

Structure of β -diketiminates and β -aminoketones made from anisidines or chloroanilines: tin and lithium complexes

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Abstract

Three series of methoxyphenyl substituted β -diketimate and β -enaminoketonate and chlorophenyl β -enaminoketonate ligands were prepared and studied by IR, ¹H and ¹³C NMR spectroscopy in solution and X-ray diffraction techniques in solid state. The crystal structures of [2-(MeO)C₆H₄]N=(H)CCH(H)C[2-(MeO)C₆H₄]NH.HCl, [2-(MeO)C₆H₄]N=(H)CCH(H)C[2-(MeO)C₆H₄]NH, [4-(MeO)C₆H₄]N=(H)CCH(H)C[4-(MeO)C₆H₄]NH, [4-ClC₆H₄]N(H)(Me)CCH(Me)C=O, [2-(MeO)C₆H₄]N=(Me)CCH(Me)C[2-(MeO)C₆H₄]NH and 7-methoxy-2,4-dimethylquinoline-toluenesulfonyl acid adduct as ligands, their precursors and a byproduct isolated during the synthesis of [3-(MeO)C₆H₄]N(H)(Me)CCH(Me)C=O were determined. One of the ligands the *meta*-methoxyphenyl substituted β -enaminone has been treated with *n*-butyllithium to give {[3-ClC₆H₄]N(Me)CCH(Me)C=O}Li which reveals tetrameric structure in the solid state. Further reactions of this lithium complex with tri- and diorganotin(IV) chlorides and hydride give appropriate organotin(IV) complexes with five coordinated tin atom. The direct reaction of bis(*para*-methoxyphenyl) substituted β -diketimine with Sn[N(SiMe₃)₂]₂ gives [4-(MeO)C₆H₄]N=(H)CCH(H)C[4-(MeO)C₆H₄]NSnN(SiMe₃)₂. Structure of these complexes was evaluated by ¹H, ⁷Li and ¹¹⁹Sn NMR spectroscopy and X-ray diffraction analysis for two examples.

Keywords: β -diketiminates; β -enaminones; lithium; tin.

Introduction

The chemistry of metal complexes containing $\alpha\beta$ -diketimate as a spectator ligand is a phenomenon of approximately the past two decades. These complexes are usually studied for their possible catalytic applications (Dove et al., 2006; Champouret et al., 2010) in a plethora of different organic chemistry transformations (Cheng et al., 2000; Jana et al.,

2010), as a single source precursor for material chemistry and last but not least for kinetic stabilization of low valent metal centers. These ligands can be applied as a bidentate monoanionic species with a delocalized π -electron system (Figure 1), but another type of β -diketiminato complexes, for example, compounds with non-planar ligand central ring, three different types bimetallic complexes (Piesik et al., 2009), etc., are known. These bonding modes with considerable diversity are described in a review by Lappert (Bourget-Merle et al., 2002). Recently, these complexes were successfully used for stabilization of groups 13 (Kuhn et al., 1989; Gornitzka and Stalke, 1994; Qian et al., 1998) and 14 (Ding et al., 2001a) elements in low valence states. These six-membered heterocycles are reviewed by Jones and Driess (Asay et al., 2011), showing high potential of β -diketiminato ligands with high sterical demand to stabilize such a reactive species, for example, Mg(I) (Bonyhady et al., 2010; Platts et al., 2011), Si(II) (Meltzer et al., 2010; Xiong et al., 2010; Azhakar et al., 2011), Ge(I) (Woodul et al., 2011), Sn(I) (Choong et al., 2012) and others.

β -Diketiminates as precursors for alkaline metal β -diketiminato complexes are usually prepared by a condensation reaction of diones (Carey et al., 2003; Chen et al., 2005) or 1,1,3,3-tetraalkoxypropanes (Feldman et al., 1997; Cheng et al., 2001; Stender et al., 2001; Jung and Kim, 2006) with anilines (Scheme 1). Common byproducts in the reactions of diones are β -enaminones which can also be deprotonated (Kakaliou et al., 1999; Kao et al., 2008) by a strong base; further reactivity of appropriate conjugated base with a metal halide give another interesting class of main group metal complexes (Dixit and Tandon, 1989; Singh et al., 2000).

In a series of both types of compounds, the majority of examples contain a bulky phenyl (McGeachin, 1968) or naphthyl (Monillas et al., 2010) ligand. The complexes where an aliphatic, trimethylsilyl or an adjacent coordination group is employed are also known (Figure 2) (Bradley et al., 2008; El-Zoghbi et al., 2010; Norman et al., 2010). The number of papers on compounds where a donor group is directly bonded to the phenyl ring is rather limited. The *o*-methoxy-substituted β -diketiminato complexes of Li (Carey et al., 2003), Y (Shang et al., 2007), Lu (Liu et al., 2007; Shang et al., 2007), Sc (Zhang et al., 2008) and Mg (Chisholm et al., 2005) are described. Mg complex is useful for polymerization of *rac*-lactides (Chisholm et al., 2005). For catalytic purposes, also the *o*- and *p*-methoxy-substituted β -diketiminato complex of zinc has been studied (Chisholm et al., 2005; Biyikal et al., 2010).

In this paper, we concentrate on systematic IR, NMR and solid state studies of two classes of methoxy-substituted β -diketiminates and β -enaminoketonato ligands where the

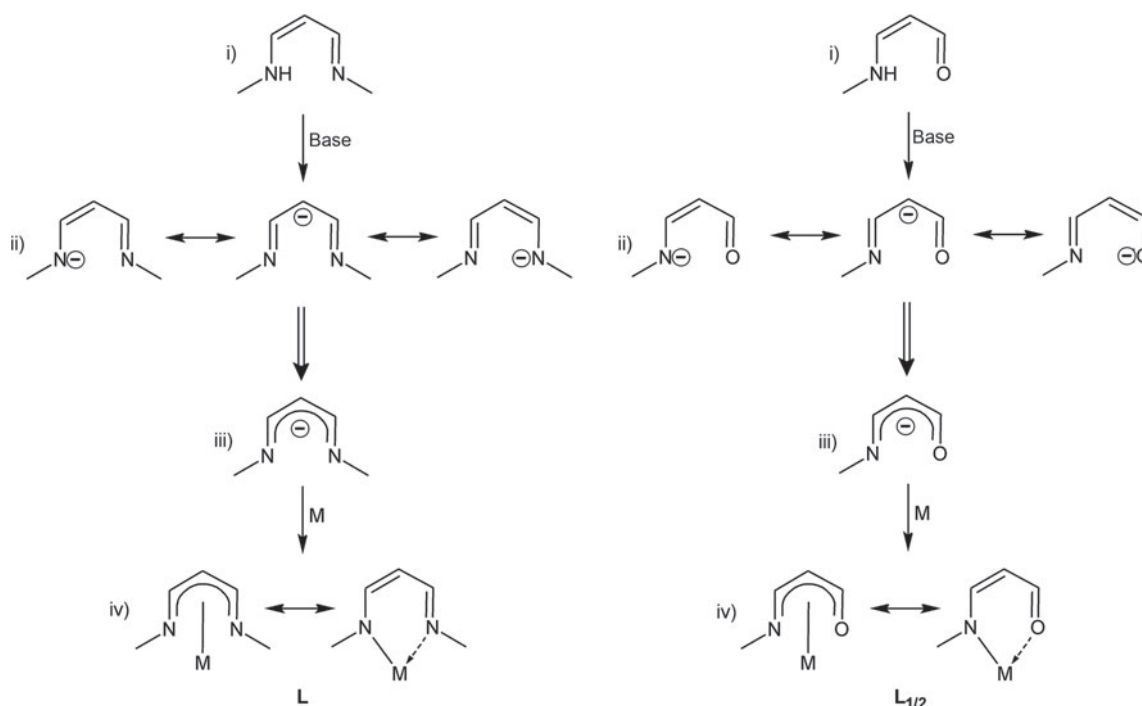


Figure 1 General description of (i) structure of β -diketimine (**L**) or β -enaminone (**L**_{1/2}), (ii) resonance structures, (iii) β -diketiminato anion or β -enaminoketonato ligand, and (iv) metal complexes.

majority of compounds were prepared much earlier (for references see Table 1, Figure 3) and ¹H NMR spectra of three compounds were measured in DMSO (hydrochlorides of **L**^{HO}**H**, **L**^{HM}**H** and **L**^{HP}**H**; see Table 1 and Figure 3). The comparison with appropriate chloro-substituted complexes will also be performed. Two of these compounds studied, the *meta*-methoxyphenyl substituted β -enaminone (**L**_{1/2}^{CM}**H**) and the *para*-methoxyphenyl-substituted β -diketimine (**L**^{HP}**H**), were selected to be tested for complexation abilities.

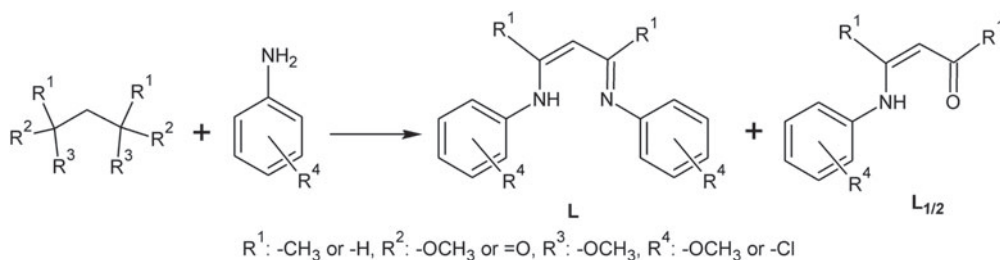
Results and discussion

Synthesis

Although the preparation of some of the compounds is reported in the literature, modified and more detailed approaches are described here. The reactions of 2,4-pentandione with two or one molar equivalents of 2-, 3- or 4-methoxyaniline give

2-, 3- or 4-methoxy substituted β -enaminones, similar to studies reported earlier (Sanchez et al., 1997; Zhuo, 1997; Zhang et al., 2006) (**L**_{1/2}^{CO}**H**, **L**_{1/2}^{CM}**H** and **L**_{1/2}^{CP}**H**), in approximately 20% yield or 2-, 3- or 4-methoxy substituted β -diketimines (**L**^{CO}**H**, **L**^{CM}**H** and **L**^{CP}**H**) (Carey et al., 2003; Chen et al., 2005) in approximately 25% yield, respectively. The yield of all compounds is independent of the amount of reactants, *p*-toluenesulfonic acid as a catalyst, and the temperature of reaction mixture. Extension of reaction time also did not affect higher yields. The comparative series of chloro-substituted β -enaminones, **L**_{1/2}^{CCO}**H** (Musker and Sakhawat, 1966) and **L**_{1/2}^{CCP}**H** (Zhuo, 1997), were prepared by similar reactions from chloro anilines where only the molar ratio of reactants 1:1 was used. The yield of these compounds is usually a half of the yield of previous series.

The reactions of 1,1,3,3-tetramethoxypropane with appropriate methoxyanilines give hydrochlorides of 2-, 3- or 4-methoxy substituted β -diketimines, **L**^{HO}**H.HCl** (Richards and Webb, 1976), **L**^{HM}**H.HCl** and **L**^{HP}**H.HCl** (Kikugawa



Scheme 1 General preparation of β -diketiminates a β -enaminones.

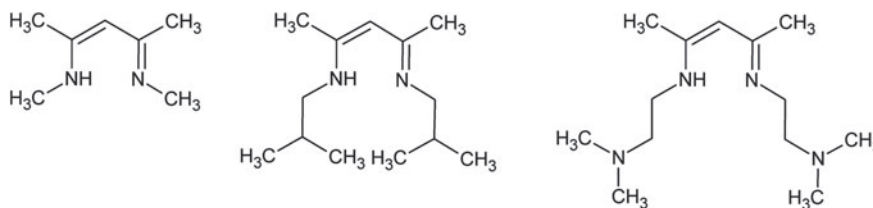


Figure 2 Different types of β -diketimines.

and Sugimura, 1986), in moderate yields. Free β -diketimines ($L^{HO}H$, $L^{HM}H$ and $L^{HP}H$) are prepared by addition of sodium carbonate or hydroxide.

