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Synthesis and Studies Pd(II)-NHC complexes with thiosaccharinate, saccharinate or benzothiazolinate ligands

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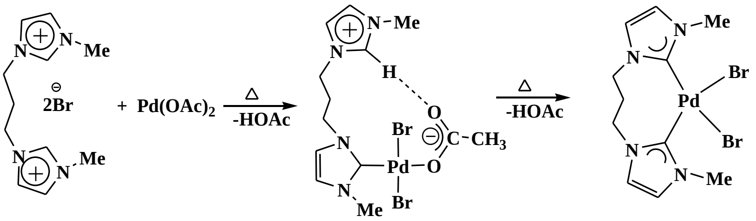
Abstract

Three cis-chelating di-N-heterocyclic carbene palladium(II) complexes [Pd(X)$_2$(di- NHC)] (X= tsac, sac and bit) tsac= thiosaccharinate, sac= saccharinate, bit= benzisothiazolinate, bearing different anionic co-ligand was synthesized and characterized. A series of palladium(II) complexes (2-5) bearing cis-chelating homo-dicarbene ligand with varying propylene-bridged (C3) and N-heterocyclic backbones (imidazole) have been synthesized by reaction of [Pd(OAc)$_2$] with the respective diazolium bromides in DMSO, have been prepared and characterized by elemental analysis, infrared spectra and ^{1}H NMR. These compounds are all stabilized in the sold state. The bidentate (diNHC) ligand together with two N-coordenated sac , bit and two S-coordenated tsac ligand, from the square planar coordination geometry around the palladium$^{(II)}$ ion.

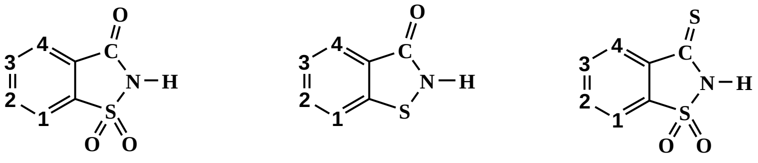
Keywords: Palladium , N-Heterocyclic carbine , spectral study

1. Introduction

The use of N-heterocyclic carbene (NHC) as ligand in organometallic chemistry is nowadays well established [1,2]. NHC ligands are generally stronger donors [3] compared to phosphines and have found applications as phosphine substitutes in Pd-mediated reactions including carbonecarbon bond formations [4], which are key synthetic steps in a variety of industrial processes[5]. These ligands have several advantages over the commonly utilized phosphines: (i) The strong s-donating ability of NHC, coupled with its minimal p-back bonding capabilities results in strong stabilizing effects and resistance to dissociation from the Pd center; (ii) the strong Pd-NHC bond and limited catalyst decomposition pathways ensures high thermal stability of Pd-NHC complexes, hence allowing for their use as catalyst at higher temperatures to increase reaction rates. Wanzlick introduced the use of acetate salts in his synthesis of a mercury bis-NHC complex starting from mercury(II) diacetate [6]. More than 25 years later, this method proved to be especially valuable for palladium(II) and nickel(II) complexes starting from the corresponding metal (II) diacetates and imidazolium or triazolium salts. For palladium, it is possible to apply the in situ deprotonation method even without solvent [7-11], but use of THF or even better DMSO provides enhanced yields of the complexes (Scheme1) [10,11]. Additionally, a variety of palladium and nickel complexes with methylene bridged, chelating NHCs were accessible only by this route (Scheme 1) [12-14] until this bidentate ligand was isolated as free carbenes recently [15]. The biological properties of saccharinate complexes have attracted particular attention and we have recently reported the promising anticancer activity of the platinum (II) saccharinate complex cis-[Pt(sac)$_2$(NH$_3$)$_2$] and its thiosaccharinate (tsac) analog cis - [Pt (tsac)$_2$(NH$_3$)$_2$][16]. Benzisothiazolinone (Hbit) [17] which is structurally similar to saccharin (Chart 1) has potent antimicrobial and anti-fungicidal properties [18].

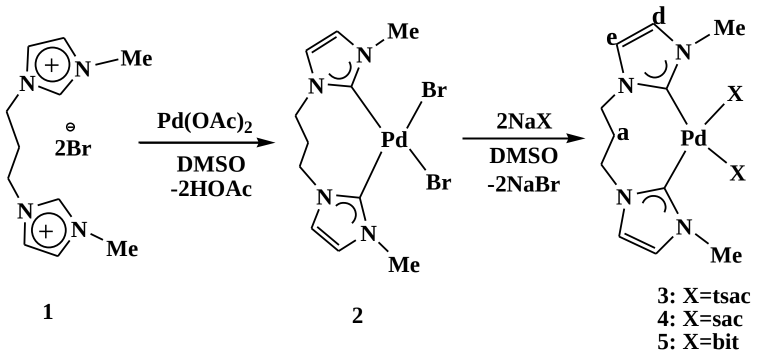


Scheme 1. Suggested mechanism for the formation of cis-[Pd(Br)$_2$(L)]



