SYNTHESIS AND CHARACTERISATION OF SOME ORGANOTIN(IV) DERIVATIVES OF THE SCHIFF BASE DERIVED FROM SALICYLDEHYDE AND 2-AMINOTHIOPHENOL

R.J. Rao* and Harish B. Wankhade
Inorganic & Organometallic Chemistry Laboratory, School of Studies in Chemistry,
Vikram University, Ujjain (M.P.) 456010, India

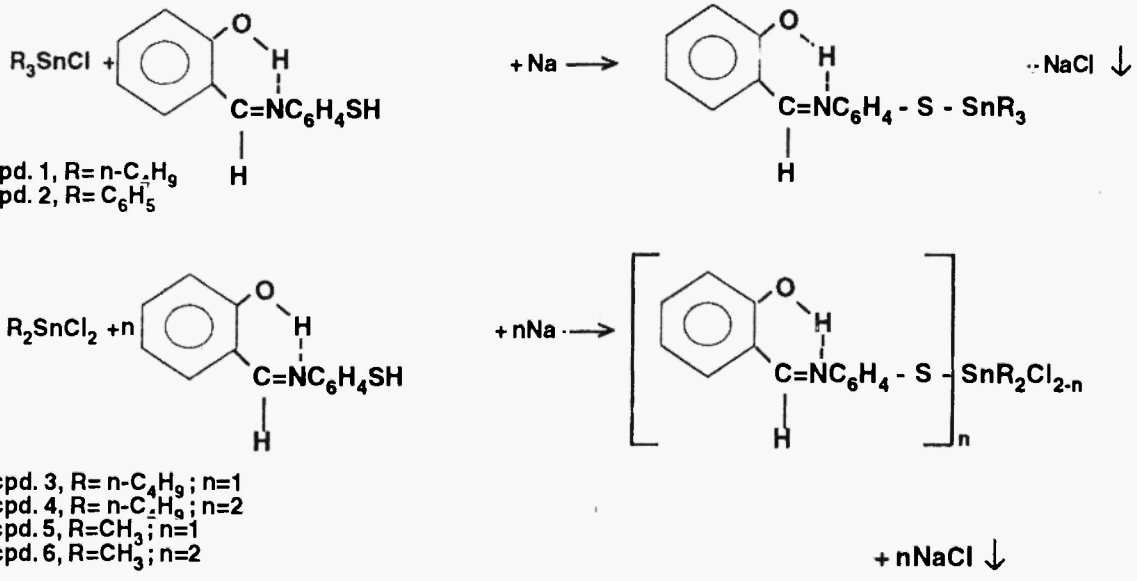
ABSTRACT

A few di- and tri-organotin(IV) derivatives of schiff base derived from salicyldehyde and 2-aminothiophenol have been synthesized by the reactions of the corresponding di- and tri-organotin(IV) chlorides with sodium salt of N-(salicylidene)-o-mercaptoaniline in desired molar ratios. These derivatives have been characterized by elemental analysis, IR and (^1H, ^{13}C and ^{119}Sn) NMR spectral studies.

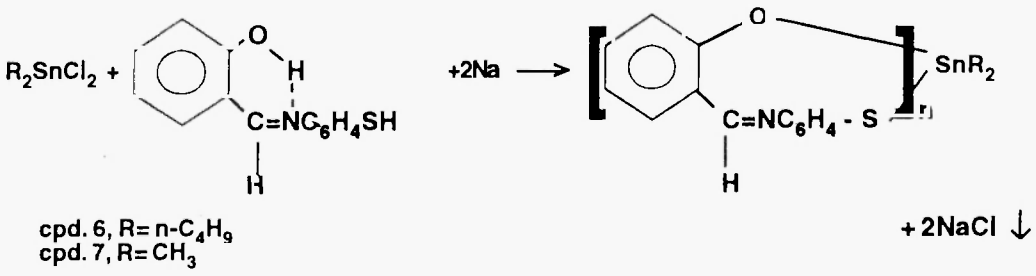
A literature survey revealed that several monometallic metal complexes with the monodentate[1], bidentate[2], tridentate[3] and tetradentate[4], Schiff bases are known. Only a few dimetallic metal complexes with tridentate[5,6] and tetradentate[7,8] Schiff bases derived from salicyldehyde/acetylacetone and tridentate Schiff bases derived from 3-aminothiophenol and salicyldehyde/substitued salicyldehyde[9] have been studied extensively. However, complexes of the N-(salicylidene)-o-mercaptoaniline with organotin(IV) moieties have not been studied so far. In view of the interesting results obtained by the above mentioned ligand and in continuation of work on organotin(IV) derivatives of N-(salicylidene)anthranilic acid[10] from our laboratory, we are reporting here synthesis and characterization of organotin(IV) derivatives of N-(salicylidene)-o-mercaptoaniline.