The reaction of $L^{CM}_{1/2}H$ with *n*-BuLi gives essential almost quantitative yield (conversion considered by 1H NMR) of $L^{CM}_{1/2}Li$ at $-78^\circ C$. The further reaction of $L^{CM}_{1/2}Li$ with organotin(IV) halides gives desired β -enaminoketonato organotin(IV) complexes in high yield (Figure 4).

The ability of one of the ligands to coordinate tin(II) species is demonstrated in the direct reaction of $L^{HP}H$ with the Lappert's stannylene (Harris and Lappert, 1974; Davidson et al., 1976) by elimination of bis(trimethylsilyl)amine and the subsequent formation of $L^{HP}Sn[Si(CH_3)_3]_2$ (Figure 5). Although many of β -diketiminato tin(II) complexes are subject of various studies (Asay et al., 2011), no study pointed to the non-substituted -NCHCHCHN- β -diketiminato ligand. The stability of this compound towards moisture and air gases is comparable to the reported complexes (Asay et al., 2011).

The IR spectra of all free ligands were measured to evaluate the electronic structure of compounds and expected changes in H-bonding. Surprisingly, only small changes were observed for characteristic N-H deformation vibrations around

750 cm^{-1} , =C-N bands at $1360\text{--}1250\text{ cm}^{-1}$ and C=C, C=N stretching vibrations where the biggest values were determined in the L^H ligand series. Based on this finding and similarities in 1H and ^{13}C NMR spectra, no IR spectra of complexes were measured.

NMR studies

All compounds prepared were subjected to multinuclear NMR studies in solution. All 1H NMR spectra reveal one set of signals attributable to the specific position of the hydrogen atom in the molecule except for spectrum measured for $L^{CM}H$ where some signals are anisochronous, probably due to the steric barrier of methoxy and methyl groups. The typical signal found at ~ 12.4 ppm is attributed to NH hydrogen atom. In hydrochlorides $L^{HO}H.HCl$, $L^{HM}H.HCl$ and $L^{HP}H.HCl$, there is another signal found with the similar chemical shift value. The next typical signals in 1H NMR spectra are those for CH groups at approximately 5 ppm for free β -enaminoketones and β -diketimines which are shifted to the lower field when the free ligand is protonated by HCl. The methoxy groups resonate in the range from 3.5 to 3.9 ppm. For all complexes prepared ($L^{CM}_{1/2}Li$, $L^{CM}_{1/2}Bu_3Sn$, $L^{CM}_{1/2}Ph_3Sn$, $L^{CM}_{1/2}Ph_2SnCl$ and $L^{HP}Sn[Si(CH_3)_3]_2$), the signal at ~ 12.5 ppm disappeared, and the rest of the signals slightly change their positions. Values for CH resonances slightly increased, and by contrast the values for methoxy resonances decreased.

There are also a couple of specific signals in ^{13}C NMR spectra. The most significant signal is the resonance belonging to the CH carbon in the center of the ligand which is found in very narrow range from 94.4 to 99.6 ppm for both types of ligands and lithium complexes, respectively. The presence of methoxy groups as well as the methyl groups originated from the starting acetylacetone in the case of L^C type of ligands is reflected in sharp resonances in specific regions (see Table 2 and experimental section), except the case of $L^{CM}_{1/2}H$, where two discrete sets of signals were found similar to the 1H NMR spectra of those compounds. Surprisingly, there are no obvious trends in ^{13}C chemical shift values for free ligands as well as their lithium complexes.

The 7Li NMR spectra of $L^{CM}_{1/2}H$ were recorded to prove the structure differences in different types of solvents. The 7Li NMR spectrum measured in toluene is rather different from that measured in THF. It means that the structure of $L^{CM}_{1/2}H$ in THF solution probably split to monomeric blocks where the lithium atom is coordinated by two THF molecules, as found for four coordinated lithium amidinates previously (Chlupaty

Table 1 Abbreviations used for prepared compounds (see Scheme 1).

Compound	R ¹	R ⁴		
		<i>o</i> -	<i>m</i> -	<i>p</i> -
$L^{CO}H^a$	-CH ₃	-OCH ₃	—	—
$L^{CM}H$	-CH ₃	—	-OCH ₃	—
$L^{CP}H^b$	-CH ₃	—	—	-OCH ₃
$L^{HO}H.HCl^{c,x}$	-H	-OCH ₃	—	—
$L^{HM}H.HCl^x$	-H	—	-OCH ₃	—
$L^{HP}H.HCl^{c,d,x}$	-H	—	—	-OCH ₃
$L^{HO}H^c$	-H	-OCH ₃	—	—
$L^{HM}H$	-H	—	-OCH ₃	—
$L^{HP}H^{c,d}$	-H	—	—	-OCH ₃
$L^{CO}_{1/2}H^e$	-CH ₃	-OCH ₃	—	—
$L^{CM}_{1/2}H^f$	-CH ₃	—	-OCH ₃	—
$L^{CP}_{1/2}H^g$	-CH ₃	—	—	-OCH ₃
$L^{CClO}_{1/2}H^h$	-CH ₃	-Cl	—	—
$L^{CClP}_{1/2}H^i$	-CH ₃	—	—	-Cl
$L^{CM}_{1/2}Li$	-CH ₃	—	-OCH ₃	—

^aCarey et al. (2003), ^bGong and Ma (2008), ^cRichards and Webb (1976), ^dKikugawa and Sugimura (1986), ^eSanchez et al. (1997), ^fZhuo (1997), ^gZhang et al. (2006), ^hMusker and Sakhawat (1966);

^xhydrochlorides; L for β -diketimine, $L_{1/2}$ for β -enaminone.

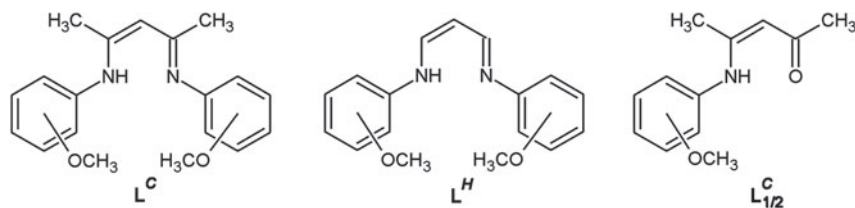


Figure 3 Compounds used as ligands in this study.

et al., 2011). By contrast, the -3.22 ppm value found in the ^7Li NMR spectrum measured in toluene which can be attributed to the tetrameric character of the compound in this solvent.

To evaluate the complexation ability of the ligand $\text{L}^{\text{CM}}_{1/2}\text{H}$, three organotin(IV) complexes were prepared by a conversion of $\text{L}^{\text{CM}}_{1/2}\text{Li}$ with organotin(IV) halide (Figure 4). From the comparison of chemical shift values of chemical shifts in ^{119}Sn NMR spectra of prepared complexes and starting chlorides (20–120 ppm), it is seen that the coordination number of the tin central atom increased from four to five. This is caused by the bidentate coordination of $\text{L}^{\text{CM}}_{1/2}\text{H}$ ligand via nitrogen and oxygen atoms to the tin atom. The bidentate coordination of L^{HP} ligand to the tin atom is also expected in $\text{L}^{\text{HP}}\text{Sn}[\text{Si}(\text{CH}_3)_3]_2$ where the δ (^{119}Sn) is found at -164.1 ppm similar to β -diketiminato tin(II) amides reported by Roesky (Jana et al., 2009) and Barrau (Akkari et al., 2001) (-134.5 and -151.8 ppm).

Solid state studies

During the course of these studies eight new crystal structures of all types of studied compounds were determined by X-ray crystallographic techniques. To evaluate the bonding situation on each ligand, the structure of the central core of each compound is discussed.

The first compound was crystallized from the first step of preparation of $\text{L}^{\text{HO}}\text{H}$. The structure of $\text{L}^{\text{HO}}\text{H}\cdot\text{HCl}$ is planar with a zig-zag chain within the central fragment of the molecule. There is a high degree of delocalization of π -electrons within the whole system. In comparison to other protonated β -diketimine molecules (Kulpe and Schulz, 1981; Brownstein et al., 1983; Kuhn et al., 2000), this particular hydrochloride reveals rather short C-C and C-N distances (see Figure 6 caption). There is the extensive hydrogen bonding in the structure of $\text{L}^{\text{HO}}\cdot\text{HCl}$. There are intramolecular hydrogen bonds $\text{NH}\dots\text{O}$ of both NH groups to the appropriate methoxy groups, while the NH group of N1 atom is also connected to the chloride

anion prolongates the connection to the oxygen atom (Figure 1) of the water molecule, which is present in the unit cell. The water molecule is further connected to the N2-H2 group of adjacent molecule oriented perpendicularly to the original molecule.

The product of the first deprotonation of $\text{L}^{\text{HO}}\text{H}\cdot\text{HCl}$ is compound $\text{L}^{\text{HO}}\text{H}$ with less complex molecular structure (Figure 7). The π -electron delocalization detected in the structure of previous compound ($\text{L}^{\text{HO}}\text{H}\cdot\text{HCl}$) is nearly missing in this molecule. To the best of our knowledge, there is no crystal structure of free β -diketimine derived from 1,3-unsubstituted -NCHCHCHN- reported to date. The main differences are reflected in bond lengths C-C and C-N, where the C9-C10 bond can be assigned to be a multiple bond but the C8-C9 is the typical single bond with a limited degree of π -electron delocalization. On the basis of C-N atoms separations, one can predict that the N1 atom is of an imino type and the N2 atom of an amino type. In addition, the degree of planarity of the molecule is much lower than in $\text{L}^{\text{HO}}\text{H}$ precursor, although the N2, C10 and C9 atoms nearly lie in the plane defined by the phenyl ring C11-C16, the C8 and N1 atoms deviate from this plane significantly (0.314 and 0.454 Å), and the interplanar angle between both phenyl ring planes is 35.21°. The intramolecular contact between N2-H2 and N1 atoms is the only hydrogen bond found in the molecule of $\text{L}^{\text{HO}}\text{H}$.

The structure of the $\text{L}^{\text{HP}}\text{H}$ (Figure 8) is similar to the structure of $\text{L}^{\text{HO}}\text{H}$ with the exception of a slightly higher degree of π -electron delocalization within the system which is reflected in the shortening of the central core C-C bonds and elongation of the C-N bonds in $\text{L}^{\text{HP}}\text{H}$ in comparison to $\text{L}^{\text{HO}}\text{H}$ which is probably caused by the presence of an *ortho* effect in $\text{L}^{\text{HO}}\text{H}$. The phenyl rings are deviated with the same orientation from the central NC_3N plane by 26.67(12)°. There is only one intramolecular N1-H1a...N1d contact in the molecule of $\text{L}^{\text{HP}}\text{H}$ which is of similar magnitude as the appropriate hydrogen bond in $\text{L}^{\text{HO}}\text{H}$.

The only solid compound from the β -diketimine series – $\text{L}^{\text{CCIP}}_{1/2}\text{H}$ (Sanchez et al., 1997; Zhuo, 1997; Zhang et al., 2006) is prepared to compare this class of compounds with related β -diketimines. The centrosymmetric dimer of $\text{L}^{\text{CCIP}}_{1/2}\text{H}$ (Figure 9) is formed via two intermolecular hydrogen bridges in the solid state. The central NC_3N planes in the dimer are coplanar with the interplanar distance of 1.211(3) Å. The intermolecular H-bonding (N1-H1...O2) is much weaker than the intramolecular bonding (N1-H1...O1), which are in the magnitude comparable to analogous



Figure 4 Preparation of Sn(IV) derivatives of L^{CM} .

