

Mono and homo trinuclear palladium (II) with 1,4-bis-(substituted thio) butane ligands

Nabeel H. Buttrus and Rana A. Al-Quboa
Chem. Dept., College of Science, Mosul University
Mosul-IRAQ

(NJC)

(Received on 4/10/2009)

(Accepted for publication 29/11/2010)

Abstract

Mono and homo-trinuclear complexes of the type $[Pd(L)Cl_2]$, $[Pd(L)(SCH_2Ph)_2]$, $[Pd(L)_2Cl_2]$, $[Pd(L)_2Cl_4]Cl_2$ and $[Pd(L)_2Cl_6]$ where $L=1,4$ bis-(benzyl thio) butane (L^1), 1,4 bis-(butyl thio) butane (L^2), 1-(benzyl thio 4-butyl thio) butane (L^3) and 1,4 bis (*p*-tolyl thio) butane (L^4), have been prepared by the reaction of prepared sulphur containing ligands (L^1)- (L^4) with $PdCl_2$ in 1:1, 1:2 or 2:3 ligand to metal ratio. The ligands were characterized by microanalysis, physicochemically and spectroscopically while their complexes and their complexes have been characterized on the basis of their metal content, IR, electronic spectra, magnetic measurements and conductivity measurements. Square planer and octahedral environment around Pd(II) complexes have been deduced on the basis of magnetic and electronic spectra.

$[Pd(L)Cl_2]$,

= L $[Pd(L)(SCH_2Ph)_2]$, $[Pd(L)_2Cl_2]$, $[Pd(L)_2Cl_4]Cl_2$, $[Pd(L)_2Cl_6]$
, (L^3) () , (L^2) () , (L^1) ()
(L^1) – , (L^4) (-)
. 3:2 1:2,1:1 (L^4)

Introduction

Prior to the 1980s, relatively few thioether complexes had been prepared in comparison to those of phosphines and amines^[1]. The development of cyclic thioether such as ^[9]aneS₃ and ^[12]aneS₃ redressed this imbalance, though subsequently it became clear that the macrocyclic effect of crown thioethers was considerably less than for the analogous crown ethers^[2].

The coordination preferences of a family of novel thioethers based on (alkylsulfanylmethyl) benzene and their bismetallated tetracarbonyl complexes of general formula $[M(CO)_4\{L\}_2]$ M= W or Mo, where the ligand bridges two monometal of Group 6 carbonyl fragment (M(CO)₄) were generated on reaction of $[W(CO)_4(MeCN)_2]$ or $[Mo(CO)_2(MeCN)_2]$ with the above ligands were examined^[3]. Interest in the chemistry of square planar platinum group element complexes is predicated on a number of factors. On the one hand complexes of Ir(I), Pd(II) and Pt(II) have been found to be catalytically active for variety of reactions including hydrogenation, hydroformylation, and olefin polymerization^[4,5]. Another interest in square planar complexes lies in their excited state properties as manifested by luminescence^[6].

Stoffregen et al 2005^[7], report the synthesis and characterization of perchlorate salts containing the following three novel complex cations each with bidentate thioether ligand: $cis-[Pt(CH_3SCH_2CH_2CH_2SCH_3)(M-OH)_2]^{2+}$, $cis-[Pt(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$, and $cis-[Pt(CH_3S-CH_2-CH_2CH_2SCH_3)(H_2O)_2]^{2+}$. The mononuclear Pt(II) and Pd(II) complexes differ in the selectivity with which they promote the hydrolysis of peptides.

Palladium (II) and platinum (II) containing the mixed ligands tertiary diphosphines $Ph_2P(CH_2)_nPPh_2$ (n=1-4) and benz-1,3-imidazoline-2-thione benz-1,3-oxazoline-2-thione or benz-1,3-thiazoline-2-thione have been prepared and characterized^[8].

Some new homo and hetero trinuclear Pd(II) and Pt(II) complexes with tridentate hybrid ligands containing phosphorus-sulphur species, of the general formula $[M_nM_3\text{'-}nL_2Cl_6]$ where M=M'= Pt or Pd, n=3, M=Pt, M'=Pd, n= 1 or 2 and L=Cis-1,2-bis (diphenyl phosphino) phenyl thio ethylene (L¹) or cis-1,2-bis (diphenyl phosphino)-2-aminophenyl thio ethylene (L²), have been prepared and characterized physico-chemically and spectroscopically^[9].

