization

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Novel tin(II) β-diketonate $Sn(Q)_2$ complexes [HQ = 1-R^1-3-R^3-4-R^4(C=O)-pyrazol-5-one; HQ^C: R^1 = Ph, R^3 = Me, R^4 = Cy; HQ^S: R^1 = Ph, R^3 = Me, R^4 = $CHPh_2$; HQ^L: R^1 = Ph, R^3 = Me, R^4 = CH_2Ph; HQ^T: R^1 = Ph, R^3 = Me, R^4 = CH_2tBu; HQ^E: R^1 = Ph, R^3 = Me, R^4 = Et; HQ^B: R^1 = Ph, R^3 = Me, R^4 = *t*Bu; HQ^W: R^1 = Ph, R^3 = Me, R^4 = *p*-(*t*Bu)Ph; HQ^R: R^1 = Ph, R^3 = Me, R^4 = *p*-[$(CH_2)_5CH_3$]Ph; HQ^N: R^1 = *p*-NO_2Ph, R^3 = Me, R^4 = Ph; HQ^M: R^1 = Me, R^3 = Me, R^4 = Ph; HQ^D: R^1 = Me, R^3 = Me, R^4 = Me; HQ^P: R^1 = Ph, R^3 = Ph, R^4 = Ph; HQ^G: R^1 = Ph, R^3 = Ph, R^4 = Me; HQ^F: R^1 = *p*-CF_3Ph, R^3 = Me, R^4 = Ph; HQ^H: R^1 = *p*-CF_3Ph, R^3 = Me, R^4 = Me] have been isolated and characterized by single-crystal X-ray diffraction analyses, IR, ^{1}H, ^{13}C, ^{119}Sn NMR and ^{119}Sn Mössbauer spectroscopy, ESI mass spectrometry, conductivity and molecular weight measurements. The tin complexes SnQ_2 are air-stable, contrary to equivalent compounds of classical β-diketones, and adopt mononuclear pseudo-trigonal-bipyramidal structures ($pSnO_4$, where p is a stereochemically active lone electron pair) in which both ligands chelate a single metal center, as confirmed in the X-ray crystal structure of $Sn(Q^L)_2$. This structure fits a trend for all "SnO_4" compounds: Sn–O(primary) and Sn–O(secondary) bonds are associated with small O(primary)–Sn–O(primary) and wide O(secondary)–Sn–O(secondary) bond angles. The reactivity of $Sn(Q^T)_2$ toward RI (R = Me or Et) and $CrCO_6$ has been investigated. The compounds PbQ_2 (HQ = HQ^T, HQ^B, HQ^W, HQ^D) have been also synthesized and the X-ray structures of $Pb(Q^B)_2$ and $Pb(Q^T)_2$ in the solid state determined. These are different from SnQ_2 and are composed of "PbO_4" moieties with additional interactions from neighboring units to produce polymeric forms. Compound $Pb(Q^T)_2$ is unusual in having the metal–O(pyrazolonato) bond longer than the metal–O(acyl) one, probably due to a Pb–arene interaction with a neighboring phenyl ring. The sterically less hindered $Pb(Q^D)_2$ reacts with phen (1,10-phenanthroline) yielding the mixed ligand complex [$Pb(Q^D)_2$(phen)]. In this work, in addition to the different coordination numbers expressed by Sn and Pb, associated with the larger covalent radius of the latter, the binding mode of 4-acyl-5-pyrazolonates to Pb is *syn* whereas for Sn it is *anti*.

Introduction

The discovery of several important new applications has led to renewed interest in tin(II) and lead(II) compounds containing chelating ligands. For example, SnF_2 has been incorporated into toothpaste for over two decades,[1] primarily as a convenient fluoride source, but more recently the inherent antimicrobial activity of the tin itself has also been claimed.[2–4] As a result, orally viable Sn^{II} derivatives are greatly desired and a number of researchers are involved in this field.[5] Moreover, new molecular precursors for MOCVD techniques are required to prepare suitable thin films of SnO_2, which is a semiconductor highly transparent in the visible region and highly reflective in the IR region,[6] adhesive to many substrates and with good chemical and mechanical stability. SnO_2 has a number of specific properties that make it useful as a transparent and conducting coating on glass,[7] in gas-sensing devices[8,9] and in transparent electrodes in photovoltaic devices.[10–12] β-Diketonates of tin(IV)[13–15] and tin(II)[16] seem to be good sources of SnO_2. Lead chelates are the basis for thin films of Pb-containing ferromagnetic ceramics such as [$PbTiO_3$], [$Pb(Zr,Ti)O_3$] and [$(Pb,La)(Zr,Ti)O_3$] that have important applications in nonvolatile ferroelectric memories, infrared detectors, electro-optic devices, sensors and micro-actuators.[17–26] Finally, the design and synthesis of new,

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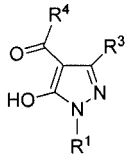
volatile and thermally stable lead(II) complexes has received increased attention.[27−29]

In the last decade we have reported on the interaction between 4-acyl-5-pyrazolones, an interesting family of asymmetric β-diketones (Figure 1), and several metal acceptors such as Sn,[30] Rh,[31] Ba,[32] Sr,[33] Cu,[34] Cd,[35] and Ag.[36] We have demonstrated that it is possible to tune the chemical properties by appropriate choice of the substituents in the R^1 and R^4 positions of the ligand. Sometimes the complexes obtained show unusual structural and physicochemical features such as good solubility in polar protic solvents.[37] More recently we have described antitumor titanium acylpyrazolonates,[38] and volatile copper acylpyrazolonates.[39]



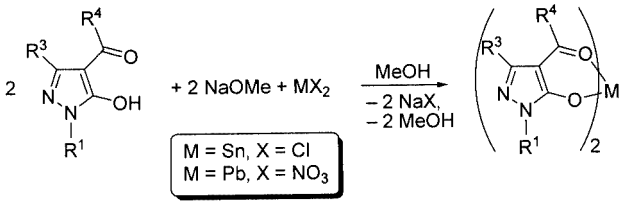
Q^CH: R^1 = Ph, R^3 = Me, R^4 = Cy
Q^SH: R^1 = Ph, R^3 = Me, R^4 = $CHPh_2$
Q^LH: R^1 = Ph, R^3 = Me, R^4 = CH_2Ph
Q^TH: R^1 = Ph, R^3 = Me, R^4 = CH_2tBu
Q^EH: R^1 = Ph, R^3 = Me, R^4 = Et
Q^BH: R^1 = Ph, R^3 = Me, R^4 = *t*Bu
Q^WH: R^1 = Ph, R^3 = Me, R^4 = *p*-*t*BuPh
Q^RH: R^1 = Ph, R^3 = Me, R^4 = *p*-[$(CH_2)_5$Me]Ph
Q^NH: R^1 = *p*-NO_2Ph, R^3 = Me, R^4 = Ph
Q^MH: R^1 = Me, R^3 = Me, R^4 = Ph
Q^DH: R^1 = Me, R^3 = Me, R^4 = Me
Q^PH: R^1 = Ph, R^3 = Ph, R^4 = Ph
Q^GH: R^1 = Ph, R^3 = Ph, R^4 = Me
Q^FH: R^1 = *p*-CF_3Ph, R^3 = Me, R^4 = Ph
Q^HH: R^1 = *p*-CF_3Ph, R^3 = Me, R^4 = Me

Figure 1. Q proligands used in this work

In 1994 we synthesized some tin(II) acylpyrazolonates[40] and found that these compounds are more stable than analogous tin(II) derivatives of classical β-diketonates.[16,41−43] Here we report a systematic investigation of the interaction of tin(II) with acylpyrazolonates to determine if variation of steric and electronic features of acylpyrazolones can affect the solid-state and solution structures of tin(II) compounds. The reactivity of the species obtained was also tested toward carbonylmetal compounds and alkyl halides. In addition, the structural properties and reactivities of new Pb^{II} acylpyrazolonates are compared.

Results and Discussion

Interaction of the acylpyrazolone proligands HQ with tin(II) dichloride in methanol, in the presence of sodium methoxide, yielded SnQ_2 derivatives **1**−**15** as precipitates (Scheme 1). In contrast to classical bis(β-diketonato)tin(II) complexes, Sn^{II} derivatives of the asymmetric Q^- ligands are quite stable to air and moisture. They are pale-yellow solids with sharp melting points. The solubility of **1**−**15** varies widely depending on the R^1, R^3 and R^4 substituents. When R^1 is a Ph or 4-$O_2NC_6H_4$ group and R^4 is an Me group (**1**−**9**), the compounds are soluble in DMSO, acetone and chlorohydrocarbon solvents, where they are not electrolytes. When R^1 = R^3 = Me (**10**, **11**), and when R^1 = *p*-$F_3CC_6H_4$ (**14**, **15**) higher solubility in acetonitrile, alcohols and aromatic solvents was found. Moreover, derivatives **12**−**15** are partially dissociated in DMSO, similar to diorganotin(IV) complexes of $(Q^P)^-$, $(Q^G)^-$, $(Q^F)^-$ and $(Q^H)^-$.[30,44,45] Compounds **1**−**15** do not undergo hydrolysis in chloroform or acetone solution. Molecular weight determinations carried out for all derivatives in chloroform suggest monomeric structures in solution.



Scheme 1

The infrared spectra of **1**−**15** show the disappearance of the broad band due to intramolecular O−H···O stretching vibration, which is observed in the free HQ proligands in the range 2300−2800 cm^{-1}. Only a small shift to lower frequencies (from about 1620 to about 1600 cm^{-1}) was found for the carbonyl band ν(C=O). In addition, new absorptions were identified in the region 300−500 cm^{-1}, likely due to ν(Sn−O).[30,37,44,45] These features are in accordance with deprotonation of acylpyrazolones and coordination to the tin atom through both oxygen atoms.[46,47]

In the case of derivatives **1**, **2**, **4** and **7**−**15** ^1H and ^{13}C NMR spectra carried out at room temperature show one set of resonances for each magnetically equivalent group of H or C, whereas the ^1H and ^{13}C NMR spectra of **3**, **5** and **6** show three sets of signals due to the three isomers depicted in Figure 2, assuming the tin atom exists in a trigonal-bipyramidal coordination environment. This different behavior is probably due to the steric bulk of Q in derivatives **3**, **5** and **6**, which increases the energetic barrier to interconversion among the three isomers. To confirm this hypothesis we recorded the ^1H NMR spectrum of compound **2** in dichloromethane at 183 K: two broad resonances for each equivalent group of protons emerged, in accordance with a lack of fluxionality at this temperature.

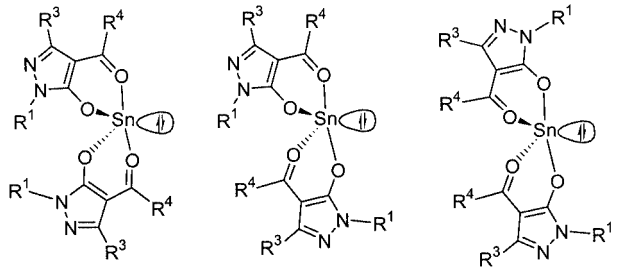


Figure 2. SnQ_2 stereoisomers found in chloroform solution of derivatives **3**, **5** and **6**

The ^{119}Sn NMR spectra of derivatives **1**−**15** show a single resonance in the range from δ = −700 to −775 ppm, typical of tin(II) derivatives with an SnO_4 core.[40,48−50] The presence of only one ^{119}Sn resonance in the case of deriva-

tives **3**, **5** and **6** seems to indicate that the tin center is not sensitive to changes in the configurational arrangement of the acylpyrazolonate donors. As previously observed, electron-withdrawing groups in the periphery of the acylpyrazolonato donors cause an upfield shift compared to those of electron-releasing ones, because of an increase in the ionic character of Sn−O bonds or, alternatively, to a greater contribution of the tin 5p atomic orbital to the Sn−O molecular orbital. An example is $Sn(Q^F)_2$ (δ = −775.2 ppm) with respect to $Sn(Q^D)_2$ (δ = −701.6 ppm). This allows the tin lone pair to became more concentrated in an orbital having increased 5s character.