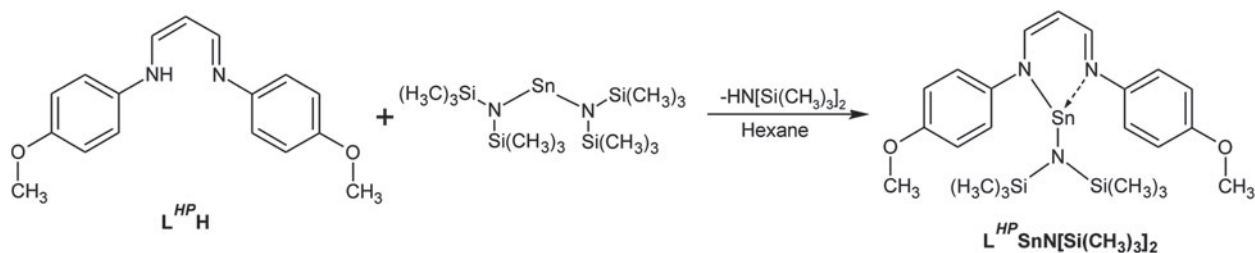


Figure 5 Preparation of Sn(II) derivative of L^{HP} .

connections previously discussed $L^{HO}H$ and $L^{HP}H$. Although the planarity of the central NC_3N core is nearly ideal, the degree of delocalization within the system is rather low. The major illustration of this fact are the interatomic distances C7-N1 and C9-O1, where the first one is attributed to the single bond, and by contrast the second one is a typical value for C=O bond type. The interplanar angle of the phenyl ring and the central NC_3N plane is a bit higher [$45.41(9)^\circ$] than that found for $L^{HP}H$.

The adduct of 7-methoxy-2,4-dimethylquinoline with *p*-toluenesulfonic acid has been obtained as a minor byproduct of catalyzed reaction of 2,4-pentandione with *m*-anisidine (Figure 10). Both parts of adduct (Figure 11) are interconnected by strong H-bridge O2-H...N1. All other interatomic distances are in the typical range for analogous functional groups previously reported in the literature (Mehta et al., 2003) or the Cambridge Structural Data Base. To the best of our knowledge, there is no molecular structure of 2,4-dicarba-7-oxo substituted quinoline determined to date.

From the interatomic distances in the planar central moiety of $L^{CO}H$ (Figure 12), it is clearly visible that the

localization of a multiple bond between C9-N2 and C8-C7 atoms is taking place. The phenyl rings are twisted by $28.75(12)^\circ$ for the ring connected by a hydrogen bridge from O1 atom to the N1-H1 group and $48.67(13)^\circ$ for the second ring which reveals that there is no interaction of this type. The intramolecular N1-H1...O1 connection is a bit stronger than in previously discussed compounds without methyl decoration of the central NC_3N fragment (see Figure 12 caption). The N1-H1...O1 connection is also responsible for widening of C7-N1-C1 angle. In comparison to the $L^{HO}H$ and $L^{HP}H$, the N1-N2 distance in $L^{CO}H$ is shorter by 0.05 Å, which is in line with the literature values for known β -diketiminates (Crimmin et al., 2010; Monillas et al., 2011).

Although the structure of $L^{CO}_{1/2}Li$ (Figure 13) seems to be heterocubane-like, the symmetry of this molecule is fairly low. By contrast, the interatomic distances and angles of the same type are of similar values, which allow us to discuss the average values or the values for a virtual quarter of heterocubane moiety separately. The compound consists of the rather deformed Li_4O_4 cube (Figure 14), where the oxygen

Table 2 Selected NMR chemical shifts (ppm).

Compound	$\delta(^1H(-NH))/\delta(^{119}Sn)/\delta(^7Li)$	-N(H)CHCHCHN- or -N(H)C(CH ₃)CHC(CH ₃)N-		-OCH ₃	
		$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^1H)$	$\delta(^{13}C)$
$L^{CO}H^a$	12.73	4.94	97.9	3.79	55.7
$L^{CM}H^a$	12.54	5.13	97.4	3.65, 3.62	54.7, 54.3
$L^{CP}H^a$	12.57	4.87	96.4	3.80	55.5
$L^{HO}H^a$	12.21	5.17	95.9	3.88	55.4
$L^{HM}H^a$	12.48	5.17	95.8	3.82	55.0
$L^{HP}H^a$	12.22	5.05	94.4	3.81	55.7
$L^{CO}_{1/2}H^a$	12.29	5.12	97.6	3.75	55.4
$L^{CM}_{1/2}H^a$	12.35	5.05	97.3	3.54	54.6
$L^{CP}_{1/2}H^a$	12.26	5.09	96.8	3.71	55.3
$L^{CClO}_{1/2}H^a$	12.40	5.16	98.5	—	—
$L^{CClP}_{1/2}H^a$	12.42	5.17	98.0	—	—
$L^{CM}_{1/2}Li$	-3.22 ^b /1.40 ^c	4.90 ^b /4.73 ^c	99.6 ^b /98.0 ^c	3.39 ^b /3.67 ^c	54.6 ^b /55.2 ^c
$L^{CM}_{1/2}Bu_3Sn^b$	28.1	5.14	—	3.52	—
$L^{CM}_{1/2}Ph_3Sn^b$	-119.8	5.85	—	3.27	—
$L^{CM}_{1/2}Ph_2SnCl^b$	-45.1	5.61	—	3.43	—
$L^{HP}_{1/2}SnN[Si(CH_3)_3]^c$	-164.1	4.97	96.6	3.72	55.7

^aMeasured in CDCl₃. ^bMeasured in toluene-d₈. ^cMeasured in THF-d₈.

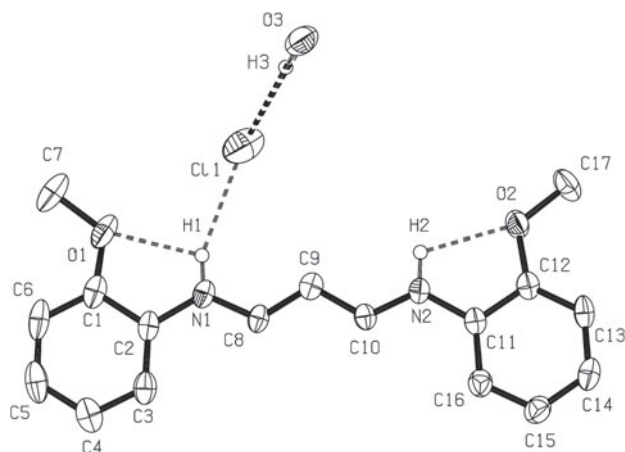


Figure 6 Molecular structure of $L^{H^O}H.HCl$ (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity (except for hydrogen atoms which are included in H-bonding). Selected interatomic distances (Å) and angles (°): C2-N1 1.411(5); N1-C8 1.323(6); C8-C9 1.368(5); C9-C10 1.371(6); C10-N2 1.326(5); N2-C11 1.406(6); C2-N1-C8 125.09(4); N1-C8-C9 123.69(4); C8-C9-C10 118.34(4); C9-C10-N2 124.20(4); C10-N2-C11 125.32(4); N1-H1...O1 2.601(5); N1-H1...Cl1 3.374(5); O3-H3...N2-H2 6.209(6); N2-H2...O2 2.600(5).

atoms originated from the $L^{CM}_{1/2}H$ ligand and interact with three lithium atoms. These are further coordinated by nitrogen atoms from the essentially planar ligand similar to the analogous ligand substituted by isopropyl fragment (Brehon et al., 1997). The similarities in bonding of both ligands are also seen from the interatomic distances and angles within the ketimine fragments. In $L^{CM}_{1/2}Li$ heterocubane core, the ligands from neighboring lithium atoms are oriented in a mutual perpendicular way ($\sim 84^\circ$) and all interplanar angles

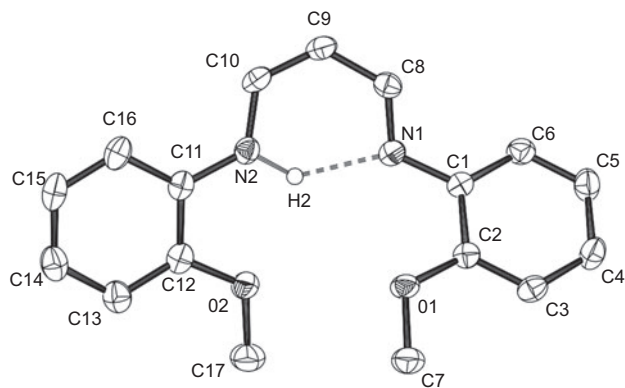


Figure 7 Molecular structure of $L^{H^O}H$ (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity (except for hydrogen atoms which are included in H-bonding). Selected interatomic distances (Å) and angles (°): C1-N1 1.413(3); N1-C8 1.291(3); C8-C9 1.427(3); C9-C10 1.350(3); C10-N2 1.353(3); C1-N1-C8 118.73(18); N1-C8-C9 122.91(19); C8-C9-C10 124.39(19); C9-C10-N2 124.30(2); C10-N2-C11 125.67(18); N2-H2...N1 2.728(2).

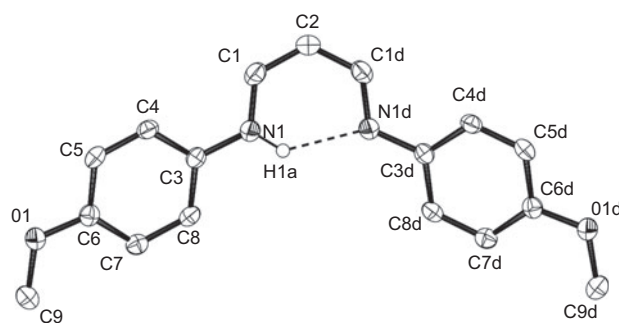


Figure 8 Molecular structure of $L^{H^P}H$ (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity (except for hydrogen atoms which are included in H-bonding). Selected interatomic distances (Å) and angles (°): C3-N1 1.408(3); N1-C1 1.322(3); C1-C2 1.390(3); C1-C1d 1.390(3); C1d-N1d 1.322(3); N1d-C3d 1.408(3); C3-N1-C1 121.784(19); N1-C1-C2 124.02(2); C1-C2-C1d 124.50(3); C2-C1a-N1d 124.02(2); C1d-N1d-C3d 121.84(19); N1-H1a...N1d 2.750(2).

between the ketimine central cores and phenyl rings are again nearly perpendicular ($\sim 87.5^\circ$). The elongation of the C10-O1 bond is caused by the bridging character of the C=O system and an interaction of oxygen atom with two lithium atoms. By contrast, the double bond character of C8-C9 interaction remains unchanged.

The molecular structure of $L^{H^P}Sn[Si(CH_3)_3]_2$ (Figure 15) is a member of the family of tin(II) β -diketiminato complexes which are of current interest (Asay et al., 2011). There is approximately 40 crystal structures of tin(II) β -diketiminato complexes reported to date, but none of them has unsubstituted CHCHCH central moiety. The central NC_3N moiety in $L^{H^P}Sn[Si(CH_3)_3]_2$ has rather delocalized character similar to the starting ligand $L^{H^P}H$. The phenyl rings are twisted from this plane by $32.73(9)^\circ$ and $49.36(12)^\circ$, respectively. The tin atom is a bit above [0.195(4) Å] the plane defined by NC_3N atoms. In the case of β -diketiminato tin(II) alcoholate, an

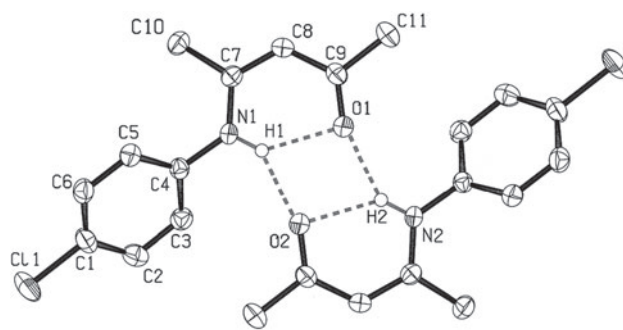


Figure 9 Molecular structure of $L^{CCIP}_{1/2}H$ (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity (except for hydrogen atoms which are included in H-bonding). Selected interatomic distances (Å) and angles (°): C4-N1 1.417(2); N1-C7 1.348(2); C7-C8 1.375(2); C8-C9 1.424(3); C9-O1 1.243(2); C4-N1-C7 127.55(15); N1-C7-C8 121.44(15); C7-C8-C9 124.82(15); C8-C9-O1 123.74(17); N2-O1-N1 115.95(15); O1-N1-O2 64.05(15); N1-H1...O1 2.705(2); N1-H1...O2 3.116(2).