RESULTS AND DISCUSSION

Triorganotin(IV) and diorganotin(IV) derivatives of N-(salicylidene)-o-mercaptoaniline have been synthesized by the reaction of tri- and di-organotin(IV) chlorides with the sodium salt of N-(salicylidene)-o-mercaptoaniline in 1:1 and 1:2 molar ratios respectively.



Further, diorganotin(IV) complexes of N-(salicylidene)-o-mercaptoaniline of the type R_2SnL have been prepared by the reaction of diorganotin(IV) dichloride with the disodium salt of N-(salicylidene)-o-mercaptoaniline in a 1:1 molar ratio.



The reaction is not much facile at room temperature. The reactants were refluxed in benzene for about 4 hours to ensure the completion of the reaction. The desired product could be isolated by evaporation of the solvent under reduced pressure after filtering off the precipitated sodium chloride. These were further purified by the crystallization from benzene-petroleum ether (40°-60°C) mixture.

IR Spectral Data

The infrared spectra of these organotin(IV) complexes of N-(salicylidene)-o-mercaptoaniline have been recorded using KBr pellets in the range 4000-400 cm^{-1}. Some important characteristics bands are listed in Experimental Section.

The ligand exhibit a ν(OH) band at ca 3100 cm^{-1} of the intramolecularly hydrogen bonded phenolic OH. The complexes 7 and 8 do not show this band indicating a deprotonation of the hydroxy group. The Schiff base exhibits a ν(SH) band around 2500 cm^{-1}. This band disappears in the spectra of all the complexes indicating deprotonation and consequent coordination of the sulphur atom to tin. A ν(C=N) (azomethine) band is found around 1620-1640 cm^{-1} in the ligand. In the complexes, this band shifts to lower wave numbers ($\Delta\ \nu$=30 cm^{-1}) indicating coordination of the azomethine nitrogen to the central metal ion. The ligand exhibit a band between 1295 and 1305 cm^{-1} due to δ(C-C-O)[11,12]. In the complexes 7 and 8, this band shifts to higher enregy by 5-15 cm^{-1} indicating the coordination of phenolic oxygen[13]. The ν(C-S) in the ligand occurs between 700 and 790 cm^{-1}. In the complexes, this band shifts to higher energy by 30-45 cm^{-1} which is indicative of coordination of the sulphur[14]. Bands of medium and weak intensities in the region 570-440 cm^{-1} may be due to Sn-C and Sn-O stretching vibrations[15].

NMR Spectral Data

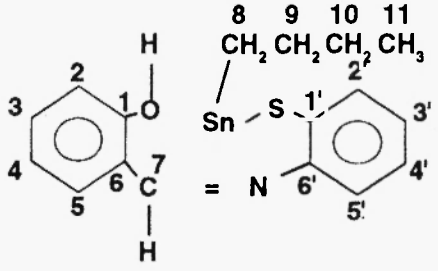
The PMR spectra of the new derivatives have been recorded in $CDCl_3$ and the values of observed chemical shifts are tabulated in experimental section. ^{13}C and ^{119}Sn NMR of the four representative compounds have been recorded in $CDCl_3$.

The PMR spectra show the characteristic resonances of corresponding ligand protons as well as alkyl or aryltin protons. The PMR Spectra of all the complexes except 7 and 8 show a signal at ca 11 ppm of the -OH proton of salicyldehyde group. The spectra of complexes 7 and 8 do not exhibit this signal suggesting deprotonation of this -OH group. A complex pattern due to the protons of the phenyl group (both ligand and phenyl protons) has been observed in the region 6.21-8.1 ppm. The resonances, which can be assigned to the butyltin protons fall in the range 0.35-1.35 ppm.