In view of the reported interesting results and in connection of our studies on palladium and platinum complexes with sulphur containing ligand [10-12], we are presenting here the preparation of new ligands L¹=1,4-bis(benzylthio) butane, L²=1,4-bis (butyl thio) butane, L³=1-(benzyl thio 4-butyl thio) butane and L⁴=1,4-bis (p-tolyl thio) butane and there Palladium complexes.

Experimental

All chemical were reagent grade, PdCl₂ were used as supplied from Fluka.

Infrared spectra were recorded on a FTIR Bruker Tensor 27Co Spectrophotometer in the 250-4000cm⁻¹ range using CsI discs. The electronic spectra were recorded on Shimadzu UV-vis spectrophotometer UV 160 for 10⁻³M solution of the complexes in dimethyl sulfoxide (DMSO) at 25^oC. Conductivity measurements were carried out on 10⁻³M solution of the complexes in DMSO at 25^oC using a conductivity meter model PCM3-Jenway. Magnetic measurements were carried out on the solids by the Faraday's method using Bruker BM 6

instrument. The palladium content was estimated as bis (dimethyl glyoximto) Pd complex ^[13]. Analyses of ligands were carried out using a CHN elemental analyzer mode Perkin Elmer 2400 (1EES) Al-bayt University Jordan

Preparation of the ligands.

1. 1,4-bis(benzylthio) butane (L^1) and 1,4-bis(*p*-tolylthio) butane (L^4). 1,4-dibromobutane (2.15g, 1mmol) in ethanol (10ml) was boiled under reflux for 5h. with an equivalent amount of benzylmercaptane (2.48g, 2mmol) or *p*-tolyl thiol (3.04g, 2mmol) and KOH (1.12g, 2mmol) in ethanol (20ml). after cooling at room temperature KBr was removed by filtration. The resulting solution was reduced in volume to ca 1/3 by heating, on cooling left a white solid. The solid thus obtained, was filtered off, washed with ethanol and ether and then dried under vacuum for several hours.
2. 1,4-bis (butylthio) butane (L^2) and (1-benzylthio 4-butylthio) butane (L^3) They prepared using similar procedure as above except using butylmercaptane (1.80g, 2mmol) in case of (L^2) or (1.24g, 1mmol) of benzyl mercaptane and (0.90g, 1mmol) of butylmercaptane in case of (L^3).
3. Preparation of the complexes
 - a. $[Pd(L)Cl_2]$, $[Pd(L)_2Cl_2]$ and $[Pd(L)_2]Cl_2$, ($L=L^1, L^2, L^3$ and L^4)
PdCl₂ (0.18g, 0.001mol) was dissolved in distil water (10ml) and a solution of corresponding ligands (L) (1mmol) or (2mmol) in ethanol (10ml) was added, a rapid formation of

precipitate was observed. The mixture was stirred under reflux for 2h., to ensure the completion of the reaction. The solid thus obtained was collected by filtration, washed with distil water, ethanol and diethylether and dried under vacuum for several hours.

- b. $[Pd(L)(SCH_2Ph)_2]$. ($L=L^1, L^2, L^3$ and L^4)