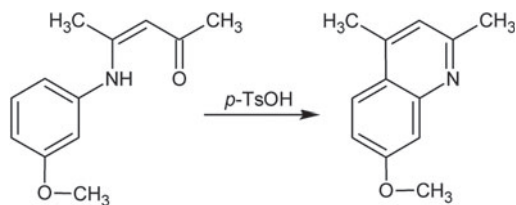


Figure 10 Formation of 7-methoxy-2,4-dimethylquinoline.

extreme deviation of the tin atom from that plane is found to be 1.056(3) Å (Ferro et al., 2011). By contrast, this deviation is nearly negligible in the case of tin(II) cation (Taylor et al., 2011) or non-planar central ring of β -diketiminato tin(II) chloride (Woodul et al., 2010). The tin atom in $L^{HP}SnN[Si(CH_3)_3]_2$ is three coordinated with the coordination polyhedron of trigonal pyramid where the lone electron pair is virtually situated in an apical position. When the interatomic distances and angles in $L^{HP}SnN[Si(CH_3)_3]_2$ are compared to the appropriate parameters found for four known β -diketiminato tin(II) amides, a conclusion is made that the Sn-N distances and angles within the β -diketiminato tin(II) fragment are similar to the reported structures but Sn1-N3 [2.135(3) Å] distance and C9-Sn1-N3 angle [106.14(8)°] are much closer to the values found for bulkier amides (Ding et al., 2001b; Jana et al., 2009) than was found for less bulky dimethylamides [2.038(4) Å, 88.82(9)° and 2.054(3) Å, 85.34(12)°] (Dove et al., 2006).

Conclusion

Within the series of studied methoxyphenyl- or chloro-substituted β -diketiminato and β -enaminoketonate ligands and its lithium and tin complexes, the conclusion about

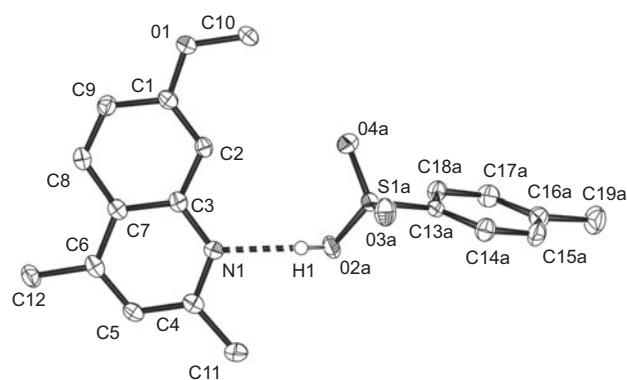


Figure 11 Molecular structure of 7-methoxy-2,4-dimethylquinolinium 4-methylbenzenesulfonate (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity (except for hydrogen atoms which are included in H-bonding). Selected interatomic distances (Å) and angles (°): C3-N1 1.377(3); N1-C4 1.334(3); C4-C5 1.397(3); C5-C6 1.377(3); C6-C7 1.427(3); C7-C3 1.409(3); C3-N1-C4 122.80(18); N1-C4-C5 119.28(2); C4-C5-C6 121.56(2); C5-C6-C7 118.31(19); C6-C7-C3 119.03(2); C7-C3-N1 119.01(19); N1...O2a-H 2.720(3).

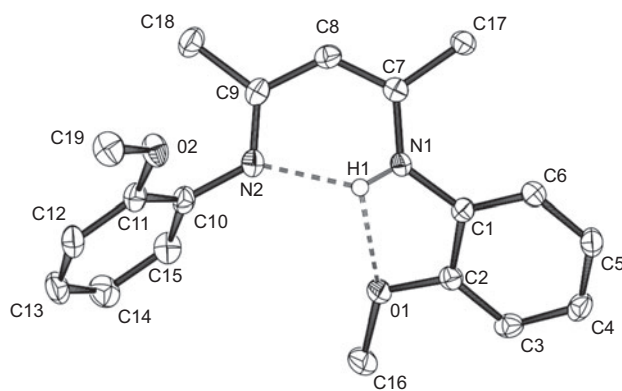


Figure 12 Molecular structure of L^{COH} (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity (except for hydrogen atoms which are included in H-bonding). Selected interatomic distances (Å) and angles (°): C10-N2 1.415(3); N1-C7 1.363(2); C7-C8 1.372(3); C8-C9 1.435(3); C9-N2 1.301(2); N1-C1 1.406(2); C1-N1-C7 130.09(15); N1-C7-C8 120.02(16); C7-C8-C9 127.39(17); C8-C9-N2 120.35(17); C9-N2-C10 121.91(16); N1-H1...N2 2.698(2); N1-H1...O1 2.605(2).

the differences in delocalization of π -electrons within the NC_3N system is made in the solid state. The highest degree of this virtual parameter is observed for protonated L^{HO} . HCl and *ortho*-substituted ligand L^{HOH} and its complex $L^{HO}SnN(SiMe_3)_2$. By contrast, in the rest of the compounds the conjugation – alternating of double and single bonds – within this system is seen. This fact cannot be supported by any NMR spectroscopy parameter observed in solution. The $L^{CM}_{1/2}H$ ($[3-(MeO)C_6H_4]N(H)(Me)CCH(Me)C=O$) can be deprotonated by *n*-butyllithium and the respective lithium salt is useful for preparation of organotin(IV) complexes where the ligand is bidentately bonded to the tin atom. The elimination of $HN(SiMe_3)_2$ is taking place when the L^{HOH} is added to the Lappert's stannylene in equimolar ratio, thus forming the β -diketiminato complex $L^{HO}SnN(SiMe_3)_2$. This approach can be a useful method in future preparation of similar compounds.

Experimental

General methods

NMR spectroscopy NMR spectra were recorded from solutions in $CDCl_3$, $THF-d_8$, $toluene-d_8$ or $DMSO-d_6$ on a Bruker Avance 500 spectrometer (Bruker Biospin, Rheinstetten, Germany) (equipped with Z-gradient 5 mm probe) at frequencies for 1H (500.13 MHz), $^{13}C\{^1H\}$ (125.76 MHz), $^{119}Sn\{^1H\}$ (186.50 MHz) and 7Li (194.4 MHz) at 295 K. In the case of air sensitive complexes were deuterated solvents distilled, degassed and then stored over K-mirror under an argon atmosphere. Solutions were obtained by dissolving approximately 30 mg of each compound in approximately 0.5 ml of deuterated solvents. Values of 1H chemical shifts were calibrated to internal standard – tetramethylsilane [$\delta(^1H)$ =0.00] or to residual signals of $CDCl_3$ [$\delta(^1H)$ =7.27], THF [$\delta(^1H)$ =3.58 or 1.73], $toluene-d_8$ [$\delta(^1H)$ =2.08] or $DMSO-d_6$ [$\delta(^1H)$ =2.50]. Values of ^{13}C chemical shifts were calibrated to signals of $CDCl_3$ [$\delta(^{13}C)$ =77.16], THF

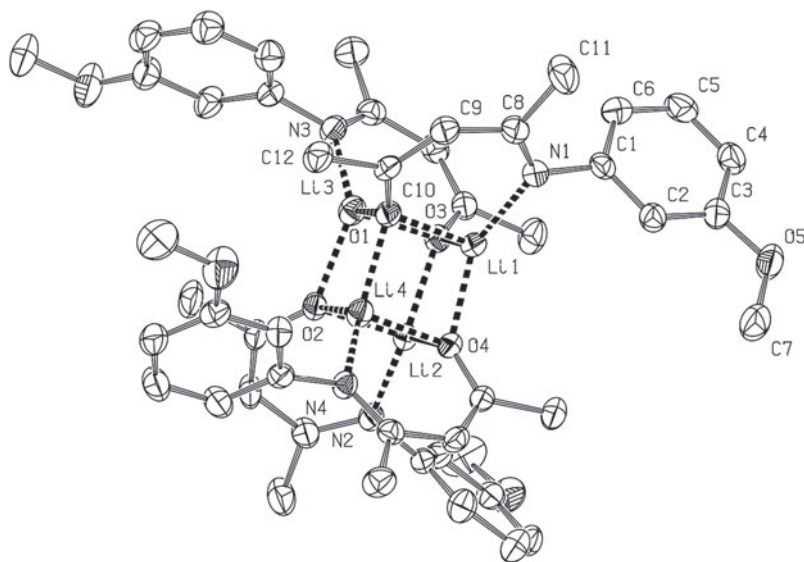


Figure 13 Molecular structure of $L^{CM}_{1/2}Li$ (ORTEP view, 60% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): C1–N1 1.423(5); N1–C8 1.298(5); C8–C9 1.437(6); C9–C10 1.363(6); C10–O1 1.304(4); C1–N1–C8 120.20(3); N1–C8–C9 122.40(4); C8–C9–C10 128.80(4); C9–C10–O1 124.90(3).

$[\delta(^{13}C)=67.21$ or $25.31]$, toluene- d_8 $[\delta(^{13}C)=20.43]$ and DMSO- d_6 $[\delta(^{13}C)=39.52]$. The 7Li NMR spectra were calibrated to external 1 M LiCl in D_2O $[\delta(^7Li)=0.0$ ppm]. ^{119}Sn chemical shift values are referred to external neat tetramethylstannane $[\delta(^{119}Sn)=0.0$ ppm]. Positive chemical shift values denote shifts to the higher frequencies relative to the standards. ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode. All ^{13}C NMR spectra were measured using the standard proton-decoupled experiment and CH_3 vs. C and CH_2 were differentiated by the standard APT method (Patt and Shoolery, 1982).

Elemental analyses The compositional analyses were determined (under an inert atmosphere of argon if necessary) on the automatic analyzer EA 1108 by FISOONS Instruments (Parkton, UK).

IR spectroscopy IR spectra of samples in KBr pellets were measured in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer (Thermo Electron Scientific Instruments LLC, Fitchburg, WI, USA) in the range $400\text{--}4000\text{ cm}^{-1}$. KBr pellets were prepared in a glovebox Labmaster 130 (mBraun) under purified nitrogen. IR spectra of neat liquid samples were measured among KBr slides on a Nicolet Avatar FT IR spectrometer in the range $400\text{--}4000\text{ cm}^{-1}$.

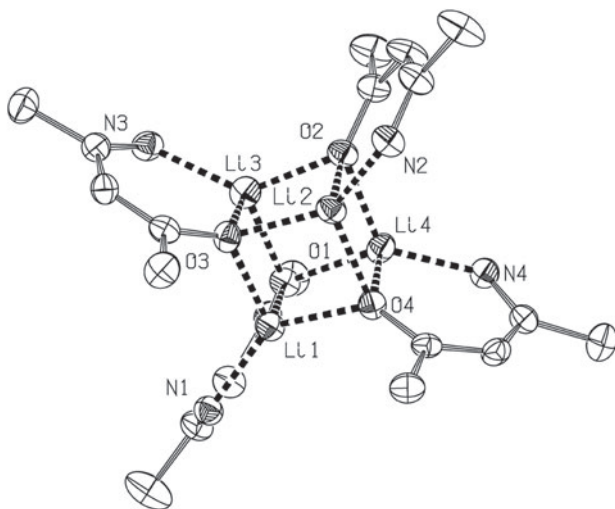


Figure 14 Detail of deformed heterocubane of molecular structure of $L^{CM}_{1/2}Li$ (ORTEP view, 60% probability level). Some of the ligands and hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Li1–O1 1.922(6); Li1–O4 1.963(6); Li1–O3 1.963(6); Li1–N1 1.963(6); O4–Li1–O1 93.50(3); O4–Li1–O3 94.10(3); O4–Li1–N1 140.10(3); O1–Li1–N1 96.40(3).