We recorded ^{119m}Sn Mössbauer spectra of representative derivatives **1**−**6**, **8**−**12**, **14** and **15** and of six other similar complexes to verify this hypothesis in the solid state (Table 1). Systems containing divalent tin are readily recognized by their high δ values of 3−4 mm·s^{-1}. In fact, the lone pair of the Sn^{2+} ion retains a high 5s character; Sn^{II}−ligand covalent bonds induce a hybridization process having a partial p character leading to the decrease of isomer shift δ value and to moderate quadrupole splitting Δ values, typically 1−2 mm·s^{-1}.[51] The complexes examined by Mössbauer spectroscopy have 1:2 Sn^{II}/ligand stoichiometries and the tin atom, possessing a lone pair, is coordinated to four oxygen atoms from Q^- with formation of a six-membered chelate ring of the type Sn^{II}−O−C=C−C=O→Sn^{II}.[52]

Table 1. Mössbauer data of Sn^{II} complexes

Compound	δ [a][b] [mm·s^{-1}]	Δ [b] [mm·s^{-1}]	$\Gamma\pm$ [b] [mm·s^{-1}]
$Sn(Q^C)_2$ (**1**)	3.14	1.86	0.82
$Sn(Q^T)_2$ (**2**)	3.19	1.85	0.87
$Sn(Q^B)_2$ (**3**)	3.07	1.94	0.80
$Sn(Q^E)_2$ (**4**)	3.33	1.78	0.93
$Sn(Q^W)_2$ (**5**)	3.17	1.83	0.99
$Sn(Q^L)_2$ (**6**)	3.17	1.98	0.77
$Sn(Q^S)_2$ (**8**)	3.24	1.78	0.83
$Sn(Q^N)_2$ (**9**)	3.07	1.87	0.89
$Sn(Q^M)_2$ (**10**)	2.99	1.98	0.81
$Sn(Q^D)_2$ (**11**)	3.29	1.68	0.86
$Sn(Q^P)_2$ (**12**)	3.22	1.94	0.98
$Sn(Q^F)_2$ (**14**)	3.26	1.89	0.87
$Sn(Q^H)_2$ (**15**)	3.36	1.96	0.83
$Sn(Q^{Br})_2$ [c]	3.00	1.85	0.81
$Sn(Q^{R'})_2$ [d]	3.06	1.77	0.77
$Sn(Q^{Me})_2$ [e]	3.13	1.98	0.86
$Sn(Q^{CCl3})_2$ [f]	3.13	1.97	0.95
$Sn(Q^{Ph})_2$ [g]	3.15	1.83	0.89
$Sn(Q^{F'})_2$ [h]	3.26	1.69	0.92

[a] With respect to room-temperature spectrum of $CaSnO_3$. [b] ±0.01 mm·s^{-1}. [c] HQ^{Br} = 4-(*p*-bromophenyl)-3-methyl-1-phenylpyrazol-5-one. [d] $HQ^{R'}$ = 3-methyl-1-phenyl-4-(*p*-tolyl)pyrazol-5-one. [e] HQ^{Me} = 3,4-dimethyl-1-phenylpyrazol-5-one. [f] HQ^{CCl3} = 3-methyl-1-phenyl-4-(trichloroacetyl)pyrazol-5-one. [g] HQ^{Ph} = 3-methyl-1,4-diphenylpyrazol-5-one. [h] $HQ^{F'}$ = 3-methyl-1-phenyl-4-(trifluoroacetyl)pyrazol-5-one.

The variation of the Mössbauer parameter values of isomer shift, δ, and quadrupole splitting, Δ, (Tables 1 and 2) is around 0.37 mm·s^{-1} and 0.30 mm·s^{-1}, respectively, and the $\Gamma\pm$ values indicate that a unique Sn^{II} site is present in the complexes examined. The different R groups in the ligand may cause variations in the δ and Δ parameters: the electron-withdrawing nature of the R groups can influence the polarity of the Sn−O bond and the 5s electron density at the tin nucleus. Moreover, the R substituents can affect steric hindrance giving rise to a greater degree of distortion in the coordination sphere of the tin atom. In any case, the small variation observed may be indicative of the same type of coordination to the Sn^{II} atom. In any case, the small variation observed in the δ values may be indicative of a poor influence of electron-withdrawing groups of acylpyrazolonate donors.

Table 2. δ and Δ ranges in β-oxo enolates of Sn^{II}

Complex	δ	Δ	Ref.
Sn^{II}−Q ligand	2.99−3.36 (0.37)	1.68−1.98 (0.30)	this work
Sn^{II}−acac	2.92−3.60 (0.68)	1.66−2.21 (0.55)	[42]
Sn^{II}−β-oxo enolate	2.91−3.31 (0.40)	1.80−2.25 (0.45)	[43]

By comparing the Mössbauer parameter values with those of parent β-oxo enolates of Sn^{II} [42,43,53] and adopting the fingerprint method as a criterion of inferring structural arrangements (Table 2), a tin complex having four oxygen atoms from two molecules of the ligand in a trigonal-bipyramidal geometry can be assigned, with the lone pair occupying an equatorial site.

Selected positive electrospray MS data of complexes **2**, **5**, **6** and **9** are reported in Table 3. In our case, since only charged species are transferred from solution to the gas phase, quantitative ESI-MS results do not represent the real relative distribution of the species in solution. However, the data seem to indicate that, in solution, these derivatives can undergo loss of the anionic pyrazolonate ligands, which immediately interact with protons or sodium ions, yielding mono-charged species such as $[H_2Q]^+$ or $[Na(HQ)]^+$. The presence of Na adducts is typical of ESI mass spectra, due to the fact that the O-donor immediately interacts and aggregates with the small quantity of alkali metal ions present in the solvents. The possibility of interaction in solution is strongly dependent on the nature of the ligands. In some cases aggregation of Sn and Q in acetonitrile is significant even at 10^{-3} M, with smaller aggregates such as $[Sn(Q)]^+$, $[NaSn(Q)_2]^+$, $[Sn_2(Q)_3]^+$ being dominant over larger adducts. Some minor peaks present in the spectra of **2** and **5** are due to the interaction of the SnQ_2 species with K^+ or H^+. The isotopic distribution of these species is in agreement with the calculated composition.

The absence of ions containing MeCN indicates no binding between the solvent and Sn. In the ESI mass spectra of the same complexes, recorded in the negative detection mode, the predominant peak is always that due to the anionic ligand $[Q]^-$. In some cases, peaks due to association of two $(Q)^-$ ligands with one Na^+ cation were also identified. Interestingly, all spectra exhibit peaks due to $SnCl_3^-$, $Sn(Q)Cl_2^-$, $KSn(Q)Cl_3^-$, and $Sn(Q)_2Cl^-$: all species containing Cl from the solvent.

Table 3. Selected ESI-MS data for the compounds **2**, **5**, **6**, **9** and **21**−**23**

Compound[a]	FW	H_2Q^+	HQ + Na^+	$(Q)_2M$ + H^+	$(Q)_2M$ + Na^+	$[(Q)_3M_2]^+$	$[SnCl_3]^-$	$(Q)^-$	$SnO(Q)^-$	$SnCl_2Q^-$	$[KSnCl_3Q]^-$
$Sn(Q^T)_2$ (**2**)	661.37	273 [5]	295 [3]	662 [20]	685 [100]	1049 [18]	225 [15]	271 [100]	406 [5]	461 [18]	
$Sn(Q^B)_2$ (**3**)	633.31		281 [100]	634 [15]	656[50]			257 [100]	392 [5]		
$Sn(Q^W)_2$ (**5**)	785.51	334 [5]			786 [60]		225 [75]	333 [100]	467 [60]	523 [60]	592 [50]
$Sn(Q^L)_2$ (**6**)[b]	701.35		315 [10]		724 [5]			291 [100]			
$Sn(Q^S)_2$ (**8**)	853.54	369 [10]	391[100]	854 [10]	876 [5]			367 [100]	502 [45]	557 [15]	
$Sn(Q^N)_2$ (**9**)	763.29		356 [100]		764 [5]			322 [100]	457 [10]		
$Sn(Q^P)_2$ (**12**)	797.44		363 [100]	798 [10]	820 [30]	916 [50]		339 [100]			
$Pb(Q^w)_2$ (**21**)[c]	874.02		357 [100]					333 [100]			
$Pb(Q^D)_2$ (**22**)[d]	513.52					873 [100]		153 [100]			
$Pb(Q^D)_2$(phen) (**23**)[e]	665.72		186 [5]					153 [100]			

[a] Relative intensity in square brackets; FW = calculated molecular weight. [b] A peak at *m/z* = 605 is assigned to the species $[(Q)_2Na]^-$. [c] Other peaks: 691 [20] $[(HQ)_2Na]^+$, 1119 [10] $[(Q)_2Pb_2Cl]^+$, 1771 [100] $[(Q)_4Pb_2Na]^+$. [d] A peak at *m/z* = 360 [30] is assigned to the species $[(Q)Pb]^+$. [e] A peak at *m/z* = 542 [100] is assigned to the species $[(Q)Pb(Phen)]^+$.

The crystal structure of bis{3-methyl-1-phenyl-4-(phenylacetyl)pyrazolon-5-ato}tin(II) (**6**) consists of discrete molecules with no additional interactions besides those due to van der Waals forces. The tin atom lies on a crystallographic twofold axis. Table 4 shows selected bond lengths and angles for this molecule. Each tin atom is bound to four oxygen atoms from the two 4-acyl-5-pyrazolonato ligands (Figure 3). These four oxygen atoms are located on one side of the tin atom due to the presence of a stereochemically active lone pair on the opposite side. Generally, the 4-acyl-5-pyrazolonato ligands form a short metal−O(pyrazolonato) bond compared to the longer metal−O(acyl) bond. This is also the case here as the Sn1−O1 distance is 2.125(7) Å and the Sn1−O2 distance is 2.334(7) Å. The geometry at the tin atom is a distorted trigonal bipyramid with an axial O2−Sn−O52 bond angle of 146.2(3)°; such distortion from 180° is due to the presence of a lone pair and the chelating features of the ligand. The O1−Sn−O51 angle of 89.2(3)° also shows significant deviation from the ideal value of 120° due to the lone pair. This structure is similar to that of bis(4-acetyl-3-methyl-1-phenylpyrazolon-5-ato)tin(II), which has been determined crystallographically both as the pure complex[40] and as a methanol solvate,[54] although neither shows a twofold axis as for **6**. The structural parameters in the coordination sphere of all three structures are similar, as shown in Table 5.