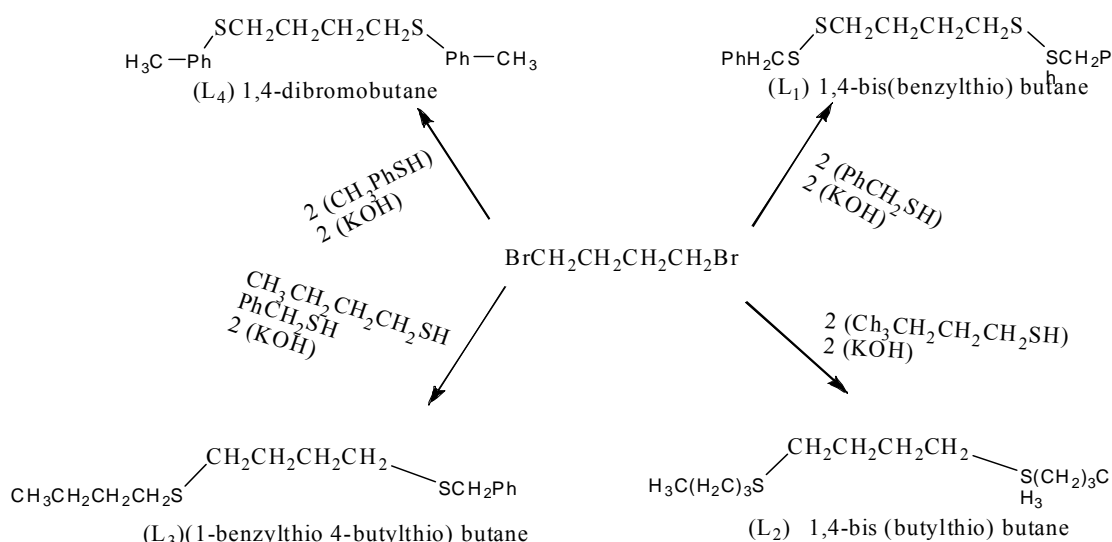
Palladium complexes of the type $[Pd(L)Cl_2]$ (1.0mmol) dissolved in dimethyl formamide DMF (10mole) was added with constant stirring to a solution containing equimolar quantities of benzylmercaptane (2.48g, 2mmol) and KOH (1.12g, 2mmol) in ethanol (30ml). The complexes thus precipitated, filtered off and washed with distil H₂O, DMF and diethyl ether then dried under vacuum over phosphorus penoxide.

- c. $[Pd_3(L)_2Cl_4]Cl_2$ and $[Pd_3(L)_2Cl_6]$
PdCl₂ (3mmol) was dissolved in distil water (10ml) and solution of ligand (L) (2mmol) in ethanol (10ml) was added, a rapid formation of precipitate was observed. The mixture was stirred under reflux for Ca 1h., to ensure completion of reaction. The solid product filtered off, washed with distil water, ethanol and then dried under vacuum for several hours.

Results and Discussion

Treatment of 1,4-dibromo butane with equimolar quantities of benzylmercaptane, butanethiol, *p*-mercapto tolyl and mixture of butanethiol and benzyl mercaptane in the presence potassium hydroxide result in the formation of the corresponding ligands (Scheme 1).

These ligands; their physical properties are listed in Table 1.



Scheme 1: preparation of the ligands (L¹ – L⁴)

The complexes can be prepared directly by treating the above ligands with PdCl₂ in 1:1, 1:2 or 2:3 ligand to metal ratio. The isolated complexes and their physicochemical properties are listed in Table 2. In general the complexes are slightly soluble in halogenated solvents but more soluble in N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO). The molar conductance in 10⁻³ DMF and DMSO solution are in the 25-40, 10-20 and 160-170 ohm⁻¹.mol⁻¹.cm² range indicating the non-electrolytic and 1:2 electrolytic nature of the complexes [14]. This is consistent with the stoichiometry assumed for the complexes on the basis of analytical data.

The ligands does not show any ν(SH) band in region 2500-2600cm⁻¹, in which this stretching frequency generally expected [15]. The characteristic bands in the infrared spectra of the free ligands occur at 1599-1601, 2915-3027 and 700-863cm⁻¹ due to the stretching vibrations of ν(C=C), ν(C-H) and ν(C-S) respectively, [16]. In the spectra of metal complexes, a band of similar intensity appears at the same position as above excepts the band due to ν(C-S) which appears at (830-660)cm⁻¹.

This indicative of coordination through the sulfur atoms of the ν(C-S) group, [17]. Moreover the IR spectra of the complexes showed another new bands at 360-405 and 290-330cm⁻¹ which may well be due to ν(M-S) and ν(M-Cl) [18].

The electronic spectra of the ligands and their complexes were recorded as 10⁻³M in DMF and the results presented in Table 3. the bands observed in the range (35211-39370 cm⁻¹) are due to π-π* or n-π* with in the ligand.