Hsac **Hbit** **Htsac**

Chart 1. Saccharin and related bicyclic compounds



Scheme 2. Synthesis of Palladium(II)-NHC Complexes 3-5

2. Experimental

2.1. General Methods, reagents and instrumentation

All the chemicals were commercially available and used without further purification. The (L) ligand was preparation according to the method of ref. [19,20] and characterized by infrared(IR) spectra in a range of 4000 – 400 cm^{-1} range on Bruker Tensor 28 spectrometer with a Platinum ATR unit. Melting points were determined using MEL-TEMP^{TM}II (Mel-Temp Laboratory Devices Inc., UK).Thermo-analytical 1112 series CHN-S analyzer. C, H, N, and S elemental analysis was performed *via* a Thermo-analytical Using elemental vario (MICRO) CUBE, and FlashEA 1112CHN-S analyzer. The ^{1}H-NMR spectra was recorded on Varian unity 400 and Gemini 200 spectrometers respectively with DMSO-d^{6} or D$_2$O-d^{2} as solvents.

2.2. Preparation of 1,3-bis(3-methylimidazolium-1-yl)propane dibromide (L) (1)

In a (100 ml) round-bottom flask, 1-methylimidazole (1.87g, 22.8mmol) was mixed with 1,3-dibromopropane (2.31 g, 11.40 mmol) and stirred for 3 hrs at 60 °C. After cooling to ambient temperature, the reaction mixture was extracted thoroughly with diethyl ether (20 ml) and ethyl acetate (2 × 20 ml) to remove any traces of starting materials. A yellow waxy solid of the ionic liquid was obtained after evaporation of solvent (3.75 g, 88.9 %; m.p: 158-159^{o}C), literature (158-159 ^{o}C) [1,19,20].

2.3. Preparation of Dibromido-(1,1′-dimethyl-3,3′-propylenediimidazolin-2,2′-diylidene) palladium(II) cis-[Pd(Br)$_2$(L)] (2)

A mixture of L (0.60 g, 1.64 mmol) and Pd(OAc)$_2$ (0.37 g, 1.64 mmol) was stirred in DMSO (25 ml) at 70 ^{o}C for 24 hrs. The resulting solution was then filtered through a small column of Celite, and solvent was removed completely under vacuum. The residue washed with water, ethanol, hexane and diethyl ether, and dried under vacuum to give a yellow solid (0.39g, 50.6%; m.p: 267-270^{a} ^{o}C). It already prepared[21,22].

2.4. Synthesis of cis-[Pd(X)$_2$(L)] X= tsac (3), sac (4) and bit (5)

A solution of Sodium thiosaccharinate (0.075 g; 0.34 mmol) in methanol (10ml) was added to cis-[Pd(Br)$_2$(L)] (**2**) (0.08 g; 0.17 mmol) in acetonitrile (15 ml). The mixture was refluxed overnight to give a brown suspension, which was filtered and the brown solid was further stirred with acetonitrile (20 ml) at room temperature 25 ^{o}C overnight. The mixture was stirring at room temperature overnight. The yellow brown precipitate was filtered off. The brown solid washed with water (15 ml), methanol (15 ml) and diethyl ether (15 ml) and dried under vacuum, to afford light brown powder. (Yield: 0.048 g, 70 %; m.p: 283-285^{a} ^{o}C).

The cis-[Pd(sac)$_2$(L)] (**4**) and cis-[Pd(bit)$_2$(L)] (**5**) complexes were prepared and isolated by a similar method.

3. Results and discussion

3.1. Preparation of cis-[Pd(Br)$_2$(L)] (2)

The preparation of the palladium(II)-diNHC complexes is summarized in Scheme 1. dibromido-(1,1-dimethyl-3,3-propylenediimidazolin-2,2-diylidene)palladium (II) (**2**) was straightforwardly preparation by in situ deprotonation of the imidazolium salt precursor (L) with palladium acetate in DMSO. These complexes; their Physical properties and elemental analysis are listed in Table 1. The complex showed medium and strong bands in the IR spectra at ca. 3068,2981 cm^{-1} which is assigned to the υ(C-H) aromatic and aliphatic bands, another band at ca. 1465 cm^{-1} is assigned to υ(C=N) for (L) ligand [22-25], the spectra showed a band at ca. 1559 cm^{-1} which can be assigned to the υ(C=C) stretching vibration, these complexes; their IR spectra data are listed in Table 2. The ^{1}H NMR spectrum of the yellow complex (**2**) shows generally broad ligand signals and geminal coupling of the propylene bridge was not resolved due to the fluxional behavior of the boat-shaped sixmembered palladacycle [13], the spectra of cis-[Pd(Br)$_2$(L)] (**2**) showed two doublets at δ 7.27 and 7.30 ppm assigned to the protons of the H^{e} and H^{d} ligand, while for the (L) ligand, the methylene group (CH_2^{b}) appeared as two signals, multiplet at δ 4.85 ppm and doublet of doublets at δ 4.35 ppm, a singlet at δ 3.92 ppm assigned to the protons of (CH$_3$) group and a quintet at δ 1.75 ppm assigned to the protons of (CH_2^{a}) group.