Table 4. Selected bond lengths [Å] and angles [°] for $Sn(Q^L)_2$

Bond lengths	
Sn−O1	2.125(7)
Sn−O2	2.334(7)
O1−C5	1.27(1)
O2−C6	1.25(1)
N1−C5	1.36(1)
N1−C7	1.43(1)
Bond angles	
O2−Sn−O1	80.4(3)
O1−Sn−O1′	89.2(3)
O1−Sn−O2′	75.9(3)
O2−Sn−O2′	146.2(3)
C5−O1−Sn	128.7(5)
C6−O2−Sn	130.3(5)
Torsion angles	
O5−N1−C7−C8	−13.8

The existence of two very different sets of Sn−O bond lengths in "SnO_4" compounds is also observed in other Sn^{II} β-diketonates and is not limited to compounds with asymmetric ligands. An analysis of compounds found in the Cambridge Database is shown in Figure 4. The lower left side of the graph shows the Sn−O(primary) bond and the upper right side shows the Sn−O(secondary) bond. For each "SnO_4" compound the Sn−O(primary) and Sn−O(secondary) bonds are associated with small O(primary)−Sn−O(primary) and wide O(secondary)−Sn−O(secondary) bond angles. The title compound is circled in Figure 4 and fits the trend as well. It is of interest to note the unique species located at the center of the graph — pentane-1,5-diaminium bis(oxalato)tin(II) — the only one showing four equal Sn−O bonds (2.21 Å) and four equal O−Sn−O bond angles (120°).[55]

$Sn(Q^T)_2$ (**2**) reacts with methyl iodide or ethyl iodide to afford $[SnMeI(Q^T)_2]$ (**16**) and $[SnEtI(Q^T)_2]$ (**17**), respectively (Scheme 2). Compounds **16** and **17** are air- and moisture-stable, and soluble in DMSO, acetone, aromatic and chlorohydrocarbon solvents, where they are non-electrolytes. Their IR spectra exhibit new bands in the range 500−600 cm^{-1} due to ν(Sn−C) and below 250 cm^{-1} caused by ν(Sn−I). Their ^1H NMR spectra show a multiplicity of broad resonances in accordance with the presence of several isomers in solution, as previously found for $SnRCl(Q)_2$-type derivatives.[52,56,57] Accordingly, the resonances in the ^{13}C NMR spectra are very broad and in the ^{119}Sn NMR spectra four (**17**) and five absorptions (**16**) are found in the range $\delta = -400$ to -700 ppm.[52,56,57]

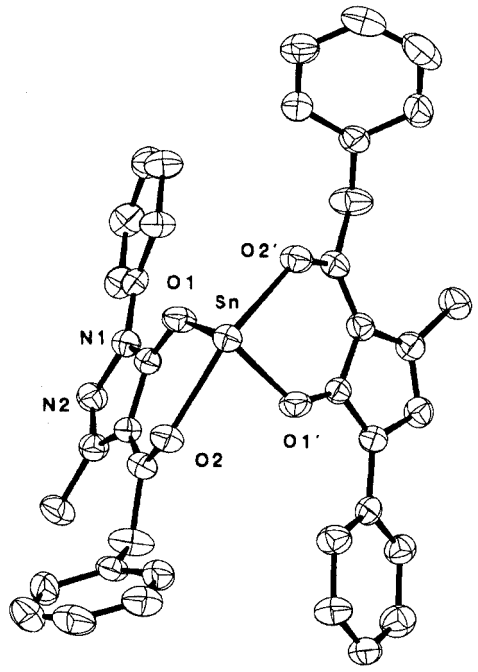


Figure 3. X-ray molecular structure of $Sn(Q^L)_2$ (**6**)

Compound **2** also reacts with $Cr(CO)_6$ in toluene to afford, upon irradiation, the novel derivative $[Cr(CO)_5Sn(Q^T)_2]$ (**18**; Scheme 2). Derivative **18** is the first example of a bis(acylpyrazolonato)tin(II) fragment acting as a Lewis base able to replace a CO ligand by donation of the lone pair to a $Cr(CO)_5$ fragment. This compound is stable in air and soluble in several organic solvents like DMSO, acetone, alcohols, aromatics and chlorohydrocarbons.

The IR spectrum of **18** shows several absorption bands in the metal−carbonyl stretching region at $\tilde{\nu}$ = 2059, 1947 and 1880 cm^{-1}. The second band is more intense than the others, in accordance with "local" C_{4v} symmetry for the $Cr(CO)_5$ fragment.[58] The ν(C=O) band of the acylpyrazolonato undergoes an upfield shift from $\tilde{\nu}$ = 1605 to 1610 cm^{-1} and in the far-IR region the ν(Sn−O) band shows a small downfield shift, indicating a lowering of the Sn−O bond strength.

The ^1H and ^{13}C NMR spectra of derivative **18** show one set of broad resonances, where the acyl fragment is shielded with respect to starting derivative **2**. The observed NMR and IR trends can be ascribed to the presence of back-donation Cr→Sn (*d*→*d*) π-bonding, as previously hypothesized for similar compounds.[59]

Table 5. X-ray structural parameters in the coordination sphere of bis(4-acyl-5-pyrazolon-5-ato)tin(II)

	R^1 = Ph, R^3 = R^4 = Me[40]	R^1 = Ph, R^3 = R^4 = Me; methanol solvate[54]	R^1 = Ph, R^3 = Me, R^4 = CH_2−Ph $Sn(Q^L)_2$ **6** [this work]
Sn−O1	2.141(5)	2.144(6)	2.125(7)
Sn−O2	2.296(6)	2.260(6)	2.334(7)
Sn−O1′	2.133(5)	2.149(7)	2.125(7)
Sn−O2′	2.313(6)	2.365(7)	2.334(7)
O1−Sn−O1′	86.7(2)	91.1(2)	89.2(3)
O2−Sn−O2′	149.8(2)	145.3(2)	146.2(3)

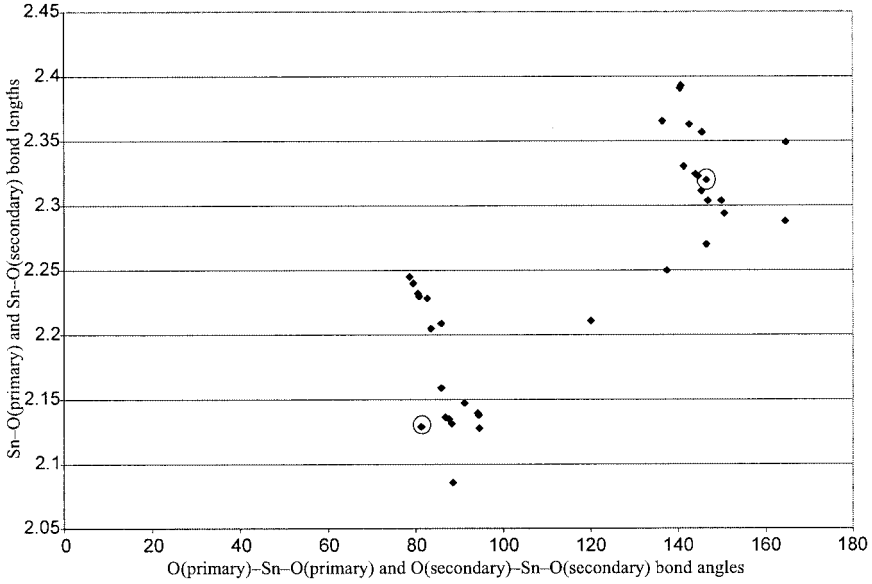
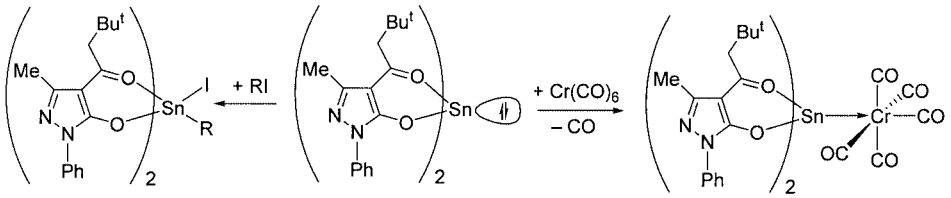


Figure 4. Selected structural parameters in "SnO_4" compounds



16 R = Me
17 R = Et

18

Scheme 2

By interaction of selected HQ proligands (HQ = HQ^B, HQ^T, HQ^W, HQ^D) with lead(II) nitrate in methanol, and in the presence of sodium methoxide, the air- and moisture-stable derivatives PbQ_2 **19**–**22** formed as precipitates (Scheme 1). They are pale-yellow solids with sharp melting points, soluble in DMSO, acetone and chlorohydrocarbon solvents, where they are non-electrolytes. Molecular weight determinations carried out in chloroform suggest aggregation in solution, as the experimental molecular weight is always higher than that expected for monomeric compounds. This observation is supported by the crystallographic results described below.

The IR and NMR spectra have features similar to those found in the tin(II) species. Interestingly, the number of signals and the chemical shift at room temperature do not seem to depend on the nature of the metal. However the low-temperature ^{1}H NMR spectrum of **20** suggests that there is no fluxionality at 183 K, as three sharp signals are seen for each equivalent group of protons.

The reactivity of derivative Pb(Q^D)$_2$ (**22**) was tested toward 1,10-phenanthroline, giving **23**. The ^{1}H NMR spectrum of **23** shows all the expected resonances for phen and for the pyrazolone protons in a 1:2 ratio. The ^{13}C NMR spectrum further confirms the existence and stability of compound **23** in chlorohydrocarbon solution, with no evidence of dissociation for either Q^D and phen ligands. However, the crystalline stability of **23** is lower than that of **19**–**22**. In fact, it has no sharp melting point and its decomposition starts at 156 °C, in accordance with a weak interaction of the {Pb(Q^D)$_2$} moiety with phen, probably due to the presence of the lead(II) lone pair.

Attempts to synthesize phen derivatives of lead(II) and tin(II) with other acylpyrazolonates failed, even under extreme reaction conditions, such as prolonged stirring and warming. Since these acylpyrazolonates contain bulky R^1 and R^4 groups (different from methyl in Q^D) we conclude that steric factors explain such a difference.

The ESI mass spectra of **21** and **22** exhibit peaks not only due to [H$_2$Q]$^+$ and [Na(HQ)]$^+$, but also due to [Pb(HQ)$_2$Cl]$^+$ and [NaPb$_2$(Q)$_4$]$^+$ species. The latter is particularly interesting since it suggests the possibility of aggregation between two different mononuclear lead species in solution. More surprisingly, the ESI mass spectrum of **23** exhibits a peak due to [Pb(Q)(phen)]$^+$, which is indicative of a strong interaction between Pb(Q)$_2$ and phen.