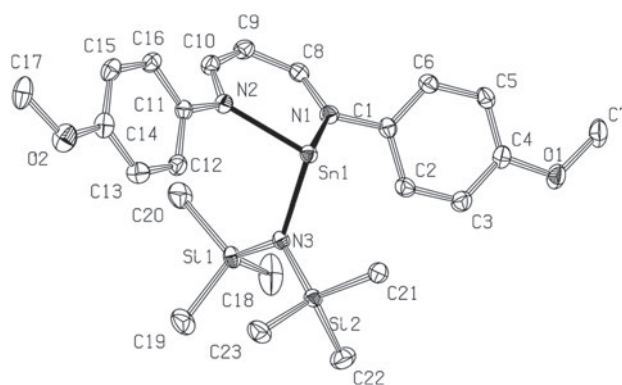


Figure 15 Molecular structure of $L^{HP}Sn[Si(CH_3)_3]_2$ (ORTEP view, 30% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): C11–N2 1.428(5); N2–C10 1.322(4); C10–C9 1.387(6); C9–C8 1.389(5); C8–N1 1.320(4); N1–C1 1.427(5); N2–Sn1 2.226(3); N1–Sn1 2.221(3); Sn1–N3 2.135(3); Sn1–Si1 3.228(10); C11–N2–C10 118.6(3); N2–C10–C9 128.3(3); C10–C9–C8 127.03(3); C9–C8–N1 127.01(4); C8–N1–C1 118.1(3); N2–Sn1–N1 84.82(10); N2–Sn1–N3 100.70(10); N1–Sn1–N3 97.96(10); C9–Sn1–N3 106.14(9).

Crystallography The X-ray data obtained from colorless crystals for all compounds were acquired at 150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer (Bruker-Nonius, Delft, The Netherlands) with MoK_α radiation ($\lambda=0.71073$ Å), a graphite monochromator, and in the Φ and χ scan mode. Data reductions were performed with DENZO-SMN (Otwinowski and Minor, 1997). The absorption was corrected by integration methods (Coppens, 1970). Structures were solved by direct methods (Sir92) (Altomare et al., 1993) and refined by full matrix least-square based on F^2 (SHELXL97) (Sheldrick, 1997). Hydrogen atoms were mostly localized on a difference Fourier map, but to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{\text{iso}}(\text{H})=1.2 U_{\text{eq}}$ (pivot atom) or of $1.5 U_{\text{eq}}$ for the methyl moiety with $\text{C-H}=0.96, 0.97, 0.98$ and 0.93 Å for methyl, methylene, methine and hydrogen atoms in aromatic rings, or multiply bounded C-H groups, respectively. Protons on N and O were located on the Fourier difference map. The water molecule in the structure of $\text{L}^{\text{HO}}\text{H}.\text{HCl}$ is disordered into two positions and is treated by standard constraints and restraints in the SHELXL97 program (Sheldrick, 1997).

Crystallographic data (Table 3) for structural analysis have been deposited with the Cambridge Crystallographic Data Center. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). CCDC deposition numbers 860307–860314.

Syntheses

General procedures Preparation of $\text{L}^{\text{CM}}_{1/2}\text{Li}$, $\text{L}^{\text{CM}}_{1/2}\text{Bu}_3\text{Sn}$, $\text{L}^{\text{CM}}_{1/2}\text{Ph}_3\text{Sn}$, $\text{L}^{\text{CM}}_{1/2}\text{Ph}_2\text{SnCl}$ and $\text{L}^{\text{HP}}\text{SnN}[\text{Si}(\text{Me})_3]_2$ complexes was performed using standard Schlenk techniques under inert atmosphere of argon. Solvents and reactants were purchased from commercial sources. Solvents (Et_2O , hexane) were distilled over K/Na alloy, degassed and then stored over a K-mirror under argon atmosphere.

General procedure of preparation of $\text{L}^{\text{CO}}\text{H}$ 2,4-Pentandione (25 ml, 0.24 mol), 2-methoxyaniline (60 ml, 0.53 mol) and toluene (ca. 200 ml) were mixed in a 500 ml round bottomed flask (Carey et al., 2003). A catalytic amount of *p*-toluenesulfonic acid (30 mg, 0.17 mmol) was added. Resultant yellow-brown mixture was stirred and heated to reflux for 5 h. The water (ca. 8 ml) formed by the reaction was continually distilled off using a Dean-Stark apparatus. The majority of toluene (150 ml) was then removed off by distillation and the residue was cooled slowly to room temperature and then stored in a freezer (-28°C) for 5 h. Yellow-brown solid product was filtered, washed twice with petrolether (20 ml) and recrystallized twice from chloroform.

General procedure of preparation of $\text{L}^{\text{CO}}_{1/2}\text{H}$, $\text{L}^{\text{CM}}\text{H}$, $\text{L}^{\text{CM}}_{1/2}\text{H}$, $\text{L}^{\text{CP}}\text{H}$, $\text{L}^{\text{CP}}_{1/2}\text{H}$, $\text{L}^{\text{CCIO}}_{1/2}\text{H}$ and $\text{L}^{\text{CCIP}}_{1/2}\text{H}$ In a slight modification of the literature procedure (Carey et al., 2003; Chen et al., 2005), all toluene was distilled off from the reaction mixture. The residue was vacuum-distilled. Two major fractions were collected: the first was β -aminoketone and the second desired β -diketiminates.

General procedure of preparation of $\text{L}^{\text{HO}}\text{H}.\text{HCl}$, $\text{L}^{\text{HM}}\text{H}.\text{HCl}$ and $\text{L}^{\text{HP}}\text{H}.\text{HCl}$ A mixture of HCl (10 ml, 36%, 0.12 mol) and methoxyaniline (0.13 mol) in distilled water (150 ml) was added dropwise to the solution of 1,1,3,3-tetramethoxypropane (10 ml, 0.06 mol) and HCl (8 ml, 36%, 0.094 mol) in distilled water (100 ml) (Jung and

Kim, 2006). Reaction mixture was heated to 70°C . Orange-red precipitate was formed immediately. After filtration the precipitate was washed twice with petrolether (30 ml).

Compounds $\text{L}^{\text{HO}}\text{H}.\text{HCl}$ and $\text{L}^{\text{HP}}\text{H}.\text{HCl}$ can be prepared by reaction of concentrated HCl (5 ml, 36%, 0.06 mol), which was added through a reflux cooler to methoxyaniline (0.04 mol) in a round bottomed flask equipped with a condenser. After a short time, 1,1,3,3-tetramethoxypropane (3.3 ml, 0.02 mol) was added and the reaction mixture was heated to reflux for 11 h (Richards and Webb, 1976; Kikugawa and Sugimura, 1986). After cooling to room temperature dark red product was filtered, washed with petrolether (20 ml) and recrystallized from ethanol.

The second alternative syntheses of ligands $\text{L}^{\text{HO}}\text{H}.\text{HCl}$ and $\text{L}^{\text{HP}}\text{H}.\text{HCl}$ is reaction 1,1,3,3-tetramethoxypropane (3.3 ml, 0.02 mol), which was added to the solution of HCl (5 ml, 36%, 0.06 mol) in ethanol (40 ml). The reaction mixture was heated to reflux for 5 h. Red precipitate was filtered, washed with hexane (30 ml) and recrystallized from ethanol.

General procedure of preparation of $\text{L}^{\text{HO}}\text{H}$, $\text{L}^{\text{HM}}\text{H}$ and $\text{L}^{\text{HP}}\text{H}$ from their hydrochlorides

Protonated ligands $\text{L}^{\text{H}}.\text{HCl}$ were dissolved in CHCl_3 (ca. 30 ml) or in a mixture of CH_2Cl_2 and Et_2O (5:1, ca. 40 ml). The solution was extracted with water solution of NaOH (0.2 M, ca. 20 ml) or Na_2CO_3 (20%, ca. 40 ml). Organic phase was separated, dried with anhydrous Na_2SO_4 and filtered. Pure products were obtained after evaporation of solvents *in vacuo*.

General procedure of preparation of Sn(IV) complexes from

$\text{L}^{\text{CM}}_{1/2}\text{Li}$ All syntheses were performed using standard Schlenk techniques under inert argon atmosphere. Sn(IV) compounds were suspended in dried Et_2O (15 ml) and cooled to -78°C . Then, $\text{L}^{\text{CM}}_{1/2}\text{Li}$ in Et_2O (15 ml) was added. The reaction mixture was slowly warmed to room temperature and LiCl formed during the warming was filtered.

$\text{L}^{\text{CO}}\text{H}$; *N,N'*-pent-2-en-2-yl-4-ylidene-bis(2-methoxyaniline) (Carey et al., 2003) Yellow solid. Yield 12.5 g (17%). Elemental anal. (%) for $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.4; H, 7.0; N, 9.0. Melting point $123\text{--}125^\circ\text{C}$. ^1H NMR CDCl_3 (500 MHz, CDCl_3 , 298 K): δ 12.73 (s, 1H, NH), 7.11 (d, $J_{\text{H-H}}=8.00$ Hz, 4H, Ar), 6.92–6.88 (m, 4H, Ar), 4.94 (s, 1H, $\text{NHC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{N}$), 3.79 (s, 6H, OCH_3), 1.99 (s, 6H, $\text{NHC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{N}$). ^{13}C NMR (125 MHz, CDCl_3 , 298 K): δ 159.9 (C=N), 151.2 (C-NH, aromatic C), 135.3 (C-OCH₃, aromatic C), 123.6, 123.0, 120.5 and 111.5 (aromatic CH), 97.9 ($\text{NHC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{N}$), 55.7 (OCH_3), 21.2 ($\text{NHC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{N}$). IR (KBr, cm^{-1}): 3068–3004 (m, $\text{C}_{\text{arom}}\text{H}$), 2971–2938 (m, CH_3), 2833 (m, OCH_3), 1630 (s), 1594 (m), 1557 (vs), 1480 (m), 1382 (m), 1286 (s), 1231 (s), 1189 (m, C-N stretching), 1118 (m), 1026 (s), 746 (s, CH out of plane bending, *o*-substituted benzenes).

$\text{L}^{\text{CO}}_{1/2}\text{H}$; 4-[(2-methoxyphenyl)amino]pent-3-en-2-one (Sanchez et al., 1997) In a slight modification of the literature procedure (Carey et al., 2003; Chen et al., 2005), 2,4-pentandione (25 ml, 0.24 mol) and *o*-anisidine (27 ml, 0.24 mol) reacted equimolar. The product was collected as pale yellow oil at $130\text{--}137^\circ\text{C}$ (pressure 266 Pa). Yield 25.5 g (52%). Elemental anal. (%) for $\text{C}_{12}\text{H}_{15}\text{NO}_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.2; H, 7.4; N, 6.7. ^1H NMR (500 MHz, CDCl_3 , 298 K): δ 12.29 (s, 1H, NH), 7.03 (t, $J_{\text{H-H}}=7.75$ Hz, 2H, Ar), 6.82 (d, $J_{\text{H-H}}=9.60$ Hz, 2H, Ar), 5.12 (s, 1H, $\text{NHC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{O}$), 3.75 (s, 3H, OCH_3), 2.01 (s, 3H, $\text{NHC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{O}$), 1.90 (s, 3H, $\text{NHC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{O}$). ^{13}C NMR (125 MHz, CDCl_3 , 298 K): δ 195.4 (C=O), 160.0 (C-N), 152.4 (C-NH, aromatic C), 127.7 (C-OCH₃, aromatic C), 125.9, 124.6, 120.0 and 111.0 (aromatic CH), 97.6 ($\text{NHC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{O}$), 55.4 (OCH_3), 28.9 ($\text{NHC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{O}$), 19.7 ($\text{NHC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{O}$). IR (neat, cm^{-1}):

Table 3 Crystallographic data.