The methyl protons of the dimethyltin derivatives appear as a sharp singlet at 1.0 ppm, with double satallite resonances on each side of the main peak. A particular advantage of the methyltin derivatives

is the ease with which proton spin - spin coupling constant can be determined. The coupling constant provides valuable information about hybridization [16,17]. For four coordinate dimethyltin(IV) compounds J(^{119}Sn - ^{1}H) values have been reported in the range 54-64 Hz and such values have been found to increase as the coordination number of tin increases from four to five, six or seven and have been observed in the range 71-116 Hz depending upon the stereochemistry [18-22]. The tin-proton coupling constant, J (^{119}Sn - ^{1}H) in the dimethyltin(IV) derivatives have been found to be in the range 72 - 81 Hz. This observation confirms that the tin has a coordination number higher than four, which is in the range of values observed for five and six coordinate dimethyltin(IV) compounds, indicating that the ligand is behaving as a bidentate moiety while tridentate in 7 and 8. (Fig.)

^{13}C NMR Spectra of four representative compounds, namely tributyl- and dibutyltin(IV) derivatives of Schiff's base derived from salicyldehyde and 2-aminothiophenol have been recorded (Compound No. 1,3,4 and 7).



The resonances at δ13.54, 18.31, 26.54 and 27.19 ppm have been assigned to C-11, C-10, C-9 and C-8 of butyl group attached to tin, comparable with other butyltin compounds [23-25]. The aromatic carbon resonances of these derivatives ware assigned by using incre mental rules for aromatic substitution [26] together with ^{13}C DEPT spectra in which resonances from quarternary carbon are suppressed. The C-1 and C-1' carbons exhibit signals in the characteristic region downfield at δ162.7 and 161.06 respectively. This is in agreement with the earliar work on salicylic acid [23] and aminothiophenol derivative [27] of organotin (IV). The azomethine carbon also absorbs on expected at 146.27 ppm, like the other Schiff's base derivatives of organotin (IV) [24].

Compound No. 1 $Bu_3Sn[SC_6H_4N{=}C(H)C_6H_4OH]$
13.49,C-11;16.87,C-10;26.87,C-9;27.14,C-8;148.2,C-7;117.56,C-6;131.2,C-5;125.4,C-4;131.5,C-3;119.6 C-2;164.0,C-1;119.13,C-6';132.0,C-5';121.2,C-5';121.2,C-4';132.0,C-3',119.4,C-2';163.2,C-1';$^{1}J(^{119}Sn-^{13}C)$ = 505 Hz

Compound No. 3 $Bu_3Sn[SC_6H_4N{=}C(H)C_6H_4OH]Cl$
13.58,C-11;17.80,C-10;26.7.,C-9;27.45,C-8;147.0,C-7;117.92,C-6;131.8,C-5;122.8,C-4;135.0,C-3;119.43C-2;164.0,C-1;120.1,C-6';129.3,C-5';119.42,C-4';131.2,C-3';119.55,C-2',163.1,C-1';$^{1}J(^{119}Sn-^{13}C)$ = 518 Hz

Compound No. 4 $Bu_2Sn[SC_6H_4N{=}C(H)C_6H_4OH]_2$
13.54,C-11;18.31,C-10;26.54.,C-9;27.19,C-8;146.3,C-7;117.3,C-6;131.5,C-5;121.4,C-4;133.6,C-3;119.4C-2;162.7,C-1;119.4,C-6';128.3,C-5';119.4,C-4';132.5,C-3';119.1,C-2';161.0,C-1';$^{1}J(^{119}Sn-^{13}C)$ = 561 Hz

Compound No. 7 $Bu_2Sn[SC_6H_4N{=}C(H)C_6H_4O]$
13.52,C-11;17.47,C-10;26.42.,C-9;27.15,C-8;146.5,C-7;117.68,C-6;131.7,C-5;122.0,C-4;131.8,C-3;119.3C-2;163.5,C-1;119.8,C-6';129.0,C-5';119.4,C-4';130.5,C-3';119.3,C-2';162.0,C-1';$^{1}J(^{119}Sn-^{13}C)$ = 545 Hz

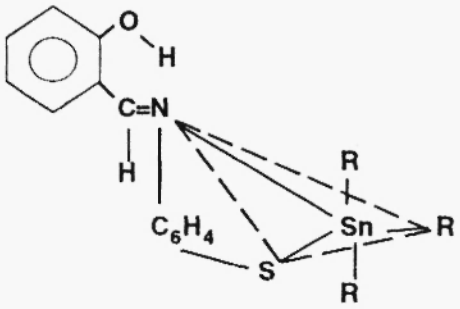
^{1}J (^{119}Sn-^{13}C) values for four coordinate butyltin compound are in the order of 365-302 Hz while five and six coordinate compounds, such values lie in the range of 500-910 Hz [25,28]. The observed values of $^{1}J(^{117/119}Sn-^{13}C)$ for tributylltin and dibutyltin derivatives of Schiff's base derived from salicyldehyde and aminthiophenol are in the range 505-561 Hz indicating five and six coordination around tin atoms.