Table 6. Selected bond lengths [Å] and angles [°] for Pb(Q^B)$_2$

Bond lengths	
Pb–O1	2.274(6)
Pb–O2	2.56(1)
Pb–O51	2.324(7)
Pb–O52	2.38(1)
Pb–N2′	2.961(8)
Pb–O51′′	3.055(7)
O1–C5	1.29(1)
O2–C6	1.23(1)
O51–C55	1.27(1)
O52–C56	1.23(1)
N1–C5	1.37(1)
N1–C7	1.42(1)
N51–C55	1.36(1)
N51–C57	1.42(2)
Bond angles	
O2–Pb–O1	72.1(3)
O51–Pb–O1	82.1(2)
O51–Pb–O2	143.7(4)
O52–Pb–O1	86.6(3)
O52–Pb–O2	80.8(3)
O52–Pb–O51	72.4(3)
O1–Pb–O51′′	157.8(2)
O2–Pb–O51′′	112.1(4)
O51–Pb–O51′′	83.4(3)
O1–Pb–N2′	81.4(2)
O2–Pb–N2′	107.3(2)
O51–Pb–N2′	72.4(2)
O51′′–Pb–N2′	116.1(2)
O52–Pb–N2′	162.4(3)
C5–O1–Pb	118.6(5)
C6–O2–Pb	131.3(7)
C55–O51–Pb	127.5(7)
C56–O52–Pb	137.6(6)
Torsion angles	
O1–N1–C7–C12	–23.4.
O51–N51–C57–C62	48.9

A crystallographic study of bis(3-methyl-1-phenyl-4-pivaloylpyrazolon-5-ato)lead(II), Pb(Q^B)$_2$ (**19**), shows no imposed symmetry (Figure 5). Table 6 shows selected structural data for this species. Similar to the tin compound **6**, each metal atom is bound to four oxygen atoms from the two Q^B ligands. The general pattern seen in metal 4-acyl-5-pyrazolonate compounds is also followed as the

Pb1−O1[O51](pyrazolonato) bond length is 2.274(6) Å [2.324(7) Å] and the Pb1−O2[O52](acyl) bond length is 2.56(1) Å [2.38(1) Å]; that is, the former is shorter. Both Q^B ligands are in a *syn* configuration — equivalent ligand substituents (for instance R^1 = Ph) are on the same side, whereas in the tin compound **6** they are opposite (*anti* configuration).

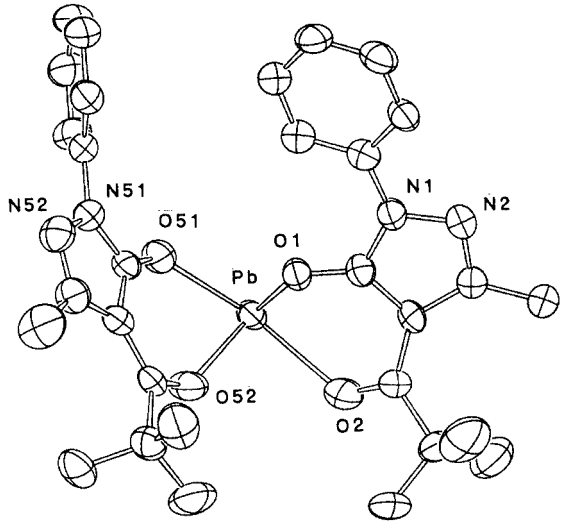


Figure 5. Atomic arrangement of the moiety $Pb(Q^B)_2$ (**19**)

The four oxygen atoms are located on one side of the lead atom, suggesting the presence of a stereochemically active lone pair as for **6**. However, unlike compound **6**, there are two additional atoms bound to the metal atom: N2′ [Pb1−N2′ = 2.961(8) Å], which belongs to the neighboring crystallographic unit (−*x*, −*y* + 2, −*z* + 1), and O51′′ [Pb1−O51′′ = 3.055(7) Å] of the unit (−*x* + 1, −*y* + 2, −*z* + 1; see Figure 6). These lead interactions suggest the metal coordination number to be six with a distorted octahedral geometry, because of departure from ideal *cis* angles of 90° [range from 72.1(3)° (O1−Pb1−O2) to 116.1(2)° (N2′−Pb1−O51′′)]. The latter wide *cis* bond angle and the corresponding long Pb−N2′ and Pb−O51′′ lengths indicate the presence of a stereochemically active lone pair in that area. Another factor contributing to octahedral distortion is the bent chelate ring (containing O1 and O2) that allows its attached pyrazole ring to stack with the pyrazole ring linked to another unit (of O1′ and O2′) at about 3.6 Å.

The linear polymeric structure propagates along the *a* axis in *anti*-parallel chains, and the hydrophobic region is located near the central area of the unit cell.

Bis(4-*tert*-butyl-3-methyl-1-phenylacetylpyrazolon-5-ato)lead(II), $Pb(Q^T)_2$ (**20**), was also studied using X-ray crystallographic methods (Figure 7) and shows no imposed symmetry on the molecular structure. Selected bond lengths and angles can be found in Table 7. As in compound **19**, a number of intermolecular interactions contribute to make the geometry of the lead atom distorted octahedral (Figure 8). They are different than in **19** and involve the nitrogen atom of one unit [Pb−N2′ = 3.121(6) Å] and a phenyl ring of another unit, with Pb−C bond lengths in the range 3.57−3.70 Å. The latter interaction is similar to that of bis(tetraphenyldithioimidodiphosphinato)lead(II), where the Pb−phenyl ring distances are in the range 3.07−3.31 Å.[60]

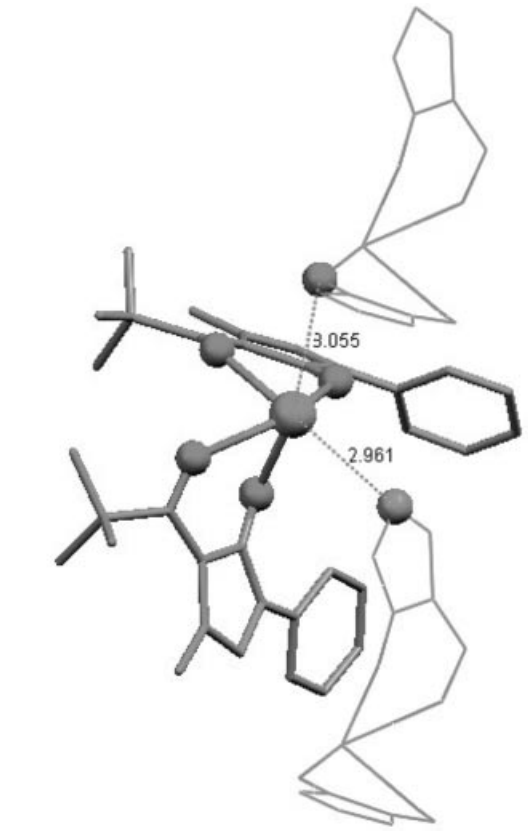


Figure 6. Whole coordination sphere for the polymeric chain of $Pb(Q^B)_2$ (**19**); Pb and its 6 bound atoms are depicted in ball-and-stick style, the 2 Q^B ligands bound at short distances as capped stick (shown also in Figure 5), and the 2 ligands bound at longer distances as wire frame [Pb−N2′ = 2.961(8) Å and Pb−O51′′ = 3.055(7) Å]

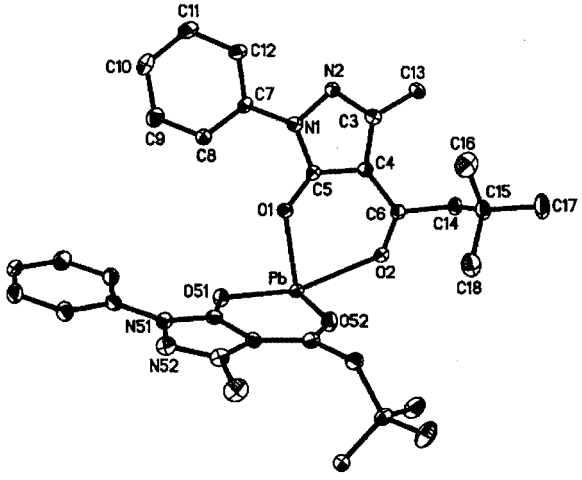


Figure 7. Atomic arrangement of the moiety $Pb(Q^T)_2$ (**20**)

A similar interaction is present in $[Pb(1,2\text{-}C_6H_4Me_2)_2\text{-}(AlCl_4)_2]$ where the Pb−C(phenyl) distances are in the range 3.30−4.48 Å.[61] Therefore, compound **20** shows the best η^6-Pb−phenyl interaction.

Tsble 7. Selected bond lengths [Å] and angles [°] for $Pb(Q^T)_2$

Bond lengths	
Pb−O1	2.379(9)
Pb−O2	2.360(8)
Pb−O51	2.280(7)
Pb−O52	2.458(7)
Pb−N2′	3.121(6)
Pb−C7′′	3.698(7)
Pb−C8′′	3.656(8)
Pb−C9′′	3.595(8)
Pb−C10′′	3.573(8)
Pb−C11′′	3.599(8)
Pb−C12′′	3.665(8)
O1−C5	1.26(1)
O2−C6	1.25(2)
O51−C55	1.28(1)
O52−C56	1.24(1)
N1−C5	1.36(2)
N1−C7	1.40(1)
N2−C3	1.30(1)
N51−C55	1.37(1)
N51−C57	1.41(1)
N52−C53	1.32(1)
Bond angles	
O2−Pb−O1	76.2(3)
O51−Pb−O1	139.7(3)
O51−Pb−O2	77.2(3)
O52−Pb−O1	76.6(3)
O52−Pb−O2	93.3(3)
O52−Pb−O51	75.3(2)
C5−O1−Pb	128.6(5)
C6−O2−Pb	137.1(5)
C55−O51−Pb	126.4(6)
C56−O52−Pb	133.4(5)
Torsion angles	
C5−N1−C7−C8	−0.5.
C55−N51−C57−C62	−7.2

As mentioned previously, 4-acyl-5-pyrazolonato ligands typically form a short metal−O(pyrazolonato) bond and a long metal−O(acyl) bond. In $Pb(Q^T)_2$ one ligand is consistent with this pattern as the Pb−O51(pyrazolonato) bond is 2.280(7) Å and the Pb−O52(acyl) bond is 2.458(7) Å. However, the other ligand is not since the Pb−O1(pyrazolonato) bond of 2.379(9) Å is longer than the Pb−O2(acyl) bond of 2.360(8) Å. This longer Pb−O(pyrazolonato) bond can be explained as this ligand contains the phenyl ring that interacts with the lead atom in a neighboring unit.