The magnetic moment data of Pd²⁺ complexes indicate that these complexes are diamagnetic except complex (14) which is paramagnetic. The complexes may have square planar coordination of the central metal ion by the surrounding ligands. Pd²⁺ having d⁸ configuration favors the formation of complexes with square planar geometry. The magnetic moment value of complex (14) is 3.25 B.M. which indicate an octahedral geometry for central Pd²⁺ ion and square planner for the terminals ions. Similar results was found [19]. In the electronic spectra of Pd²⁺ complexes the spin allowed d-d bands in the 14593-15032 and 12133-27624cm⁻¹ region along with change

transfer band were observed at 30303-37879 cm^{-1} . The spin allowed transition were assigned for $^1A_{1g} \rightarrow ^1A_{2g}$ and $^1A_{1g} \rightarrow ^1E_u$ respectively in square planner geometry, while complex No. (14) show three spin allowed d-d band in the region 10204, 12133, 26545 which were assigned for $^3A_{2g} \rightarrow ^3T_{2g}$ F(v₁), $^3A_{2g} \rightarrow ^3T_{1g}$ F(v₂) and $^3A_{2g} P \rightarrow ^3T_{2g}$ P(v₃) respectively indicating

the octahedral geometry of the Pd(II) complex, similar results was found^[20,21].

On the bases of the foregoing studies, the ligands used in this study, coordinate to the metal ions in bidentate tridentate fashions from the sulfur site of the ligand for mono and trinuclear complexes as shown in Fig. 1.