The 119 Sn NMR chemical shift for only four representative compunds namely tributyl and dibutyl tin(IV) derivatives **1,3,4** and **7** have been observed at -90.33, -92.0, -137.84 and -103.8 ppm respectively,

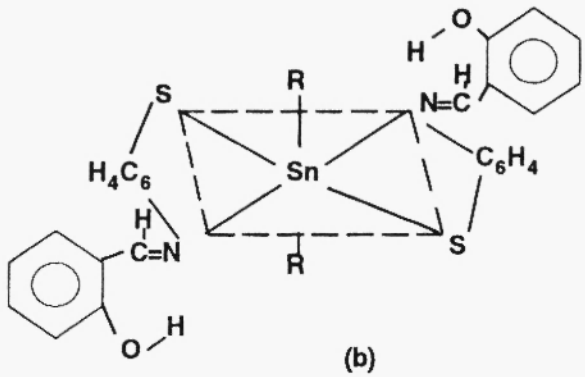
which strongly suggests pentacoordination around tin in trigonal bipyramidal (for compound 1,3 and 7) and hexa coordination around tin in octahedral (compound 4) geometry [29-32].

The 119 Sn NMR chemical shift for only four representative compounds namely the tributyltin (IV) and dibutyltin (IV) derivatives of N-(salicylidene)-o-mercaptoaniline have been observed at-90.33 and -137.84 ppm, which strongly suggests five and six coordination around tin in trigonal bipyramidal and octahedral geometry respectvely [29-32].

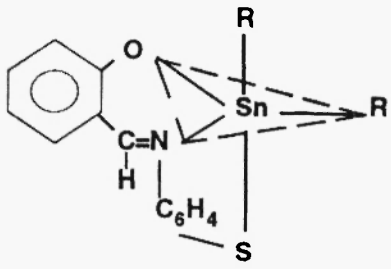
Thus based on above spectral studies 5-coordinate (a) and 6-coordinate (b) structures may be tentatively proposed for triorganotin (IV) and diorganotin (IV) derivatives of N-(salicylidene)-o-mercaptoaniline respectively. Similarly for compound $[OC_6H_4C(H)=NC_6H_4S]$ SnR2' a 5-coordinate (C) structure may be propsed in which the ligand behaves as bifunctional tridentete moiety.



(a)



(b)



(c)

EXPERIMENTAL

All the reactions ware carried out under strictly anhydrous conditions and analytical grade chemicals were used for all experiments. The Schiff base has been synthesized by the condensation of salicyldehyde with 2- aminothiophenol in a 1:1 ratio in ethanol. The solution was refluxed for 3-4 h and then allowed to cool to room temperature. The products so obtained were recystallised from ethanol.

The tin was determined as tin oxide gravimetrically and nitrogen was determined by Kjeldahl's method. Infrared spectra ware recorded on a Perkin-Elmer model 377 spectrophotometer in the range 4000-400 cm^{-1}. The ^1H NMR spectra were recorded on a Perkin-Elmer R-32 using tetramethyl silane as an internal reference and ^{119}Sn and ^{13}C NMR spectra ware recorded on Jeol FX-90 using tetramethyltin and tetramethylsilane as an external standard respectively.

Reaction between triphenyltin (IV) chloride and sodium salt of N-(salicylidene)-o-mercaptoaniline in 1:1 molar ratio.

A weighed quantity of sodium metal (0.06 gm; 2.60 m mols) and 10-15 ml of isopropanol in berzene was

taken in a round bottom flask fitted with a dried and cooled water condenser and guard tube. It was refluxed for about half an hour till clear solution of sodium isopropxide was obtained. After cooling, a weighed amount of ligand (0.60 gm;262 m.mols) was added and the mixture was refluxed for half an hour again. Now a weighed amount of triphenyltin (IV) chloride (1.02 g;2.64 m. mols) in benzene was added and the mixture was further refluxed for 4-5 hours to ensure the completion of the reaction. The desired product (1.31gm; 86%) was isolated by evaporation of the solvent under reduced pressure after filtering off the precipitated sodium chloride. The product was further purifed by crystaliisation from benzene-petroleum ether (40°C-60°C) mixture.