An investigation of "PbO_4" complexes in the CSD database shows that they have different packing arrangements with neighboring molecules in the solid. Only one "PbO_4" species, bis(dipivaloylmethanato)lead(II), has no interactions with the neighboring units, much like the "SnO_4" compounds described above, with both chelating ligands on the lead atom bent away from the stereochemically active lone pair.[62][63] The two bulky *t*Bu substituents on the symmetrical β-diketonato ligand probably prevent Pb from having a high coordination number. In general, the intermolecular interactions seen in other "PbO_4" compounds are not found in the similar "SnO_4" species. This is presumably due to the larger covalent radius of Pb allowing for a higher coordination number. Lead commonly interacts with nitrogen and oxygen ligands. For instance, the lead atom in bis(4-butanoyl-3-methyl-1-phenylpyrazolonato)lead(II), besides covalent bonds to the four oxygen atoms of the two chelating ligands, shows intermolecular interactions with lone pairs from two N atoms of neighboring units.[64] This interaction gives the lead atom a distorted octahedral geometry and allows for the molecules in the crystal to arrange in a polymeric chain. Another example is in *catena*-[bis(μ_2-1,1,1-trifluoro-5,5-dimethylhexane-2,4-dionato-*O*,*O*′)lead(II), where each Pb atom interacts with two oxygen atoms from neighboring units,[65] leading to a "PbO_6" system. The structure of bis(4-acetyl-3-methyl-1-phenylpyrazolon-5-ato)lead(II) is a trinuclear species that contains intermolecular interactions with two nitrogen atoms from a second ligand, and one oxygen atom from a third ligand.[64] Another variation is the formation of dinuclear compounds instead of polynuclear chains, as in bis(2,2-dimethyl-6,6,7,7,8,8-heptafluorooctane-3,5-dionato)lead(II) where the lead atoms stabilize a skewed geometry.[63]

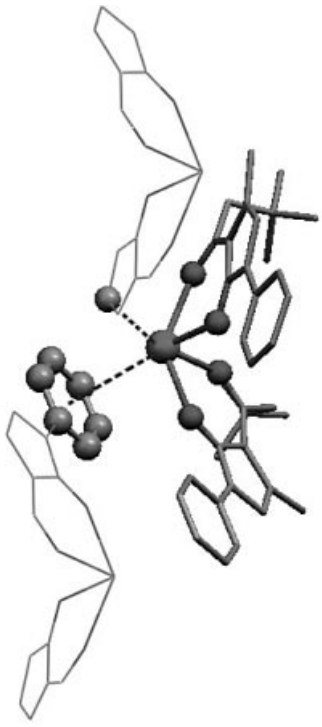


Figure 8. Whole coordination sphere for the polymeric chain of $Pb(Q^T)_2$ (**20**); Pb and its bound atoms are depicted in ball-and-stick style, the 2 Q^T ligands bound at short distances as capped stick (also shown in Figure 7), and the 2 ligands bound at longer distances as wire frame [Pb−N2′ = 3.121(6) Å and Pb−Ph′′ range = 3.55−3.70 Å]

In summary, Pb compounds **19** and **20** both contain a lead atom having coordination number 6 and interacting with atoms in neighboring units. Compound **19** is novel because this chain-like structure has a central PbQ_2 unit interacting on one side with a nitrogen atom from a second unit, and on the other side with an oxygen atom from a third unit; compound **20** shows an intermolecular interaction between the lead atom and all six C atoms of a phenyl ring.

Conclusion

4-Acyl-5-pyrazolones, HQ, form MQ_2 compounds for M = Sn^{II} and Pb^{II} that differ markedly in their structural features. Both Q ligands have an *anti* configuration on the tin atom and *syn* configuration on the lead atom. The tin compounds are mononuclear and have a trigonal-bipyramidal metal geometry, distorted by the metal lone pair located in the equatorial plane. The lead compounds show an increased coordination number, forming polynuclear compounds of varied structure. In this work a Pb−arene interaction has been found in $Pb(Q^T)_2$, whereas there is no such interaction in $Pb(Q^B)_2$. Such a dramatic structural change probably arises due to steric reasons, as the addition of a CH_2 moiety in the peripheral area of the Q^B acyl group makes this ligand equal to Q^T.

Ligand substitution is important if additional ligands are to be included in the coordination sphere of lead(II). Thus, the only PbQ_2 derivative able to react with phen is with Q = Q^D, a ligand containing R^1 = Me, in contrast with those that are not reactive and having R^1 = Ph.

The lone pair in SnQ_2 derivatives can be donated to, for instance, carbonylchromium derivatives stabilizing a Cr−Sn bond.

Experimental Section

General Remarks: 3-Methyl-1-phenylpyrazolon-5-one, *N*-methylhydrazine, *N*-(4-nitrophenyl)hydrazine, ethyl acetoacetate, ethyl benzoyl acetate, potassium hydroxide, sodium methoxide, tin(II) dichloride and the acyl chlorides employed (benzoyl chloride, acetyl chloride, cyclohexanecarbonyl chloride, pivaloyl chloride, *tert*-butylacetyl chloride, phenylacetyl chloride, diphenylacetyl chloride, propionyl chloride, ethanoyl chloride, 4-*tert*-butylbenzoyl chloride) were purchased from Aldrich (Milwaukee) and used as received. Solvent evaporations were always carried out under vacuum by using a rotary evaporator. The samples for microanalysis were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr). All syntheses were carried out under nitrogen. Hydrocarbon solvents were dried by distillation from sodium/potassium; dichloromethane was distilled from calcium hydride. All solvents were degassed with dry nitrogen prior to use. Elemental analyses (C, H, N) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. IR spectra were recorded from 4000 to 200 cm^{-1} with a Perkin−Elmer System 2000 FT-IR instrument. ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR spectra were recorded with a VXR-300 Varian instrument (300 MHz for ^1H, 75 MHz for ^{13}C, 282.2 MHz for ^{19}F and 111.8 MHz for ^{119}Sn). The chemical shifts (δ) are reported in parts per million (ppm) from $SiMe_4$ (^1H and ^{13}C), $CFCl_3$ (^{19}F) or $SnMe_4$ (^{119}Sn); relative intensity (%) in square brackets. Melting points are uncorrected and were measured with an SMP3 Stuart scientific instrument and with a capillary apparatus. The electrical conductivity measurements (Λ_m, reported as $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$) of dichloromethane or DMSO solutions of complexes **1**−**23** were recorded with a Crison CDTM 522 conductimeter at room temperature. Molecular weight determinations (MW) were performed at 40 °C with a Knauer KNA0280 vapour pressure osmometer calibrated with benzil; the solvent was Baker Analysed Spectrophotometric grade chloroform. The results were reproducible to ±2%. ^{119m}Sn Mössbauer spectra were recorded on solid samples at liquid nitrogen temperature by using a conventional constant acceleration spectrometer, coupled with a multichannel analyser [a.e.n., Ponteranica (BG), Italy] equipped with a cryostat Cryo (RIAL, Parma, Italy). A $Ca^{119}SnO_3$ Mössbauer source, 10 mCi (from Ritverc, St. Petersburg, Russia) moving at room temperature with constant acceleration in a triangular waveform was used. The velocity calibration was made using a ^{57}Co Mössbauer source, 10 mCi, and an iron foil as absorber (from Ritverc, St. Petersburg, Russia). The 4-acyl-5-pyrazolones (here indicated as QH) were synthesized by the procedure reported by Jensen[66] or by our previous methods.[30−40]

$Sn(Q^C)_2$ (1): Potassium hydroxide (0.112 g, 2.0 mmol) and tin(II) dichloride (0.190 g, 1 mmol) were added to a methanol solution (30 mL) of Q^CH (0.566 g, 2 mmol). A colorless precipitate formed immediately. After 1 h, it was filtered off, washed with methanol (10 mL) and recrystallized from chloroform/methanol. Yield 0.603 g (88%). M.p. 166−169 °C. $C_{34}H_{38}N_4O_4Sn$ (685.4): calcd. C 59.58, H 5.59, N 8.17; found C 59.33, H 5.83, N 8.23. Λ_m (CH_2Cl_2, 1 × 10^{-3} M) = 0.1. MW ($CHCl_3$, c = 1.5 × 10^{-3} mol/L): 668. IR (nujol): $\tilde{\nu}$ = 1604 vs, 1593 vs ν(C=O), 451 s, 399 s ν(Sn−O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.20−1.90 (m), 2.78 [t, 11 H, C(=O)-C_6H_{11}], 2.28 (s, 3 H, 3-CH_3), 7.15 (t), 7.38 (t), 7.72 (d, 5 H, NC_6H_5) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.1 (s, 3-CH_3), 26.0, 26.1, 29.7, 46.6 [s, C(=O)C_6H_{11}], 103.9 (s, C-4), 121.5, 125.8, 128.7, 138.2 (s, C_{arom}), 148.1 (s, C-3), 161.6 (s, C-5), 199.9 (s, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −727.5 ppm.

$Sn(Q^T)_2$ (2): Compound **2** was synthesized as described for compound **1**. Yield 0.622 g (94%). M.p. 140−142 °C. $C_{32}H_{38}N_4O_4Sn$ (661.4): calcd. C 58.11, H 5.79, N 8.47; found C 58.25, H 5.65, N 8.49. Λ_m (CH_2Cl_2, 1 × 10^{-3} M) = 0.2. MW ($CHCl_3$, c = 1.6 × 10^{-3} mol/L): 659. IR (nujol): $\tilde{\nu}$ = 1605 vs, 1593 vs ν(C=O), 452 s, 439 s, 391 s ν(Sn−O) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ = 1.05 [s, 9 H, C(=O)$CH_2C(CH_3)_3$], 2.27 (s, 3 H, 3-CH_3), 2.50 [s, 2 H, C(=O)$CH_2C(CH_3)_3$], 7.18 (t), 7.33 (t), 7.75 (d, 5 H, NC_6H_5) ppm. ^1H NMR (CD_2Cl_2, 183 K): δ = 0.93 [br. s, 9 H, C(=O)-$CH_2C(CH_3)_3$], 1.92 (br. s), 2.21 (br. s, 3 H, 3-CH_3), 2.40 (br. s), 2.56 [br. s, 2 H, C(=O)$CH_2C(CH_3)_3$], 7.15 (br. t), 7.33 (br. t), 7.67 (br. d, 5 H, NC_6H_5) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.8 (s, 3-CH_3), 30.2 [s, C(=O)$CH_2C(CH_3)_3$], 32.1 [s, C(=O)$CH_2C(CH_3)_3$], 50.6 [s, C(=O)$CH_2C(CH_3)_3$], 106.4, (s, C-4), 121.1, 125.6, 128.6, 138.0 (s, C_{arom}), 148.2 (s, C-3), 161.2 (s, C-5), 195.8 (s, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −726.9 ppm.

$Sn(Q^B)_2$ (3): Compound **3** was synthesized as described for compound **1**. Yield 0.430 g (68%). M.p. 198−200 °C. $C_{30}H_{34}N_4O_4Sn$ (633.3): calcd. C 56.90, H 5.41, N 8.85; found C 56.58, H 5.50, N 8.61. Λ_m (CH_2Cl_2, 1 × 10^{-3} M) = 0.6. MW ($CHCl_3$, c = 1.6 × 10^{-3} mol/L): 594. IR (nujol): $\tilde{\nu}$ = 1602 vs, 1595 vs ν(C=O), 475 vs, 446 s, 411 m ν(Sn−O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.25 (s) [24], 1.39 (s) [2], 1.58 (s) [1] [9 H, C(=O)C(CH_3)$_3$], 2.40 (s) [24], 2.65 (s) [2], 2.72 (s) [1] (3 H, 3-CH_3), 7.16 (t), 7.30 (t), 7.45 (t), 7.73 (d), 7.85 (d, 5 H, NC_6H_5) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.2 (s, 3-

CH_3), 26.9 [s, C(=O)*C*(CH_3)$_3$], 27.9 [s, C(=O)C(*C*H_3)$_3$], 104.0, (s, C-4), 121.0 (*), 121.3, 125.6, 126.6 (*), 128.5, 129.0 (*), 135.8 (*), 138.1 (s, C_{arom}), 145.7 (s, C-3), 162.1 (s, C-5), 195.7 (s, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −754.4 ppm.

Sn(Q^E)$_2$ (4): Compound **4** was synthesized as described for compound **1**. Yield 0.500 g (87%). M.p. 152−154 °C. $C_{26}H_{24}N_4O_4Sn$ (575.2): calcd. C 54.29, H 4.21, N 9.74; found C 54.10, H 4.15, N 9.63. Λ_m (CH_2Cl_2, 1 × 10^{-3} M) = 0.1. MW ($CHCl_3$, c = 1.9 × 10^{-3} mol/L): 560. IR (nujol): $\tilde{\nu}$ = 1601 vs ν(C=O), 445 m, 426 s, 387 s ν(Sn−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.20 [t, 3 H, C(=O)-CH_2CH_3], 2.51 [q, 2 H, C(=O)CH_2CH$_3$), 2.16 (s, 3 H, 3-CH_3), 7.16 (t), 7.31 (t), 7.69 (d, 5 H, NC_6H_5) ppm. ^{13}C NMR ($CDCl_3$): δ = 8.63 [s, C(=O)CH_2CH_3], 17.1 (s, 3-CH_3), 32.6 [s, C(=O)-*C*H_2CH_3], 104.4, (s, C-4), 121.0, 125.6, 128.5, 138.0 (s, C_{arom}), 148.2 (s, C-3), 160.7 (s, C-5), 197.1 (s, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −723.4 ppm.