Compound reference	L ^{H^o} H.HCl	L ^{H^o} H	L ^{H^p} H	L ^{CCP} H _{1/2}	Quinoline ^a	L ^{C^o} H	L ^{CM} Li _{1/2}	L ^{H^p} SnN[Si(CH ₃) ₃] ₂
Chemical formula	C ₁₇ H ₁₉ ClN ₂ O ₂	C ₁₇ H ₁₈ N ₂ O ₂	C ₁₇ H ₁₈ N ₂ O ₂	C ₁₁ H ₁₂ ClNO	C ₁₉ H ₂₁ N ₂ O ₂	C ₁₉ H ₂₂ N ₂ O ₂	C ₄₈ H ₅₆ N ₄ O ₈	C ₂₃ H ₃₅ N ₃ O ₂ Si ₂ Sn
Formula mass	354.82	282.33	282.33	209.67	359.43	310.39	918.85	560.41
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
<i>a</i> , Å	34.951(4)	9.8320(4)	31.6123(8)	6.9730(5)	6.8830(3)	12.6880(5)	13.4578(12)	13.8580(10)
<i>b</i> , Å	5.504(3)	10.2601(3)	7.3029(11)	7.9481(4)	10.3509(5)	17.2460(9)	13.9082(13)	12.6270(4)
<i>c</i> , Å	19.532(2)	14.6299(11)	6.3310(2)	10.5520(4)	24.3992(16)	7.7221(7)	15.1270(9)	17.1521(13)
<i>α</i> , °	90.00	90	90	99.767(4)	90	90	103.536(7)	90
<i>β</i> , °	109.25(12)	90	90	100.433(5)	96.324(5)	102.032(5)	95.251(6)	117.521(6)
<i>γ</i> , °	90.00	90	90	109.868(4)	90	90	103.814(6)	90
Unit cell volume, Å ³	3547.4(3)	1475.83(13)	1461.6(2)	523.74(5)	1727.75(16)	1652.59(18)	2640.3(4)	2661.7(3)
Temperature, K	150(1)	150(1)	150(1)	150(1)	150(1)	150(1)	150(1)	150(1)
Space group	C2/c	<i>Pca</i> 2 ₁	<i>Cmc</i> 2 ₁	<i>P</i> -1	<i>P</i> 2/c	<i>P</i> 2/c	<i>P</i> -1	<i>P</i> 2/c
No. of formula units per unit cell, Z	8	4	4	2	4	4	2	4
Absorption coefficient, μ/mm ⁻¹	0.238	0.084	0.085	0.330	0.211	0.081	0.077	1.073
No. of reflections measured	8466	10 027	5124	10 122	13 065	12 546	46 340	23 061
No. of independent reflections	2275	2629	1322	1810	2970	2778	7039	4523
<i>R</i> _{int} ^b	0.0630	0.0784	0.0584	0.0794	0.0417	0.0485	0.0950	0.0571
Final <i>R</i> _i values [<i>I</i> > 2σ(<i>I</i>)] ^c	0.0924	0.0488	0.0485	0.0433	0.0487	0.0564	0.0896	0.0391
Final <i>wR</i> (<i>F</i> ²) values [<i>I</i> > 2σ(<i>I</i>)] ^c	0.2385	0.0979	0.0910	0.1018	0.1078	0.1136	0.1884	0.0601
Goodness of fit ^d on <i>F</i> ²	1.083	1.071	1.160	1.075	1.087	1.170	1.093	1.107

^a7-Methoxy-2,4-dimethylquinolinium 4-methylbenzenesulfonate.^b $R_{int} = \sum |F_o^2 - F_{o,mean}^2| / \sum F_o^2$.^cWeighting scheme: $w = [\sigma^2(F_o^2) + (w_p P)^2 + w_r P^{-1}]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \sum |F_o| - |F_c| / \sum |F_o|$, $wR(F^2) = [\sum (w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2}$.^d $S = [\sum (w(F_o^2 - F_c^2)^2) / (N_{diff} - N_{param})]^{1/2}$.

3068–3001 (m, C_{arom}H), 2963–2914 (m, CH₃), 2837 (m, OCH₃), 1616 (vs, C=O_{stretching}), 1571 (vs, C=O_{stretching}), 1482 (m), 1355 (m), 1279 (s), 1248 (m), 1174 (m, C-N_{stretching}), 1117 (m), 1027 (s), 750 (s, CH out of plane bending, *o*-substituted benzenes).

L^{CM}H; *N,N*-pent-2-en-2-yl-4-ylidene-bis(3-methoxyaniline) Yellow orange oil. Collected at 130–133°C (pressure 266 Pa). Yield 20.0 g (27%). Elemental anal. (%) for C₁₉H₂₂N₂O₂: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.4; H, 7.1; N, 9.0. ¹H NMR (500 MHz, CDCl₃, 298 K): δ 12.54 (s, 1H, NH), 7.14 (t, $J_{\text{H-H}}=8.02$ Hz, 1H, Ar), 6.96 (t, $J_{\text{H-H}}=7.97$ Hz, 1H, Ar), 6.66 (d, $J_{\text{H-H}}=8.35$ Hz, 1H, Ar), 6.62 (d, $J_{\text{H-H}}=7.88$ Hz, 1H, Ar), 6.59 (s, 1H, Ar), 6.23 (d, $J_{\text{H-H}}=8.16$ Hz, 1H, Ar), 6.20 (d, $J_{\text{H-H}}=7.90$ Hz, 1H, Ar), 6.16 (s, 1H, Ar), 5.13 (s, 1H, NHC(CH₃)-CHC(CH₃)N), 3.65 (s, 3H, OCH₃), 3.62 (s, 3H, OCH₃), 2.05 (s, 3H, NHC(CH₃)-CHC(CH₃)N), 1.92 (s, 3H, NHC(CH₃)-CHC(CH₃)N). ¹³C NMR (125 MHz, CDCl₃, 298 K): δ 160.3 (C=N), 148.1 (C-NH aromatic C), 139.4 (C-OCH₃, aromatic C), 109.7, 107.7, 103.0 and 100.3 (aromatic CH), 97.4 (NHC(CH₃)-CHC(CH₃)N), 54.7 (OCH₃), 54.3 (OCH₃), 19.3 (NHC(CH₃)-CHC(CH₃)N). IR (neat, cm⁻¹): 3062–3008 (m, C_{arom}H), 2999–2945 (m, CH₃), 2835 (m, OCH₃), 1621 (vs), 1600 (vs), 1573 (vs), 1496 (m), 1357 (m), 1287 (s), 1207 (m, C-N_{stretching}), 1158 (s), 1041 (m), 957 (m), 846 (m), 762 (m, NH_{def}), 689 (m, CH out of plane bending, *m*-substituted benzenes).

L^{CM}_{1/2}H; 4-[(3-methoxyphenyl)amino]pent-3-en-2-one (Zhuo, 1997) The product was yellow oil and was collected as secondary product at 115–119°C (pressure 266 Pa). Yield 15.0 g. Elemental anal. (%) for C₁₂H₁₅NO₂: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.1; H, 7.2; N, 6.8. ¹H NMR (500 MHz, CDCl₃, 298 K): δ 12.35 (s, 1H, NH), 6.99 (t, $J_{\text{H-H}}=8.04$ Hz, 1H, Ar), 6.50 (d, $J_{\text{H-H}}=8.31$ Hz, 1H, Ar), 6.47 (d, $J_{\text{H-H}}=7.85$ Hz, 1H, Ar), 6.42 (s, 1H, Ar), 5.05 (s, 1H, NHC(CH₃)-CHC(CH₃)O), 3.54 (s, 3H, OCH₃), 1.88 (s, 3H, NHC(CH₃)-CHC(CH₃)O), 1.79 (s, 3H, NHC(CH₃)-CHC(CH₃)O). ¹³C NMR (125 MHz, CDCl₃, 298 K): δ 195.4 (C=O), 159.7 (C-N), 159.4 (C-NH, aromatic C), 139.4 (C-OCH₃, aromatic C), 129.3, 116.1, 111.3 and 110.3 (aromatic CH), 97.3 (NHC(CH₃)-CHC(CH₃)O), 54.6 (OCH₃), 30.2 (NHC(CH₃)-CHC(CH₃)O), 19.3 (NHC(CH₃)-CHC(CH₃)O). IR (neat, cm⁻¹): 3064–3000 (m, C_{arom}H), 2961–2903 (m, CH₃), 2836 (m, OCH₃), 1600 (vs, C=O_{stretching}), 1576 (vs, C=O_{stretching}), 1494 (m), 1320 (m), 1281 (s), 1188 (m, C-N_{stretching}), 1157 (s), 1048 (m), 957 (m), 851 (m), 757 (m, NH_{def}), 693 (m, CH out of plane bending, *m*-substituted benzenes).

L^{CP}H; *N,N*-pent-2-en-2-yl-4-ylidene-bis(4-methoxyaniline) (Gong and Ma, 2008) The product was collected as distillation residue and recrystallized from chloroform. The product was dark viscous oil. Yield 10.0 g (13%). Elemental anal. (%) for C₁₉H₂₂N₂O₂: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.6; H, 7.1; N, 9.0. ¹H NMR (500 MHz, CDCl₃, 298 K): δ 12.57 (br s, 1H, NH), 7.13 (d, $J_{\text{H-H}}=7.58$ Hz, 4H, Ar), 6.87 (d, $J_{\text{H-H}}=8.69$ Hz, 4H, Ar), 4.87 (s, 1H, NHC(CH₃)-CHC(CH₃)N), 3.80 (s, 6H, OCH₃), 1.99 (s, 6H, NHC(CH₃)-CHC(CH₃)N). ¹³C NMR (125 MHz, CDCl₃, 298 K): δ 160.2 (C=N), 156.0 (C-NH aromatic C), 138.9 (C-OCH₃, aromatic C), 124.2 and 114.2 (aromatic CH), 96.4 (NHC(CH₃)-CHC(CH₃)N), 55.5 (OCH₃), 20.7 (NHC(CH₃)-CHC(CH₃)N). IR (KBr, cm⁻¹): 3034–3001 (w, C_{arom}H), 2957–2901 (m, CH₃), 2833 (m, OCH₃), 1623 (s), 1542 (s), 1501 (vs), 1276 (m), 1243 (vs), 1187 (m, C-N_{stretching}), 1034 (m), 839 (s, CH out of plane bending, *p*-substituted benzenes), 770 (w, NH_{def}).

L^{CP}_{1/2}H; 4-[(4-methoxyphenyl)amino]pent-3-en-2-one (Zhang et al., 2006) The product was yellow oil and was collected as secondary product at 135–145°C (pressure 266 Pa). Yield 25.0 g. Elemental anal. (%) for C₁₂H₁₅NO₂: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.2; H, 7.3; N, 6.8. ¹H NMR (500 MHz, CDCl₃, 298 K): δ 12.26 (s, 1H,

NH), 6.96 (d, $J_{\text{H-H}}=8.69$ Hz, 2H, Ar), 6.75 (d, $J_{\text{H-H}}=8.80$ Hz, 2H, Ar), 5.09 (s, 1H, NHC(CH₃)-CHC(CH₃)O), 3.71 (s, 3H, OCH₃), 2.01 (s, 3H, NHC(CH₃)-CHC(CH₃)O), 1.83 (s, 3H, NHC(CH₃)-CHC(CH₃)O). ¹³C NMR (125 MHz, CDCl₃, 298 K): δ 195.6 (C=O), 168.5 (C-N), 161.2 (C-NH, aromatic C), 131.3 (C-OCH₃, aromatic C), 126.5 and 114.4 (aromatic CH), 96.8 (NHC(CH₃)-CHC(CH₃)O), 55.3 (OCH₃), 28.9 (NHC(CH₃)-CHC(CH₃)O), 19.5 (NHC(CH₃)-CHC(CH₃)O). IR (neat, cm⁻¹): 3066–3000 (w, C_{arom}H), 2999–2910 (m, CH₃), 2836 (m, OCH₃), 1614 (vs, C=O_{stretching}), 1570 (s, C=O_{stretching}), 1516 (vs), 1279 (m), 1248 (vs), 1187 (m, C-N_{stretching}), 1034 (m), 842 (s, CH out of plane bending, *p*-substituted benzenes), 745 (w, NH_{def}).