3.2. Synthesis of cis-[Pd(X)$_2$(L)] X= tsac (3), sac (4) or bit (5)

Reaction of two equivalents of Natsac with $[Pd(Br)_2(L)]$ in DMSO afforded (**3**) as a light-brown solid in 70% yield, a similar reaction of Nasac with $[Pd(Br)_2(L)]$ in DMSO afforded (**4**) as a brown solid in 73% yield, and a similar reaction of Nabit with $[Pd(Br)_2(L)]$ in DMSO afforded (**5**) as a light brown solid in 77% yield. The thiosaccharinate, saccharinate, or benzisothiazolinate ligands shows medium and strong bands in the IR spectra at ca. 1681,1636 cm^{-1} which is assigned to the υ(C=O) vibration for sac and bit ligands, the frequency of these bands are shifted from that in the free sac and bit ligands, which appeared at ca.1646 and 1626 cm^{-1} [26,27]. Another band at ca. 999 cm^{-1} is assigned to υ(C-S) vibration for tsac ligand, the frequency of this band are shifted from that in the free tsac ligand which appeared at ca.1014 cm^{-1} [27,28]. This indicating that υ(C-S) group participate in coordination with palladium (II) ion, the stretching vibration of the $\upsilon(SO_2)$ group at ca.1151,1158 and 1301,1314 cm^{1} corresponding to $\upsilon(SO_2)_{sy}$ and $\upsilon(SO_2)_{asy}$ respectively of the tsac and sac ligands. The υ(C-H) aliphatic and aromatic bands appeared at ca. 2980,2973, 2980 and 3104,3073,3062 cm^{-1} assigned to the stretching vibration of ligands[26-29], the spectra showed bands at ca. 1585,1596 and 1599cm^{-1} which can be assigned to the υ(C=C) stretching vibration of the phenyl ring [19-22]. The stretching vibration of the υ(C=N) of (1-methylimidazole) appeared at ca.1461,1460 and 1462 cm^{-1} shifted to lower frequency from that in the free ligand, which appeared at ca.1477 cm^{-1} [22-25], the bands appeared at ca. 408 and 434,434 cm^{-1} assigned to the stretching vibration of υ(Pd-S) and υ(Pd-N) for the three complexes respectively [27,28]. ^{1}H NMR spectra were recorded in d$_6$-dmso, and showed spectra data are listed in Table 3. The ^{1}H NMR spectra of $[Pd(tsac)_2(L)]$ (**3**), $[Pd(sac)_2(L)]$ (**4**) or $[Pd(bit)_2(L)]$ (**5**) showed multiplets at δ 7.83-8.23, 7.78-7.87 and 7.73-8.40 ppm assigned to the protons of the tsac, sac and bit ligands, while for the (L^5) ligand, a doublet appeared at δ 7.21,7.20 and 7.24 ppm and the methylene group (CH_2^b) appeared as two signal, multiplet at δ 4.95, 4.86, 4.95 ppm and doublet of doublets at δ 4.38, 4.35, 4.46 ppm, a singlet ranging from 3.92-3.95 ppm assigned to the protons of (CH_3) group and a quintet at δ 1.81, 1.89 and 1.91 ppm assigned to the protons of (CH_2^a) group.

Conclusion

By choosing proper experimental condition, the present investigation was made to synthesized complexes with tsac, sac and bit. From the result, discussion, analysis data and the IR, ^{1}H NMR study it is conformed stoichiometry suggest that the Pd(II) complexes have square planer geometry.