Sn(Q^W)$_2$ (5): Compound **5** was synthesized as described for compound **1**. Yield 0.495 g (63%). M.p. 229−231 °C. $C_{42}H_{42}N_4O_4Sn$ (785.5): calcd. C 64.22, H 5.39, N 7.13; found C 63.91, H 5.53, N 7.06. Λ_m (CH_2Cl_2, 1 × 10^{-3} M) = 0.4. MW ($CHCl_3$, c = 1.4 × 10^{-3} mol/L): 743. IR (nujol): $\tilde{\nu}$ = 1599 vs, 1592 vs ν(C=O), 436 m, 383 s ν(Sn−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.32 (s) [2], 1.38 (s) [10], 1.40 (s) [1] [9 H, C(=O)C_6H_5C(CH_3)$_3$], 1.72 (s) [10], 1.96 (s) [2], 2.05 (s) [1] (3 H, 3-CH_3), 7.14 (t), 7.18 (t), 7.35−7.60 (m), 7.75 (d), 7.79 (d), 7.97 [d, 9 H, NC_6H_5 and C(=O)C_6H_5C(CH_3)$_3$] ppm. ^{13}C NMR ($CDCl_3$): δ = 16.3, 16.5 (s, 3-CH_3), 31.1, 31.2 [s, C(=O)C_6H_5C(*C*H_3)$_3$], 35.1 [s, C(=O)C_6H_5*C*(CH$_3$)$_3$], 120.7, 120.8, 121.7, 121.8, 125.1, 125.3, 125.4, 126.5, 127.2, 128.0, 128.3, 128.6, 128.7, 128.8, 128.9, 129.1, 129.5, 136.2, 137.9 (s, C_{arom}), 149.0 (s, C-3), 155.2 (s, C-5) ppm; C-4 and CO signals not observed. ^{119}Sn NMR ($CDCl_3$): δ = −759.4 ppm.

Sn(Q^L)$_2$ (6): Compound **6** was synthesized as described for compound **1**. Yield 0.687 g (98%). M.p. 185−187 °C. $C_{36}H_{30}N_4O_4Sn$ (701.3): calcd. C 61.65, H 4.31, N 7.99; found C 61.45, H 4.42, N 7.82. Λ_m (CH_2Cl_2, 1 × 10^{-3} M) = 0.2. MW ($CHCl_3$, c = 1.5 × 10^{-3} mol/L): 688. IR (nujol): $\tilde{\nu}$ = 1604 vs, 1590 vs ν(C=O), 441 m, 433 m, 390 m ν(Sn−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.18 (s) [1], 2.24 (s) [6], 2.51 (s) [2] (3 H, 3-CH_3), 3.50 (s) [1], 3.78 (s) [6], 4.05 (s) [1] [2 H, C(=O)C$H_2C_6H_5$], 6.95 (t), 7.02−7.45 (m), 7.48 (t), 7.75 (d), 7.83 [d, 10 H, NC_6H_5 and C(=O)$CH_2C_6H_5$] ppm. ^{13}C NMR ($CDCl_3$): δ = 15.8, 16.9, 17.1 (s, 3-CH_3), 43.9, 44.2, 45.0 [s, C(=O)C$H_2C_6H_5$], 103.8, 104.8 (s, C-4), 120.6, 120.9, 121.3, 121.5, 125.5, 126.6, 126.9, 127.1, 128.1, 128.3, 128.4, 128.8, 129.0, 129.1, 132.5, 133.1, 134.2, 136.3, 137.7 (s, C_{arom}), 148.0, 148.8 (s, C-3), 161.1 (s, C-5), 192.9, 193.1 (s, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −738.6 ppm.

Sn(Q^R)$_2$ (7): Compound **7** was synthesized as described for compound **1**. Yield 0.678 g (78%). M.p. 157−160 °C. $C_{48}H_{54}N_4O_4Sn$ (869.7): calcd. C 66.29, H 6.26, N 6.44; found C 65.96, H 6.33, N 6.37. Λ_m (CH_2Cl_2, 1 × 10^{-3} M) = 0.4. MW ($CHCl_3$, c = 1.5 × 10^{-3} mol/L): 855. IR (nujol): $\tilde{\nu}$ = 1605 vs, 1583 s ν(C=O), 447 vs, 409 w, 387 m ν(Sn−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.88 [t, 3 H, C(=O)C_6H_4(CH$_2$)$_6$CH_3], 1.25−1.40 (m), 1.60 (m), 2.67 [t, 12 H, C(=O)C_6H_4(CH_2)$_6$CH$_3$], 1.65 (s, 3 H, 3-CH_3), 7.08 (t), 7.17 (t), 7.23 (d), 7.37 (d), 7.75 [d, 10 H, NC_6H_5 and C(=O)-C_6H_4(CH$_2$)$_6$CH$_3$] ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 [s, C(=O)-C_6H_4(CH$_2$)$_6$*C*H$_3$], 16.2 (s, 3-CH_3), 22.6, 29.1, 29.2, 31.2, 31.8, 36.0 [s, C(=O)C_6H_4(*C*H$_2$)$_6$CH$_3$], 105.5 (s, C-4), 120.8, 125.5, 128.2, 128.4, 128.6, 136.4, 138.0, 147.0 (s, C_{arom}), 149.1 (s, C-3), 161.8 (s, C-5), 191.2 (s, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −757.6 ppm.

Sn(Q^S)$_2$ (8): Compound **8** was synthesized as described for compound **1**. Yield 0.495 g (58%). M.p. 78−79 °C. $C_{48}H_{38}N_4O_4Sn$ (853.5): calcd. C 67.55, H 4.49, N 6.56; found C 67.12, H 4.50, N 6.48. Λ_m (CH_2Cl_2, 1 × 10^{-3} M) = 0.8. MW ($CHCl_3$, c = 1.5 × 10^{-3} mol/L): 812. IR (nujol): $\tilde{\nu}$ = 1610 vs, 1595 vs ν(C=O), 435 m, 426 m, 397 m ν(Sn−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.40 (s, 3 H, 3-CH_3), 5.63 [s, 1 H, C(=O)C*H*(C_6H_5)$_2$], 7.10−7.32 (m), 7.74 [d, 15 H, NC_6H_5 and C(=O)CH(C_6H_5)$_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 17.5 (s, 3-CH_3), 58.4 [s, C(=O)*C*H(C_6H_5)$_2$], 105.9 (s, C-4), 121.2, 125.8, 127.0, 127.5, 127.7, 127.9, 128.5, 128.7, 129.2, 129.7, 129.8, 137.9, 139.1 (s, C_{arom}), 148.0 (s, C-3), 162.2 (s, C-5), 193.2 (s, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −747.0 ppm.

Sn(Q^N)$_2$ (9): Compound **9** was synthesized as described for compound **1**. Yield 0.580 g (76%). M.p. > 350 °C. $C_{34}H_{24}N_6O_8Sn$ (763.2): calcd. C 53.50, H 3.17, N 11.01; found C 53.09, H 3.10, N 10.72. Λ_m (CH_2Cl_2, 1 × 10^{-3} M) = 0.2. MW ($CHCl_3$, c = 0.8 × 10^{-3} mol/L): 725. IR (nujol): $\tilde{\nu}$ = 1606 vs, 1589 s ν(C=O), 446 m, 433 m, 408 m ν(Sn−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 21.72 (s, 3 H, 3-CH_3), 7.51 (d), 7.63 (m), 7.96−8.15 [m, 9 H, $NC_6H_4NO_2$ and C(=O)C_6H_5] ppm. ^{13}C NMR ($CDCl_3$): δ = 16.3 (s, 3-CH_3), 103.4, (s, C-4), 119.4, 119.7, 124.4, 124.9, 128.2, 128.4, 128.5, 132.4 (s, C_{arom}) ppm; signals of C-3, C-5 and CO not observed. ^{119}Sn NMR ($CDCl_3$): δ = −789.5 ppm.

Sn(Q^M)$_2$ (10): Compound **10** was synthesized as described for compound **1**. Yield 0.351 g (64%). M.p. 165−168 °C. $C_{24}H_{22}N_4O_4Sn$ (549.1): calcd. C 52.49, H 4.04, N 10.20; found C 52.07, H 4.08, N 10.02. Λ_m (CH_2Cl_2, 1 × 10^{-3} M) = 0.2. MW ($CHCl_3$, c = 1.5 × 10^{-3} mol/L): 542. IR (nujol): $\tilde{\nu}$ = 1582 vs ν(C=O), 432 w, 411 m, 399 m ν(Sn−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.76 (s, 3 H, 3-CH_3), 3.33 (s, 3 H, NCH_3), 7.40−7.60 [m, 5 H, C(=O)C_6H_5] ppm. ^{13}C NMR ($CDCl_3$): δ = 16.3 (s, 3-CH_3), 31.7 (s, NCH_3), 104.3, (s, C-4), 120.7, 128.1, 128.5, 131.4, 139.5 (s, C_{arom}), 148.1 (s, C-3), 161.9 (s, C-5), 190.6 (s, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −734.7 ppm.

Sn(Q^D)$_2$ (11): Compound **11** was synthesized as described for compound **1**, with water as solvent. Yield 0.234 g (55%). M.p. 154−155 °C. $C_{14}H_{18}N_4O_4Sn$ (425.0): calcd. C 39.56, H 4.27, N 13.18; found C 39.88, H 4.16, N 12.78. Λ_m (CH_2Cl_2, 1 × 10^{-3} M) = 0.1. MW ($CHCl_3$, c = 1.8 × 10^{-3} mol/L): 412. IR (nujol): $\tilde{\nu}$ = 1578 vs ν(C=O), 454 m, 414 s, 396 s ν(Sn−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.31 (s, 3 H, 3-CH_3), 2.38 [s, 3 H, C(=O)CH_3], 3.27 (s, 3 H, NCH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.9 (s, 3-*C*H$_3$), 27.5 [s, C(=O)*C*H$_3$], 31.5 (s, NCH_3), 104.1 (s, C-4), 147.4 (s, C-3), 160.7 (s, C-5), 192.6 (s, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −701.6 ppm.

Sn(Q^P)$_2$ (12): Compound **12** was synthesized as described for compound **1**. Yield 0.598 g (75%). M.p. 245−248 °C. $C_{44}H_{30}N_4O_4Sn$ (797.4): calcd. C 66.27, H 3.79, N 7.03; found C 65.98, H 3.81, N 6.93. Λ_m (CH_2Cl_2, 1 × 10^{-3} M) = 0.4. MW ($CHCl_3$, c = 1.5 × 10^{-3} mol/L): 790. IR (nujol): $\tilde{\nu}$ = 1608 s, 1595 vs ν(C=O), 440 m, 399 m ν(Sn−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 6.88−7.22 (m), 7.33 (d), 7.51 (t), 7.78 (t), 7.90 (d), 7.95 (d), 8.12 [d, 15 H, NC_6H_5, C(=O)C_6H_5 and 3-C_6H_5] ppm. ^{13}C NMR ($CDCl_3$): δ = 103.6, (s, C-4), 121.2, 122.1, 126.1, 127.6, 127.7, 127.9, 128.8, 129.1, 129.4, 129.8, 130.3, 131.7, 133.3, 137.9, 138.3 (s, C_{arom}), 152.7 (s, C-3), 162.2 (s, C-5), 191.2 (s, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −768.8 ppm.