L^{HO}H.HCl; 2-methoxy-*N*-[3-[(2-methoxyphenyl)amino]prop-2-en-1-ylidene]anilinium chloride (Richards and Webb, 1976) The product was collected as red solid. Yield 11.5 g (65%). Elemental anal. (%) for C₁₇H₁₉ClN₂O₂: C, 64.05; H, 6.01; Cl, 11.12; N, 8.79. Found: C, 64.15; H, 6.0; Cl, 11.0; N, 8.8. Melting point 125–133°C. ¹H NMR (500 MHz, DMSO-d₆, 298 K): δ 11.85 (d, $J_{\text{H-H}}=13.85$ Hz, 2H, NH), 8.93 (t, $J_{\text{H-H}}=12.01$ Hz, 2H, NHCHCHCHNH), 7.56 (d, $J_{\text{H-H}}=7.87$ Hz, 2H, Ar), 7.27 (t, $J_{\text{H-H}}=7.57$ Hz, 2H, Ar), 7.18 (d, $J_{\text{H-H}}=8.23$ Hz, 2H, Ar), 7.07 (t, $J_{\text{H-H}}=7.61$ Hz, 2H, Ar), 6.74 (t, $J_{\text{H-H}}=11.64$ Hz, 1H, NHCHCHCHNH), 3.93 (s, 6H, OCH₃). ¹³C NMR (125 MHz, DMSO-d₆, 298 K): δ 161.7 (C=N), 151.0 (C-NH, aromatic C), 130.3 (C-OCH₃, aromatic C), 128.8, 122.2, 119.7 and 113.5 (aromatic CH), 100.7 (NHCHCHCHNH), 57.1 (OCH₃).

L^{HM}H.HCl; 3-methoxy-*N*-[3-[(3-methoxyphenyl)amino]prop-2-en-1-ylidene]anilinium chloride The product was collected as red solid. Yield 10.6 g (60%). Elemental anal. (%) for C₁₇H₁₉ClN₂O₂: C, 64.05; H, 6.01; Cl, 11.12; N, 8.79. Found: C, 64.2; H, 6.1; Cl, 11.0; N, 8.9. Melting point 125–135°C. ¹H NMR (500 MHz, DMSO-d₆, 298 K): δ 12.64 (d, $J_{\text{H-H}}=13.90$ Hz, 2H, NH), 9.03 (t, $J_{\text{H-H}}=13.13$ Hz, 2H, NHCHCHCHNH), 7.35 (t, $J_{\text{H-H}}=8.05$ Hz, 2H, Ar), 7.07 (s, 2H, Ar), 7.02 (d, $J_{\text{H-H}}=7.85$ Hz, 2H, Ar), 6.82 (d, $J_{\text{H-H}}=8.15$ Hz, 2H, Ar), 6.49 (t, $J_{\text{H-H}}=11.43$ Hz, 1H, NHCHCHCHNH), 3.81 (s, 6H, OCH₃). ¹³C NMR (125 MHz, DMSO-d₆, 298 K): δ 161.4 (C=N), 159.5 (C-NH₂, aromatic C), 140.8 (C-OCH₃, aromatic C), 131.8, 112.6, 110.9 and 104.0 (aromatic C), 99.6 (NHCHCHCHNH), 56.5 (OCH₃).

L^{HP}H.HCl; 4-methoxy-*N*-[3-[(4-methoxyphenyl)amino]prop-2-en-1-ylidene]anilinium chloride (Richards and Webb, 1976; Kikugawa and Sugimura, 1986) The product was collected as red solid. Yield 8.8 g (50%). Elemental anal. (%) for C₁₇H₁₉ClN₂O₂: C, 64.05; H, 6.01; Cl, 11.12; N, 8.79. Found: C, 64.1; H, 6.1; Cl, 11.0; N, 8.8. Melting point 128–133°C. ¹H NMR (500 MHz, DMSO-d₆, 298 K): δ 12.47 (d, $J_{\text{H-H}}=14.10$ Hz, 2H, NH), 8.81 (t, $J_{\text{H-H}}=11.70$ Hz, 2H, NHCHCHCHNH), 7.39 (d, $J_{\text{H-H}}=8.99$ Hz, 4H, Ar), 7.00 (d, $J_{\text{H-H}}=8.92$ Hz, 4H, Ar), 6.41 (t, $J_{\text{H-H}}=11.56$ Hz, 1H, NHCHCHCHNH), 3.76 (s, 6H, OCH₃). ¹³C NMR (125 MHz, DMSO-d₆, 298 K): δ 158.2 (C=N), 133.1 (C-NH₂, aromatic C), 125.5 (C-OCH₃, aromatic C), 119.7 and 116.0 (aromatic C), 98.7 (NHCHCHCHNH), 56.4 (OCH₃).

L^{HO}H; *N,N*-prop-1-en-1-yl-3-ylidene-bis(2-methoxyaniline) (Richards and Webb, 1976) The product was collected as yellow solid. Yield 3.5 g (55% overall, calculated on 2,4-pentandione). Elemental anal. (%) for C₁₇H₁₈N₂O₂: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.3; H, 6.4; N, 9.9. Melting point 120–122°C. ¹H NMR (500 MHz, CDCl₃, 298 K): δ 12.21 (br s, 1H, NH), 7.75 (d, $J_{\text{H-H}}=5.05$ Hz, 2H, NHCHCHCHNH), 7.05–7.01 (m, 4H, Ar), 6.96–6.91 (m, 4H, Ar), 5.17 (t, $J_{\text{H-H}}=6.00$ Hz, 1H, NHCHCHCHNH), 3.88 (s, 6H, OCH₃). ¹³C NMR (125 MHz, CDCl₃, 298 K): δ 150.0 (C=N), 148.1 (C-NH₂, aromatic C), 136.6 (C-OCH₃, aromatic C), 123.3, 120.9, 114.9 and 110.8 (aromatic C), 95.9 (NHCHCHCHNH), 55.4 (OCH₃). IR (KBr, cm⁻¹): 3084–3014 (m, C_{arom}H), 2958–2914 (m, CH₃), 2837 (m, OCH₃), 1631 (vs), 1594 (m),

1542 (vs), 1462 (m), 1386 (m), 1279 (s), 1248 (s), 1178 (m, C-N_{stretching}), 1118 (m), 1029 (s), 750 (s, CH out of plane bending, *o*-substituted benzenes).

$L^{HM}H$; *N,N*-prop-1-en-1-yl-3-ylidene-bis(3-methoxyaniline) The product was collected as red viscous oil. Yield 2.3 g (51% overall, calculated on 2,4-pentandione). Elemental anal. (%) for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.3; H, 6.5; N, 9.9. 1H NMR (500 MHz, $CDCl_3$, 298 K): δ 12.48 (br s, 1H, NH), 7.69 (d, $J_{H-H}=6.80$ Hz, 2H, NHCHCHCHN), 7.24 (t, $J_{H-H}=8.05$ Hz, 2H, Ar), 6.69 (d, $J_{H-H}=8.13$ Hz, 2H, Ar), 6.65–6.62 (m, 4H, Ar), 5.17 (t, $J_{H-H}=6.03$ Hz, 1H, NHCHCHCHNH), 3.82 (s, 6H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 156.7 (C=N), 149.2 (C-NH₂, aromatic C), 140.5 (C-OCH₃, aromatic C), 117.1, 114.0, 109.3 and 108.7 (aromatic C), 95.8 (NHCHCHCHN), 55.0 (OCH_3). IR (KBr, cm^{-1}): 3062–3008 (m, C_{arom}H), 2965–2939 (m, CH₃), 2835 (m, OCH_3), 1653 (vs), 1599 (vs), 1483 (m), 1365 (m), 1286 (m), 1196 (m, C-N_{stretching}), 1049 (s), 931 (m), 829 (m), 764 (m, NH_{def}), 685 (m, CH out of plane bending, *m*-substituted benzenes).

$L^{HP}H$; *N,N*-prop-1-en-1-yl-3-ylidene-bis(4-methoxyaniline) (Richards and Webb, 1976; Kikugawa and Sugimura, 1986) The product was collected as yellow solid. Yield 2.0 g (43% overall, calculated on 2,4-pentandione). Elemental anal. (%) for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.3; H, 6.4; N, 9.8. Melting point 121–123°C. 1H NMR (500 MHz, $CDCl_3$, 298 K): δ 12.22 (br s, 1H, NH), 7.64 (d, $J_{H-H}=6.33$ Hz, 2H, NHCHCHCHN), 7.05 (d, $J_{H-H}=8.67$ Hz, 4H, Ar), 6.89 (d, $J_{H-H}=8.83$ Hz, 4H, Ar), 5.05 (t, $J_{H-H}=5.56$ Hz, 1H, NHCHCHCHNH), 3.81 (s, 6H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 156.4 (C=N), 148.2 (C-NH₂, aromatic C), 140.6 (C-OCH₃, aromatic C), 119.4, 114.8 (aromatic C), 94.4 (NHCHCHCHN), 55.7 (OCH_3). IR (KBr, cm^{-1}): 3072–3006 (w, C_{arom}H), 2959–2901 (m, CH₃), 2839 (m, OCH_3), 1647 (s), 1557 (m), 1516 (vs), 1290 (s), 1244 (vs), 1033 (m), 1179 (m, C-N_{stretching}), 830 (s, CH out of plane bending, *p*-substituted benzenes), 757 (w, NH_{def}).

$L^{CCIO}_{1/2}H$; 4-[(2-chlorophenyl)amino]pent-3-en-2-one (Musker and Sakhawat, 1966) In a slight modification of the literature procedure (Carey et al., 2003; Chen et al., 2005), 2,4-pentandione (25 ml, 0.24 mol) and *o*-chloroaniline (25 ml, 0.24 mol) reacted equimolar. The product was collected as yellow oil at 115–135°C (pressure 266 Pa). Yield 7.5 g (15%). Elemental anal. (%) for $C_{17}H_{18}N_2O_2$: C, 63.01; H, 5.77; Cl, 16.91; N, 6.68. Found: C, 63.1; H, 5.8; Cl, 16.8; N, 6.7. 1H NMR (500 MHz, $CDCl_3$, 298 K): δ 12.40 (s, 1H, NH), 7.33–7.15 (m, 4H, Ar), 5.16 (s, 1H, NHC(CH₃)CHC(CH₃)O), 2.03 (s, 3H, NHC(CH₃)CHC(CH₃)O), 1.75 (s, 3H, NHC(CH₃)CHC(CH₃)O). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 197.5 (C=O), 159.15 (C-N), 140.2 (C-NH, aromatic C), 130.5 (C-Cl, aromatic C), 128.5, 127.2, 123.8 and 121.4 (aromatic CH), 98.5 (NHC(CH₃)CHC(CH₃)O), 29.3 (NHC(CH₃)CHC(CH₃)O), 19.8 (NHC(CH₃)CHC(CH₃)O).

$L^{CCIP}_{1/2}H$; 4-[(4-chlorophenyl)amino]pent-3-en-2-one (Zhuo, 1997) In a slight modification of the literature procedure (Carey et al., 2003), 2,4-pentandione (25 ml, 0.24 mol) and *o*-chloroaniline (30 g, 0.24 mol) reacted equimolar. Most of the toluene was distilled of the reaction mixture. The product was collected as yellow brown solid. Yield 6.0 g (12%). Elemental anal. (%) for $C_{17}H_{18}N_2O_2$: C, 63.01; H, 5.77; Cl, 16.91; N, 6.68. Found: C, 63.1; H, 5.8; Cl, 16.7; N, 6.5. 1H NMR (500 MHz, $CDCl_3$, 298 K): δ 12.42 (s, 1H, NH), 7.25 (d, $J_{H-H}=8.67$ Hz, 2H, Ar), 6.98 (d, $J_{H-H}=8.62$ Hz, 2H, Ar), 5.17 (s, 1H, NHC(CH₃)CHC(CH₃)O), 2.06 (s, 3H, NHC(CH₃)CHC(CH₃)O), 1.94 (s, 3H, NHC(CH₃)CHC(CH₃)O). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 196.5 (C=O), 159.7 (C-N), 138.4 (C-NH, aromatic C), 130.9 (C-Cl, aromatic C), 128.9 and 127.3 (aromatic CH), 98.0

(NHC(CH₃)CHC(CH₃)O), 30.0 (NHC(CH₃)CHC(CH₃)O), 19.9 (NHC(CH₃)CHC(CH₃)O). IR (KBr, cm^{-1}): 3186–3023 (m, C_{arom}H), 2933–2901 (w, CH₃), 2874 (w, OCH_3), 1600 (s), 1564 (s), 1533 (vs), 1489 (vs), 1310 (s), 1290 (m), 1220 (m), 1164 (s), 1033 (m), 1011 (m), 815 (m, CH out of plane bending, *p*-substituted benzenes), 681 (s, C-C chlorine compounds), 569 (m).