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Table 1: Physical properties and elemental analysis of the (L) ligand and its complexes

Seq.	Compounds	Color	Yield %	m.p.(°C)	Elemental analysis. % Calc.(Found)			
					C	H	N	**S**
1	L	Yellow	89	158-159	35.91 (36.09)	4.69 (4.96)	15.50 (15.30)	……… ………
2	$[Pd(Br)_2(L)]$	Yellow	51	267-270^a	28.71 (28.08)	3.73 (3.43)	11.97 (11.91)	……… ………
3	$[Pd(tsac)_2(L)]$	Brown	70	283-285^a	42.17 (42.46)	3.54 (3.42)	11.73 (11.88)	18.10 (18.14)
4	$[Pd(sac)_2(L)]$	Light brown	73	310-312^a	43.92 (44.48)	3.74 (3.58)	12.66 (12.45)	9.55 (9.50)
5	$[Pd(Bit)_2(L)]$	Light brown	77	294-299^a	48.89 (49.14)	4.18 (3.96)	13.41 (13.75)	10.39 (10.50)

a: decomposed temperature

Table 2: Selected IR stretching vibration bands (cm^{-1}) of the (L) ligand and its complexes

Seq.	**Compounds**	$\upsilon(C{-}H)_{ar}$	$\upsilon(C{-}H)_{aliph.}$	$\upsilon(C{=}N)$	$\upsilon(C{-}N)$	$\upsilon(C{-}S)$	$\upsilon(C{=}O)$	$\upsilon(C{=}C)$	$\upsilon(SO_2)_{Sy.}$	$\upsilon(SO_2)_{asy.}$
1	L	3072	2991	1477	1385	....	....	1562	....	....
2	$[Pd(Br)_2(L)]$	3068	2981	1465	1362	....	....	1559	....	....
3	$[Pd(tsac)_2(L)]$	3104	2980	1461	1369	999	....	1585	1151	1301
4	$[Pd(sac)_2(L)]$	3073	2973	1460	1363	....	1681	1596	1158	1314
5	$[Pd(Bit)_2(L)]$	3062	2980	1462	1360	....	1636	1599	....	....

Table 3: ^{1}H NMR chemical shifts (ppm) and coupling constsnts (Hz) for the prepared complexes

Seq.	Compounds	$^{3}J_{(H\text{-}H)}$	Chemical shift δH (in ppm)*
1	L	8.00	2.45 (q, 2H, H^{a}) ; 3.83 (s, 6H, CH_3) ; 4.25 (t, 4H, H^{b}); 7.40 (m, 2H, H^{e}); 7.44 (m, 2H, H^{d}); 8.72 (s, 2H, H^{c})
2	$[Pd(Br)_2(L)]$	7.80	1.75 (m, 2H, H^{a}); 3.92(s, 6H, CH_3); 4.35 (dd, 2H, H^{b}); 4.85 (m, 2H, H^{c}); 7.27 (d, 2H, H^{e}); 7.30 (d, 4H, H^{d})
3	$[Pd(L^5)(tsac)_2]$	7.60	1.81 (q, 2H, H^{a}); 3.95 (s, 6H, CH_3); 4.38 (dd, 2H, H^{b}); 4.95 (m, 2H, H^{c}); 7.21 (d, 4H, H^{e} & H^{d}); 7.83-7.93 (m, 6H, H2, H3, & H4); 8.23 (d, 2H, H1)
4	$[Pd(sac)_2(L)]$	7.90	1.89 (q, 2H, $CH_2{}^{a}$); 3.92 (s, 6H, CH_3); 4.35 (dd, 2H, H^{b}); 4.86 (m, 2H, H^{c}); 7.20 (d, 4H, H^{e} & H^{d}); 7.78-7.87 (m, 8H, Phenyl$_{(Sac)}$)
5	$[Pd(Bit)_2(L)]$	7.70	1.91 (q, 2H, H^{a}) ; 3.92 (s, 6H, CH_3); 4.46 (dd, 2H, H^{b}); 4.95 (m, 2H, H^{c}); 7.24 (d, 4H, H^{e}, & H^{d}); 7.73 (t, 2H, H3); 7.84 (t, 2H, H2); 8.30 (d, 2H, H1); 8.40 (d, 2H, H4)

***** s= singlet, d= doublet, m= multiplet, dd= doublet of doublets

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تحضير ودراسة معقدات Pd(II)-NHC مع ليكاندات الثايوسكارينيت,السكارينيت أو البنزوثايوزولينيت

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الملخص

تم تحضير ثلاثة معقدات ذات الصيغة العامة $[Pd(X)_2(diNHC)]$ وذلك من خلال مفاعلة خلات البلاديوم مع 3,1−ثنائي (3−مثيل أميدازول) بروبان ثنائي البروميد ثم مفاعلة الناتج مع ليكاندات الثايوسكارين, السكارين و البت بنسبة 2:1 فلز الى ليكاند. ثم تشخيص المعقدات بواسطة التحليل الدقيق للعناصر وكذلك طيفيا" بواسطة الأشعة تحت الحمراء والرنين النووي المغناطيسي, وإعتمادا على القياسات الطيفية والتحليل الدقيق للعناصر تبين أن معقدات البلاديوم تمتلك بنية المربع المستوي.