Sn(Q^G)$_2$ (13): Compound **13** was synthesized as described for compound **1**. Yield 0.444 g (66%). M.p. 207−209 °C. $C_{44}H_{30}N_4O_4Sn$ (673.3): calcd. C 60.65, H 3.89, N 8.32; found C 60.50, H 3.92, N 8.10. Λ_m (CH_2Cl_2, 1 × 10^{-3} M) = 0.2. MW ($CHCl_3$, c = 1.5 × 10^{-3} mol/L): 642. IR (nujol): $\tilde{\nu}$ = 1617 s, 1611 s ν(C=O), 452 m, 430 m, 416 m ν(Sn−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.96 (s), 2.18 [s, 3 H, C(=O)CH_3), 7.05−7.58 (m), 7.90 (d, 10 H, NC_6H_5 and 3-

C_6H_5) ppm. ^{13}C NMR ($CDCl_3$): δ = 28.0 [s, C(=O)CH_3], 105.3, (s, C-4), 121.2, 126.1, 128.5, 128.9, 129.0, 129.5, 134.2, 138.4 (s, C_{arom}), 152.8 (s, C-3), 160.6 (s, C-5), 194.9 (s, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −743.5 ppm.

Sn(Q^F)$_2$ (14): Compound **14** was synthesized as described for compound **1**. Yield 0.558 g (69%). M.p. 240−242 °C. $C_{36}H_{24}F_6N_4O_4Sn$ (809.3): calcd. C 53.43, H 2.99, N 6.92; found C 53.15, H 3.08, N 6.62. Λ_m (CH_2Cl_2, 1×10^{-3} M) = 0.1. Λ_m (DMSO, 1×10^{-3} M) = 13.0. MW ($CHCl_3$, $c = 1.7 \times 10^{-3}$ mol/L): 775. IR (nujol): $\tilde{\nu}$ = 1598 vs ν(C=O), 436 m, 428 m, 403 m ν(Sn−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.63 (s, 3 H, 3-CH_3), 7.40 (d), 7.45−7.65 (d), 7.98 [d, 9 H, $NC_6H_4CF_3$ and C(=O)C_6H_5] ppm. ^{13}C NMR ($CDCl_3$): δ = 15.9 (s, 3-CH_3), 104.9 (s, C-4), 119.8, 125.5, 125.6, 127.9, 128.1, 131.7, 132.4, 138.4, 140.3 (s, C_{arom}), 149.4 (s, C-3), 162.1 (s, C-5), 191.8 (s, CO) ppm; CF_3 signal not observed. ^{19}F NMR ($CDCl_3$): δ = −62.8 ppm. ^{119}Sn NMR ($CDCl_3$): δ = −775.2 ppm.

Sn(Q^H)$_2$ (15): Compound **15** was synthesized as described for compound **1**. Yield 0.562 g (82%). M.p. 267−270 °C. $C_{26}H_{10}F_6N_4O_4Sn$ (685.1): calcd. C 45.58, H 2.94, N 8.18; found C 45.45, H 2.88, N 8.18. Λ_m (CH_2Cl_2, 1×10^{-3} M) = 0.1. Λ_m (DMSO, 1×10^{-3} M) = 11.1. MW ($CHCl_3$, $c = 1.8 \times 10^{-3}$ mol/L): 670. IR (nujol): $\tilde{\nu}$ = 1620 s, 1607 s ν(C=O), 444 s, 438 m, 404 m ν(Sn−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.15 (s, 3 H, 3-CH_3), 2.31 [s, 3 H, C(=O)CH_3] 7.58 (d), 7.95 (d, 4 H, $NC_6H_4CF_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.8 (s, 3-CH_3), 27.7 [s, C(=O)CH_3], 104.5 (s, C-4), 120.2, 125.7, 125.8, 138.2 (s, C_{arom}), 148.2 (s, C-3), 162.4 (s, C-5), 192.2 (s, CO) ppm; CF_3 signal not observed. ^{19}F NMR ($CDCl_3$): δ = −62.7 ppm. ^{119}Sn NMR ($CDCl_3$): δ = −741.9 ppm.

SnMeI(Q^T)$_2$ (16): Compound **2** (0.661 g, 1 mmol) was dissolved in an excess of methyl iodide (30 mL). The mixture was stirred under reflux for 4 d. Removal of the unconverted methyl iodide under reduced pressure left a solid residue, which was recrystallized from chloroform/*n*-hexane and shown to be compound **16**. Yield 0.755 g (94%). M.p. 123−125 °C. $C_{33}H_{41}IN_4O_4Sn$ (803.3): calcd. C 49.34, H 5.14, N 6.97; found C 49.68, H 5.25, N 7.06. Λ_m (CH_2Cl_2, 1×10^{-3} M) = 0.3. IR (nujol): $\tilde{\nu}$ = 1600 vs, 1581 vs ν(C=O), 552 sh, 542 m ν(Sn−C), 470 s, 392 m ν(Sn−O), 225 s br. ν(Sn−I) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.95 (s), 1.00 (s), 1.14 (s), 1.18 [s, 18 H, C(=O)$CH_2C(CH_3)_3$], 1.35 (s, $^2J_{Sn,H}$ = 116.8 Hz), 1.48 (s, $^2J_{Sn,H}$ = 118.0 Hz), (s, 3 H, $SnCH_3$), 2.45 (s), 2.49 (s), 2.55 (s, 6 H, -3CH_3), 2.64 (s), 2.67 (s), 2.68 [s, 4 H, C(=O)$CH_2C(CH_3)_3$], 7.09 (br. m), 7.30 (br. m), 7.49 (br. t), 7.57 (br. m), 7.86 (br. d), 8.04 (br. d, 10 H, NC_6H_5) ppm. ^{13}C NMR ($CDCl_3$): δ = 9.9 (br. s, $SnCH_3$), 17.9 (br. s, 3-CH_3), 30.3 [br. s, C(=O)$CH_2C(CH_3)_3$], 33.0 [br. s, C(=O)-$CH_2C(CH_3)_3$], 50.5 [br. s, C(=O)$CH_2C(CH_3)_3$], 106.9 (br. s, C-4), 120.5, 121.3, 121.8, 126.5, 129.0, 137.3 (br. s, C_{arom}), 149.2 (br. s, C-3), 162.2 (br. s, C-5), 196.3 (br. s, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −496.4, −652.2, −663.3, −668.5, −677.2 ppm.

SnEtI(Q^T)$_2$ (17): Compound **17** was synthesized as for compound **16**, but with ethyl iodide. Yield 0.719 g (88%). M.p. 134−137 °C. $C_{34}H_{43}IN_4O_4Sn$ (817.3): calcd. C 49.96, H 5.30, N 6.85; found C 50.03, H 5.45, N 6.90. Λ_m (CH_2Cl_2, 1×10^{-3} M) = 0.5. IR (nujol): $\tilde{\nu}$ = 1600 vs, 1583 vs ν(C=O), 555 m ν(Sn−C), 465 m, 396 w ν(Sn−O), 220 s br. ν(Sn−I) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.94 (s), 1.00 (s), 1.02 (s), 1.16 [s, 18 H, C(=O)$CH_2C(CH_3)_3$], 1.24 (t), 1.28 (t), 2.62 (m), 2.67 (m, 5 H, $SnCH_2CH_3$), 2.37 (br. s, 6 H, 3-CH_3), 2.49 (br. s, 4 H, C(=O)$CH_2C(CH_3)_3$], 7.12 (br. m), 7.30 (br. m), 7.45 (br. t), 7.60 (br. m), 7.88 (br. d), 8.04 (br. d, 10 H, NC_6H_5) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.5, 32.9 (br. s, $SnCH_2CH_3$), 17.9 (br. s, 3-CH_3), 30.4 [br. s, C(=O)$CH_2C(CH_3)_3$], 32.1 [br. s, C(=O)-$CH_2C(CH_3)_3$], 50.6 [br. s, C(=O)$CH_2C(CH_3)_3$], 107.0 (br. s, C-4), 120.5, 121.2, 121.8, 126.4, 129.0, 137.4 (br. s, C_{arom}), 149.1 (br. s, C-3), 162.5 (br. s, C-5), 196.5 (br. s, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −614.1, −626.1, −631.0, −639.5 ppm.

Cr(CO)$_5$Sn(Q^T)$_2$ (18): Compound **2** (0.661 g, 1 mmol) was dissolved in a toluene solution (30 mL) of hexacarbonylchromium (0.220 g, 1 mmol). The mixture was irradiated and stirred under reflux for 4 d. Removal of the solvent under reduced pressure left a solid residue, which was recrystallized from chloroform/*n*-hexane and shown to be compound **18**. Yield 0.751 g (88%). M.p. 73−76 °C. $C_{37}H_{38}CrN_4O_9Sn$ (853.4): calcd. C 52.07, H 4.49, N 6.57; found C 52.45, H 4.61, N 6.88. Λ_m (CH_2Cl_2, 1×10^{-3} M) = 0.4. IR (nujol): $\tilde{\nu}$ = 2059 m, 1947 s, 1880 m ν(Cr−C≡O), 1610 vs, 1595 vs ν(C=O), 440 m, 433 m, 392 w ν(Sn−O) cm^{-1}. ^{1}H NMR ([D$_6$]benzene): δ = 1.05 [s, 9 H, C(=O)$CH_2C(CH_3)_3$], 2.20 (s, 3 H, 3-CH_3), 2.30 [s, 2 H, C(=O)$CH_2C(CH_3)_3$], 7.02 (t), 7.21 (t), 8.25 (d, 5 H, NC_6H_5) ppm. ^{13}C NMR ([D$_6$]benzene): δ = 16.1 (s, 3-CH_3), 30.0 [s, C(=O)$CH_2C(CH_3)_3$], 31.9 [s, C(=O)$CH_2C(CH_3)_3$], 49.6 [s, C(=O)$CH_2C(CH_3)_3$], 105.8 (s, C-4), 120.1, 126.1, 129.2, 138.3 (s, C_{arom}), 147.0 (s, C-3), 194.4 (s, CO) ppm; C-5 and Cr(*C*O) signals not observed. ^{119}Sn NMR ([D$_6$]benzene): δ = −377.2 ppm.

Pb(Q^B)$_2$ (19): Compound **19** was synthesized as described for compound **20** (see below). Yield 0.567 g (76%). M.p. 248−250 °C. $C_{30}H_{34}N_4O_4Pb$ (721.8): calcd. C 49.92, H 4.75, N 7.76; found C 49.62, H 4.90, N 7.77. Λ_m (CH_2Cl_2, 1×10^{-3} M) = 0.5. MW ($CHCl_3$, $c = 1.6 \times 10^{-3}$ mol/L): 950. IR (nujol): $\tilde{\nu}$ = 1600 vs, 1595 vs ν(C=O), 469 s, 434 m 412 vs, 386s ν(Pb−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.23 [s, 9 H, C(=O)$C(CH_3)_3$], 2.36 (3 H, 3-CH_3), 7.13 (t), 7.30 (t), 7.74 (d, 5 H, NC_6H_5) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.4 (s, 3-CH_3), 28.3 [s, C(=O)$C(CH_3)_3$], 33.4 [s, C(=O)$C(CH_3)_3$], 104.8 (s, C-4), 121.9, 125.8, 128.9, 138.6 (s, C_{arom}), 145.5 (s, C-3), 163.6 (s, C-5), 204.6 (s, CO) ppm.