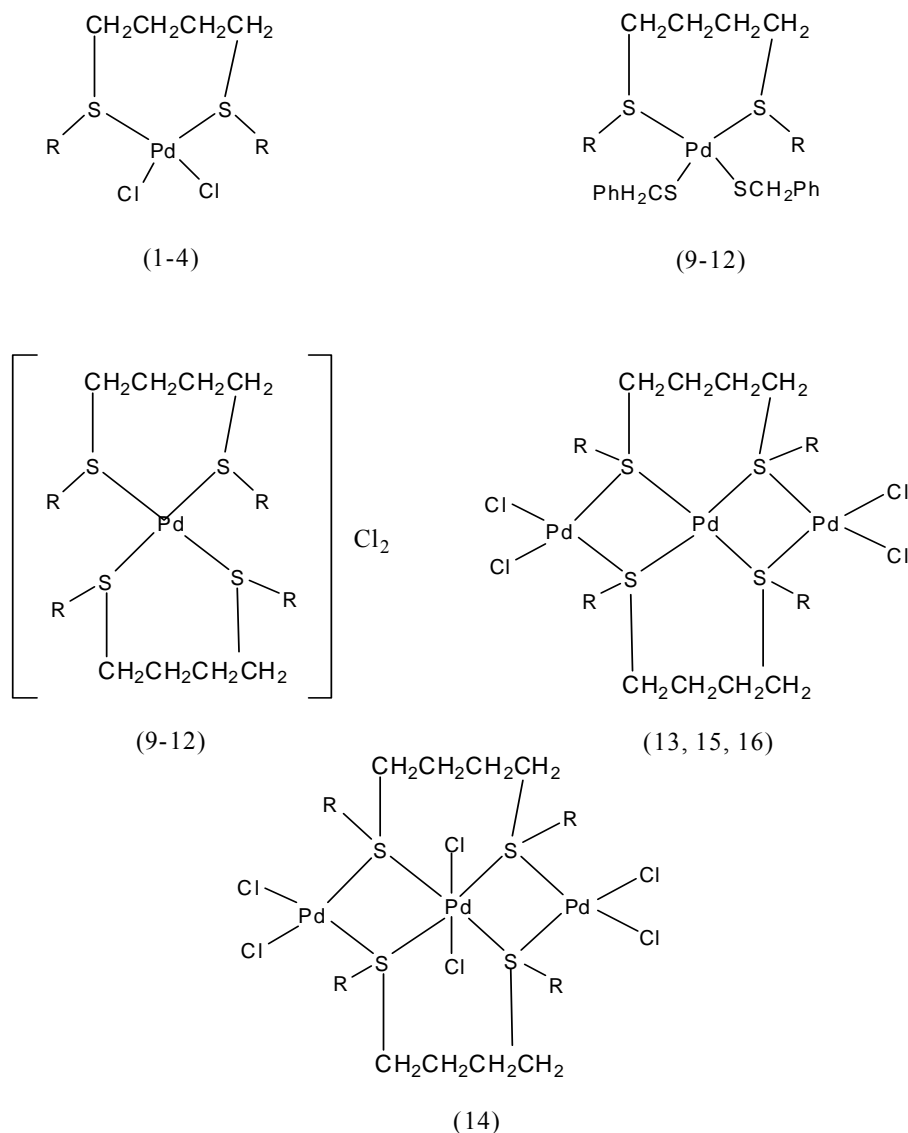


Fig. 1: Suggested structure for the complexes

Table 1: Physical properties of the free ligands

Seq.	Ligand (colour)	m.p. (°C)	Analysis found (Calcd.) %		Selected IR bands (cm ⁻¹)			λ_{max} , nm (cm ⁻¹)
			C	H	$\nu(\text{C-S})$	$\nu(\text{C-H})$	$\nu(\text{C=C})$	
(L ¹)	White	88-90	71.50 (71.52)	7.26 (7.28)	768,699(s)	2915 (m) 3027 (m)	1601 (m)	272 (36764)
(L ²)	White	112	61.42 (61.53)	11.09 (11.11)	850,638(s)	2931	1600 (s)	254 (39370)
(L ³)	White	56	67.11 (67.16)	8.91 (8.95)	759,886(s)	2915 (m)	1599 (m)	273 (35211)
(L ⁴)	White	64	71.49 (71.53)	7.26 (7.28)	700,767(s)	2929 (s)	1601 (s)	276 (36231)

Table 2: Physical properties of the prepared complexes

	Complex	color	Melting points (°C)	Pd%	Λ_M $\Omega^{-1}\text{cm}^{-1}\text{mol}^{-1}$	μ_{eff}
1.	[Pd(L ¹)Cl ₂]	Brown	148*	22.10 (22.18)	20	D
2.	[Pd(L ²)Cl ₂]	Pale brown	144-145	25.73 (25.84)	26	D
3.	[Pd(L ³)Cl ₂]	Dark brown	205*	23.79 (23.87)	24	D
4.	[Pd(L ⁴)Cl ₂]	Reddish orange	178*	22.10 (22.18)	21	D
5.	[Pd(L ¹) ₂]Cl ₂	Reddish brown	110	13.53 (13.60)	139	D
6.	[Pd(L ²) ₂]Cl ₂	Brown	154	16.30 (16.46)	136	D
7.	[Pd(L ³) ₂]Cl ₂	Pale brown	108-110	14.81 (14.89)	134	D
8.	[Pd(L ⁴) ₂]Cl ₂	Orange	210*	13.58 (13.60)	145	D
9.	[Pd(L ¹)(SCH ₂ Ph) ₂]	Dark Brown	120*	16.25(16.14)	19	D
10.	[Pd(L ²)(SCH ₂ Ph) ₂]	Brown	171*	18.09(18.13)	28	D
11.	[Pd(L ³)(SCH ₂ Ph) ₂]	Orange	180*	17.11(17.14)	24	D
12.	[Pd(L ⁴)(SCH ₂ Ph) ₂]	Orange	207-208	16.18(16.25)	25	D
13.	[Pd ₃ (L ¹) ₂ Cl ₄]Cl ₂	Dark brown	140	28.00 (28.08)	169	D
14.	[Pd ₃ (L ²) ₂ Cl ₆]	Olive	254	31.79 (31.81)	165	3.25
15.	[Pd ₃ (L ³) ₂ Cl ₄]Cl ₂	Black	110	29.64 (29.84)	172	D
16.	[Pd ₃ (L ⁴) ₂ Cl ₄]Cl ₂	Reddish Orange	185	28.03 (28.00)	173	D