Preparation of 7-methoxy-2,4-dimethylquinolinium 4-methylbenzenesulfonate The product was collected as pale yellow solid. Yield 1.0 g (1%). Elemental anal. (%) for $C_{19}H_{21}NO_4S$: C, 63.49; H, 5.89; N, 3.90; S, 8.92. Found: C, 63.5; H, 5.8; N, 3.8. 1H NMR (500 MHz, DMSO- d_6 , 298 K): δ 8.31 (d, $J_{H-H}=9.31$ Hz, 1H, Ar), 7.68 (s, 1H, Ar), 7.55 (d, $J_{H-H}=7.01$ Hz, 1H, Ar), 7.52 (d, $J_{H-H}=7.97$ Hz, 2H, Ar-SO₃), 7.47 (s, 1H, Ar), 7.15 (d, $J_{H-H}=7.80$ Hz, 2H, Ar-SO₃), 4.02 (s, 3H, OCH_3), 2.87 (s, 3H, C(CH₃)CH(CH₃)CN), 2.85 (s, 3H, C(CH₃)CH(CH₃)CN), 2.32 (s, 3H, CH₃-Ar-SO₃). The signal for -SO₃H or NH⁺ was not observed. ^{13}C NMR (125 MHz, DMSO- d_6 , 298 K): δ 163.1 (C=N), 155.7 (C-N), 145.2, 139.7, 128.0 and 125.4 (aromatic CH₃-Ar-SO₃), 138.8 (aromatic C-OCH₃), 127.3, 121.5, 121.3 and 120.5 (aromatic C), 99.7 (C(CH₃)CH(CH₃)CN), 56.1 (OCH_3), 20.7 (CH₃-Ar-SO₃), 20.2 (C(CH₃)CH(CH₃)CN), 19.0 (C(CH₃)CH(CH₃)CN).

Preparation of $L^{CM}_{1/2}Li \cdot ([3-ClC_6H_4]N(Me)CCH(Me)C=O)Li$ The lithiation of ligand $L^{CM}_{1/2}H$ was carried out under an argon atmosphere. The ligand $L^{CM}_{1/2}H$ (1.33 g, 0.065 mol) was dissolved in dried Et₂O (15 ml). Yellow solution was formed and cooled to -78°C. 1.6 M Solution of *n*-BuLi in hexane (4.1 ml, 6.56 mmol) was added dropwise to the reaction mixture. Orange-white suspension of $L^{CM}_{1/2}Li$ was formed immediately. At the end of the reaction, the solution was slowly warmed to room temperature. Lithium $L^{CM}_{1/2}Li$ salt was used without further purification for reactions with Sn(IV) compounds immediately. 1H NMR (500 MHz, toluene- d_8 , 298 K): δ 7.01 (t, $J_{H-H}=7.92$ Hz, 1H, Ar), 6.47 (d, $J_{H-H}=8.16$ Hz, 1H, Ar), 6.40–6.37 (m, 2H, Ar), 4.90 (s, 1H, NC(CH₃)CHC(CH₃)O), 3.39 (s, 3H, OCH_3), 1.65 (s, 3H, NC(CH₃)CHC(CH₃)O), 1.58 (s, 3H, NC(CH₃)CHC(CH₃)O). ^{13}C NMR (125 MHz, toluene- d_8 , 298 K): δ 175.8 (C=O), 168.5 (C-N), 160.8 (C-N, aromatic C), 153.7 (C-OCH₃, aromatic C), 129.7, 114.6, 109.0 and 107.8 (aromatic CH), 99.6 (NC(CH₃)CHC(CH₃)O), 54.6 (OCH_3), 28.1 (NC(CH₃)CHC(CH₃)O), 21.9 (NC(CH₃)CHC(CH₃)O). 7Li NMR (194 MHz, toluene- d_8 , 298 K): δ -3.22. 1H NMR (500 MHz, THF- d_8 , 298 K): δ 7.05 (t, $J_{H-H}=7.74$ Hz, 1H, Ar), 6.47 (d, $J_{H-H}=7.73$ Hz, 1H, Ar), 6.34–6.32 (m, 2H, Ar), 4.73 (s, 1H, NC(CH₃)CHC(CH₃)O), 3.67 (s, 3H, OCH_3), 1.69 (s, 3H, NC(CH₃)CHC(CH₃)O), 1.65 (s, 3H, NC(CH₃)CHC(CH₃)O). ^{13}C NMR (125 MHz, THF- d_8 , 298 K): δ 178.7 (C=O), 167.1 (C-N), 161.1 (C-N, aromatic C), 155.1 (C-OCH₃, aromatic C), 129.7, 115.8, 108.9 and 108.5 (aromatic CH), 98.0 (NC(CH₃)CHC(CH₃)O), 55.2 (OCH_3), 28.5 (NC(CH₃)CHC(CH₃)O), 21.9 (NC(CH₃)CHC(CH₃)O). 7Li NMR (194 MHz, THF- d_8 , 298 K): δ 1.40.

Preparation of $L^{CM}_{1/2}Bu_3Sn \cdot ([3-ClC_6H_4]N(Me)CCH(Me)C=O)Sn-n-Bu_3$ from $L^{CM}_{1/2}Li$ and *n*-Bu₃SnCl *n*-Bu₃SnCl (1.46 ml, 0.0054 mol) was suspended in Et₂O (15 ml) and cooled to -78°C. $L^{CM}_{1/2}Li$ in Et₂O (15 ml) prepared from $L^{CM}_{1/2}H$ (1.12 g, 0.0054 mol) was added. The reaction mixture was slowly warmed to room temperature and then filtered from LiCl. The crude reaction mixture was washed twice with hexane (yield 86%). 1H NMR (500 MHz, toluene- d_8 , 298 K): δ 6.35–6.13 (m, 4H, Ar), 5.14 (s, 1H, NC(CH₃)CHC(CH₃)O), 3.52 (s, 3H, OCH_3), 2.51 (m, 6H, Sn(CH₂CH₂CH₂CH₃)), 1.70 (m, 6H, Sn(CH₂CH₂CH₂CH₃)), 1.57 (s, 3H, NC(CH₃)CHC(CH₃)O), 1.41 (m, 6H, Sn(CH₂CH₂CH₂CH₃)), 1.34 (s, 3H, NC(CH₃)CHC(CH₃)O), 0.92 (m, 9H, Sn(CH₂CH₂CH₂CH₃)). ^{119}Sn -NMR (134 MHz, toluene- d_8 , 298 K): δ 28.05.

Alternative preparation of $L^{CM}_{1/2}Bu_3Sn$ from $L^{CM}_{1/2}H$ and $n-Bu_3SnH$ $n-Bu_3SnH$ (1.74 ml, 0.0065 mol) was suspended in Et_2O (15 ml) and cooled to $-78^\circ C$. $L^{CM}_{1/2}H$ (1.33 g, 0.0065 mol) in Et_2O (15 ml) was added. The reaction mixture was slowly warmed to room temperature and vacuum evaporated to give essentially the same NMR spectra as in the previous case with similar yield of 82%.

Preparation of $L^{CM}_{1/2}Ph_3Sn\cdot\{[3-CIC_6H_4]N(Me)CCH(Me)C=O\}-SnPh_2$ Ph_3SnCl (2.47 g, 0.0064 mol) was suspended in Et_2O (15 ml) and cooled to $-78^\circ C$. $L^{CM}_{1/2}Li$ in Et_2O (15 ml) prepared from $L^{CM}_{1/2}H$ (1.32 g, 0.0064 mol) was added. The reaction mixture was slowly warmed to room temperature and then filtered from $LiCl$. The crude reaction mixture was washed twice with hexane (yield 72%). 1H NMR (500 MHz, toluene- d_8 , 298 K): δ 7.89–7.59 (m, 8H, Ar), 7.15 (s, 1H, Ar), 6.96 (t, $J_{HH}=6.36$ Hz, 1H, Ar), 6.82–6.70 (m, 6H, Ar), 6.32–6.20 (m, 3H, Ar), 5.85 (s, 1H, $NC(CH_3)CHC(CH_3)O$), 3.27 (s, 3H, OCH_3), 1.47 (s, 3H, $NC(CH_3)CHC(CH_3)O$), 1.25 (s, 3H, $NC(CH_3)CHC(CH_3)O$). ^{119}Sn -NMR (134 MHz, toluene- d_8 , 298 K): δ -119.8.

Preparation of $L^{CM}_{1/2}Ph_2SnCl\cdot\{[3-CIC_6H_4]N(Me)CCH(Me)C=O\}-SnPh_2Cl$ Ph_2SnCl_2 (1.96 ml, 0.0057 mol) was suspended in Et_2O (15 ml) and cooled to $-78^\circ C$. $L^{CM}_{1/2}Li$ in Et_2O (15 ml) prepared from $L^{CM}_{1/2}H$ (1.17 g, 0.0057 mol) was added. The reaction mixture was slowly warmed to room temperature and then filtered from $LiCl$. The crude reaction mixture was washed twice with hexane (yield 68%). 1H NMR (500 MHz, toluene- d_8 , 298 K): δ 7.62–7.51 (m, 8H, Ar), 7.38–7.15 (m, 6H, Ar), 5.61 (s, 1H, $NC(CH_3)CHC(CH_3)O$), 3.43 (s, 3H, OCH_3), 1.30 (s, 3H, $NC(CH_3)CHC(CH_3)O$), 1.15 (s, 3H, $NC(CH_3)CHC(CH_3)O$). ^{119}Sn -NMR (134 MHz, toluene- d_8 , 298 K): δ -45.1.

Preparation of $L^{HP}Sn[N(Si(CH_3)_3)_2]\cdot\{[4-(MeO)C_6H_4]N(H)CCH(H)-C[4-(MeO)C_6H_4]NSn(SiMe_3)_2\}$ The preparation was carried out under inert atmosphere of argon. Lappert's stannylene ($Sn\{N[Si(Me)_3]_2\}_2$) (Harris and Lappert, 1974; Davidson et al., 1976) was dissolved in hexane and cooled to $-78^\circ C$. Suspension of $L^{HP}H$ in dried hexane was added dropwise. Dark red reaction mixture was slowly warmed to room temperature. The reaction mixture was crystallized from toluene (yield 77%). 1H NMR (500 MHz, THF- d_8 , 298 K): 7.40 (d, $J_{HH}=7.02$ Hz, 2H, $NHCHCHCHN$), 7.28 (d, $J_{HH}=8.72$ Hz, 4H, Ar), 6.89 (d, $J_{HH}=8.72$ Hz, 4H, Ar), 4.96 (t, $J_{HH}=6.52$ Hz, 1H, $NHCHCHCHN$), 3.72 (s, 6H, OCH_3), 0.19 (s, 18H, $NSi(CH_3)_3$). ^{13}C NMR (125 MHz, THF- d_8 , 298 K): δ 158.4 ($C=N$), 154.7 ($C-N$, aromatic C), 143.7 ($C-OCH_3$, aromatic C), 123.7, 115.3 (aromatic C), 96.6 ($NHCHCHCHN$), 55.7 (OCH_3), 6.52 ($NSi(CH_3)_3$). ^{119}Sn -NMR (134 MHz, THF- d_8 , 298 K): δ -164.1.

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