Pb(Q^T)$_2$ (20): Potassium hydroxide (0.112 g, 2.0 mmol) and $Pb(NO_3)_2$ (0.331 g, 1 mmol) were added to a methanol solution (30 mL) of Q^{T}H (0.566 g, 2 mmol). A colourless precipitate formed immediately. After 1 h, it was filtered off, washed with methanol (10 mL) and recrystallized from chloroform/methanol. Yield 0.562 g (75%). M.p. 224−227 °C. $C_{32}H_{38}N_4O_4Pb$ (749.9): calcd. C 51.26, H 5.18, N 7.47; found C 51.05, H 5.35, N 7.46. Λ_m (CH_2Cl_2, 1×10^{-3} M) = 0.4. MW ($CHCl_3$, $c = 1.8 \times 10^{-3}$ mol/L): 842. IR (nujol): $\tilde{\nu}$ = 1600 vs, 1592 vs ν(C=O), 441 vs, 411 w, 397 m ν(Pb−O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 293 K): δ = 1.02 [s, 9 H, C(=O)$CH_2C(CH_3)_3$], 2.27 (s, 3 H, 3-CH_3), 2.53 [s, 2 H, C(=O)-$CH_2C(CH_3)_3$], 7.14 (t), 7.30 (t), 7.77 (d, 5 H, NC_6H_5) ppm. ^{1}H NMR (CD_2Cl_2, 293 K): δ = 1.05 [s, 9 H, C(=O)$CH_2C(CH_3)_3$], 2.32 (s, 3 H, 3-CH_3), 2.57 [s, 2 H, C(=O)$CH_2C(CH_3)_3$], 7.16 (t), 7.29 (t), 7.81 (d, 5 H, NC_6H_5) ppm. ^{1}H NMR (CD_2Cl_2, 193 K): δ = 0.93 (s). 1.05 [s, 9 H, C(=O)$CH_2C(CH_3)_3$], 1.62 (s), 1.75 (s), 1.87 (s, 3 H, 3-CH_3), 2.36 (s), 2.42 (s), 2.58 [s, 2 H, C(=O)$CH_2C(CH_3)_3$], 7.12 (t), 7.26 (t), 7.44 (t), 7.78 (d), 7.81 (d, 5 H, NC_6H_5) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.4 (s, 3-CH_3), 30.4 [s, C(=O)$CH_2C(CH_3)_3$], 32.2 [s, C(=O)$CH_2C(CH_3)_3$], 51.0 [s, C(=O)$CH_2C(CH_3)_3$], 108.1 (s, C-4), 121.7, 125.7, 129.0, 138.5 (s, C_{arom}), 148.0 (s, C-3), 162.3 (s, C-5), 196.0 (s, CO) ppm.

Pb(Q^W)$_2$ (21): Compound **21** was synthesized as described for compound **20**. Yield 0.769 g (88%). M.p. 251−253 °C. $C_{42}H_{42}N_4O_4Pb$ (874.0): calcd. C 57.72, H 4.84, N 6.41; found C 57.43, H 5.01, N 6.47. Λ_m (CH_2Cl_2, 1×10^{-3} M) = 0.7. MW ($CHCl_3$, $c = 1.4 \times 10^{-3}$ mol/L): 1042. IR (nujol): $\tilde{\nu}$ = 1605 vs, 1595 vs ν(C=O), 473 m, 469 m, 412 m, 382 vs ν(Pb−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.35 [s, 9 H, C(=O)$C_6H_5C(CH_3)_3$], 1.64 (s, 3 H, 3-CH_3), 7.10 (t), 7.18 (t), 7.30 (d), 7.42 (d), 7.76 [d, 9 H, NC_6H_5 and C(=O)-

$C_6H_5C(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$): δ = 16.6 (s, 3-CH_3), 31.4 [s, C(=O)$C_6H_5C(CH_3)_3$], 35.2 [s, C(=O)$C_6H_5C(CH_3)_3$], 106.2 (s, C-4),121.3, 125.3, 125.6, 128.4, 128.9, 138.5 (s, C_{arom}), 149.1 (s, C-3), 163.0 (s, C-5), 191.7 (s, CO) ppm.

$Pb(Q^D)_2$ (22): Compound **22** can be synthesized as described for compound **20**, but also as follows: $Pb(OOCCH_3)_2 \cdot 3H_2O$ (0.379 g, 1 mmol) was added to a water solution (30 mL) of Q^DH (0.308 g, 2 mmol). A colorless precipitate formed immediately and this was filtered, washed with methanol (10 mL), dried to constant weight under reduced pressure and recrystallized from chloroform/diethyl ether. Yield 0.345 g (65%). M.p. 214−216 °C. $C_{14}H_{18}N_4O_4Pb$ (531.7): calcd. C 32.75, H 3.52, N 10.91; found C 32.43, H 3.66, N 10.72. Λ_m (CH_2Cl_2, 1 × 10^{-3} M) = 0.4. MW ($CHCl_3$, c = 1.8 × 10^{-3} mol/L): 763. IR (nujol): $\tilde{\nu}$ = 1586 vs ν(C=O), 454 vs, 388 vs, 373 s ν(Pb−O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.30 (s, 3 H, 3-CH_3), 2.40 [s, 3 H, C(=O)CH_3], 3.28 (s, 3 H, NCH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.4 (s, 3-CH_3), 28.1 (s, NCH_3), 31.5 [s, C(=O)CH_3], 105.9 (s, C-4), 147.1 (s, C-3), 161.8 (s, C-5), 192.8 (s, CO) ppm.

$Pb(Q^D)_2$(phen) (23): Compound **22** (0.532 g, 1 mmol) and phen (0.180 g, 1 mmol) were dissolved in benzene (30 mL) and the clear solution stirred at room temperature for 2 h. The solvent was then removed and the residue treated with diethyl ether (20 mL), affording a colorless precipitate, which was filtered off, dried to constant weight under reduced pressure and recrystallized from chloroform/*n*-hexane. Yield 0.541 g (78%). M.p. 156 °C (dec.). $C_{26}H_{26}N_4O_4Pb$ (693.7): calcd. C 45.02, H 3.78, N 12.11; found C 44.82, H 3.96, N 11.87. Λ_m (CH_2Cl_2, 1 × 10^{-3} M) = 0.3. MW ($CHCl_3$, c = 1.8 × 10^{-3} mol/L): 640. IR (nujol): $\tilde{\nu}$ = 1590 vs ν(C=O), 446 vs, 393 m, 374 s ν(Pb−O), 291 m ν(Pb−N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.29 (s, 6 H, 3-CH_3), 2.32 [s, 6 H, C(=O)CH_3], 3.21 (s, 6 H, NCH_3), 7.73 (dd), 7.85 (s), 8.33 (dd), 9.38 (dd, 8 H, CH_{phen}) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.3 (s, 3-CH_3), 28.2 (s, NCH_3), 31.0 [s, C(=O)CH_3], 105.5 (s, C-4), 123.7, 126.7, 129.3, 136.8, 146.5, 150.2 (s, C_{phen}), 145.8 (s, C-3), 162.6 (s, C-5), 191.8 (s, CO) ppm.

X-ray Crystallographic Study: Experimental data for compounds **6**, **19** and **20** can be found in Table 8. The crystal of bis(3-methyl-4-phenyl-1-phenylacetylpyrazolon-5-ato)tin(II) (**6**) decayed slightly but no decay correction was applied to the data. For crystals of bis(3-methyl-1-phenyl-4-pivaloylpyrazolon-5-ato)lead(II) (**19**) and bis(4-*tert*-butyl-3-methyl-1-phenylacetylpyrazolon-5-ato)lead(II) (**20**) no decay was seen. The data for compounds **6** and **19** were collected with a Syntex $P2_1$ diffractometer equipped with a graphite-monochromated beam at 298 K. The heavy-atom method in CAOS was used to solve both structures.[67] Once the heavy-atom peak had been located in the Patterson map, a Fourier synthesis was performed to locate the other non-hydrogen atoms until all atoms were found. All non-hydrogen atoms were refined anisotropically until convergence. The hydrogen atoms were then placed at a fixed C−H bond length of 0.96 Å using a subroutine of CAOS, further refinement was applied with the H atoms riding on their attached atoms until convergence. Data were refined by full-matrix least-squares

Table 8. Crystal and refinement data

	6	**19**	**20**
Empirical formula	$C_{38}H_{30}N_4O_4Sn$	$C_{30}H_{34}N_4O_4Pb$	$C_{32}H_{38}N_4O_4Pb$
Formula mass	701.35	721.82	749.97
Crystal habit	Plate	Block	Block
Crystal size [mm]	0.30 × 0.25 × 0.10	0.20 × 0.15 × 0.15	0.25 × 0.20 × 0.20
Crystal system	monoclinic	triclinic	triclinic
Space group	$A2$	$P\bar{1}$	$P\bar{1}$
Crystal color	colorless	colorless	colorless
a [Å]	14.388(8)	10.693(7)	10.614(2)
b [Å]	5.801(3)	11.307(8)	12.278(2)
c [Å]	19.958(12)	13.473(9)	13.462(3)
α [°]	90	70.07(2)	95.311(4)
β [°]	110.67(2)	89.66(2)	111.434(3)
γ [°]	90	70.92(2)	104.811(3)
V [Å^3]	1558.6	1437.035	1544.74(5)
Z	4	2	2
T [K]	293	293	243
$D_{calcd.}$ [Mg m^{-3}]	1.37	1.61	1.61
$2\theta_{max}$ [°]	56	60	56.5
μ [mm^{-1}]	0.86	5.83	5.50
Wavelength (graphite- monochromated) [Å]	Mo (0.71069)	Mo (0.71069)	Mo (0.71069)
Transmission factors	1.00, 0.94	1.00, 0.78	0.609, 0.406
Measured reflections	4223	8357	9794
Unique reflections	2071	8088	6669
R (merged)	0.040	0.052	0.026
F(000)	652	688	744
h_{min}, h_{max}	0, 19	0, 14	−13, 13
k_{min}, k_{max}	0, 7	−14, 15	−15, 12
l_{min}, l_{max}	−26, 24	−18, 18	−17, 11
Refined reflections [$F > n\sigma(F)$]	1887 (n = 6)	6443 (n = 7)	5657 (n = 6)
Refined parameters	204	352	370
R, R_w	0.046, 0.064	0.061, 0.076	0.029, 0.038
S	0.86	0.89	0.94
Equivalent reflections	77	17	3125
Scan mode	2θ-θ	2θ-θ	ω

procedures on *F*. The data for compound **20** were collected with a Bruker P4 diffractometer equipped with a SMART CCD detector at 243 K. Absorption correction was applied with SADABS. The structure was solved by direct methods and standard difference-map techniques, and was refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.10).[68] Hydrogen atoms were included in calculated positions. Difference electron density measurements showed no important residual electron density for all three structures. CCDC-233990 to -233992 (for **6**, **19**, and **20**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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