D= diamagnetic

Table 3: IR absorption (cm⁻¹) and electronic data of the complexes

Seq.	IR bands (cm ⁻¹)				Electronic spectra (cm ⁻¹)
	v(C-H)	v(C-S)	v(Pd-S)	v(Pd-Cl)	
1.	3010(m)	678(s)	330(m)	302, 311(m)	14593, 26596, 31447
2.	2957(m)	668(s)	333(m)	302, 280(w)	24038, 37879
3.	2924(w)	690(m)	331(m)	301, 310(m)	24096
4.	3016(w)	690(m)	340(w)	302, 311(m)	25000, 30303
5.	3005(m)	659(s)	340(m)	-	23255, 37037
6.	2958(m)	682(m)	355(m)	-	15032, 24038, 32895
7.	3028(w)	727(s)	354(w)	-	22988
8.	2923(m)	712(s)	360(m)	-	27027, 37313
9.	3020(m)	638(s)	360(m)	-	25000, 31695
10.	3023(m)	670(s)	380(m)	-	23255, 26315, 35460
11.	3011(m)	690(s)	355(m)	-	15935, 36496
12.	3024(m)	697(s)	375(m)	-	25641, 36496
13.	2942	686(s)	360(m)	281, 313(m)	22624, 33112
14.	3005(m)	683(s)	370(m)	290, 310(m)	10204, 12133, 26545, 31440
15.	2957(m)	698(s)	360(w)	319, 303(m)	27624, 32679
16.	2923(m)	711(m)	354(m)	312, 290(m)	26000, 38167

References

- Murray, S.G. and Hartley F.R., *Chem. Rev.*, 1981, **81**, 365-414.
- Cooper S.R., *Pure and Appl. Chem.*, 1990, **62(6)**, 1123-1125.
- Gormley F.K., Gronbach J., Draper S.M. and Dravis A.P., *J. Chem. Soc. Dalton Trans.*, 2000, 173-179.
- Dervisi A., Jenkins R.L., Abdul Malik K.M., Hursthouse M.B., and Coles S., *Dalton Trans*, 1133-1142.
- Suardi G., Cleary B.P., Duckett, S.B., Sleigh C., Ran, M., Reed W.E., Lohman J.A., and Eisenbery R., *J. Am. Chem. Soc.*, 1997, **119**, 7716-7725.
- Weinstein J.A., Tierney M.T., Davies E.S., Base K., Roberio A.A, and Grinstaff. M.W., *Inorg. Chem.*, 2006, **45**, 4544-4555.
- Stoffergen S.A., Firiffin A.K.L. and Kostic N.M., *Inorg. Chem.*, 2005, **44**, 8899-8907.
- Al-Jibori S.A., Al-Zanbai S.S.A., Mohammed M.Y. and Al-Allaf T.A.K., *Metal Chem.*, 2007, **32**, 281-286.
- Buttrus N.H., Hussain A.K. and Al-Allaf, T.A.K., *Asian J. Chem.*, 2003, **15(3-4)**, 1617-1622.
- Al-Hayli L.J., Buttrus, N.H., Tarq F., and Al-Allaf T.A.K., *Jorgan J. Appl. Sci.*, 2005, **7(1)**, 64-70.
- Buttrus N.H., Al-Numa K.S., and Mohammed A.F., *Jordan J. Appl. Sci.*, 2008, **10(2)**, 71-78.
- Al-Allaf T.A.K., Buttrus N.H. and Hitchcock P.B., *Asian J. Chem.*, 1997, **15**, 187-194.
- Vogel. A.I, practical organic chemistry, Longman. London, 1978.
- Geary, W.J., *Coord. Chem. Rev.*, 1971, **7**, 81-90.
- Rao C.N.R., Academic Press, New York, (1963).

16. Al-Hayaly, L.J. Buttrus N.H., and Al-Allaf T.A.K., *Asian J. Chem.*, 2002, **14(3-4)**, 14(2)-1426.
17. Narayna B. and Coojenragad M, 21, 71-76, *Turk. J. Chem.*, 1997, **21**, 71-76.
18. Singh N. and Parassad, L.B., *Inorg. Met-Org.Chem.*, 1998, **28(6)** 929-946.
19. Al-Allaf T.A.K., Buttrus N.H., Yousif H.R., *Asiaa, J. Chem*, 2000, **12(2)**, 527-536.
20. Rao C.N.R., 1963, "Chemical application of infrared spectroscopy", Academic Press New York.
21. Weinstein J.A., Tierney M.T., Davies E.S., Base K., Roberio A.A. and Grinstaff. M.W., *Inorg. Chem.*, 2006, **45**, 4544-4555.