All Other organotin (IV) derivatives of N-(Salicylidene)-o-rnercaptoaniline were synthesized similarly. The characterization of the compunds is given below :

Compound 1. $Bu_3Sn[SC_6H_4N=C(H)C_6H_4OH]$:

Physical and Analytical data : yield,81 %; Viscous Liquid:

Analysis (%F(C): Sn,22.85(22,91): N,2.65(2.70); S,6.20 (6.17)

IR(cm^{-1}): ν 0H 3080; ν C=N 1605; ν Sn-C/Sn-O 510/440

1HNMR (δ ppm) : 6.8-8.1,m, 8H (Ph); 0.5-1.35, m, 27H (n-Bu); 0.61-1.23, t, 9H (terminal methyl of butyl group); 3.25, S, 1H (=CH)

Compound 2. $Ph_3Sn(SC_6H_4N=C(H)C_6H_4OH)$

Physical and Analytical data : yield, 86%; orange solid; M.P. 95°C;

Analysis (% F(C)) : Sn, 20.49(20.53); N,2.38(2.42); S, 5.59(5.53)

IR(cm^{-1}) : ν OH 3120; ν C=N 1595; ν Sn-C/Sn-O 540/450

^{1}H NMR (δ ppm) : 6.2-7.2,m, 23H (Ph); 3.41, S, 1H (=CH)

Compound 3. $Bu_2Sn(SC_6H_4N=C(H)C_6H_4OH)Cl$

Physical and Analytical data : yield, 74%; orange solid; M.P. 90°C;

Analysis (% F(C)) : Sn, 23.80(23.91); N,2.78(2.82); S, 6.40(6.44);Cl, 7.10(7.15)

IR(cm^{-1}) : ν OH 3090; ν C=N 1600; ν Sn-C/Sn-O 520/460

^{1}H NMR (δ ppm) : 6.7-7.2,m, 8H (Ph); 0.61-1.70, m, 18H (n-Bu); 0.31-0.71, t, 6H (terminal methyl of butyl group); 2.90, S, 1H (=CH)

Compound 4. $Bu_2Sn(SC_6H_4N=C(H)C_6H_4OH)_2$

Physical and Analytical data : yield, 80%; Viscous liquid;

Analysis (% F(C)) : Sn, 17.26(17.22); N ,4.10(4.06); S, 9.22(9.29)

IR(cm^{-1}) : ν OH 3110; ν C=N 1610; ν Sn-C/Sn-O 530/450

^{1}H NMR (δ ppm) : 6.4-7.8,m, 16H (Ph); 0.7-1.5, m, 18H (n-Bu); 0.5-1.1, t 6H (terminal methyl of butyl); 3.35, S, 1H (=CH)

Compound 5. $Me_2Sn(SC_6H_4N=C(H)C_6H_4OH)Cl$

Physical and Analytical data : yield, 72%; brown solid; M.P. 130°C;

Analysis (% F(C)) : Sn, 28.80(28.79); N ,3.34(3.39); S, 7.80(7.76); Cl, 8.56(8.61)

IR(cm^{-1}) : ν OH 3105; ν C=N 1615; ν Sn-C/Sn-O 520/460

^{1}H NMR (δ ppm) : 6.3-7.9,m, 8H (Ph); 1.1, S, 6H (CH_3); J(^{119}Sn-^{1}H)=81Hz; 2.85, S, 1H(=CH)

Compound 6. $Me_2Sn(SC_6H_4N=C(H)C_6H_4OH)_2$

Physical and Analytical data : yield, 75%; yellow solid; M.P. 155°C;

Analysis (% F(C)) : Sn, 19.60(19.62); N ,4.58(4.63); S, 10.46(10.58)

IR(cm^{-1}) : ν OH 3095; ν C=N 1605; ν Sn-C/Sn-O 530/460

^{1}H NMR (δ ppm) : 6.8-7.4,m, 16H (Ph); 1.3, S, 6H (Ch_3); J(^{119}Sn-^{1}H)=72Hz; 3.0, S, 1H(=CH)

Compound 7. $Bu_2Sn(SC_6H_4N=C(H)C_6H_4O)$

Physical and Analytical data : yield, 71%; yellow solid; M.P. 140°C;

Analysis (% F(C)) : Sn, 23.84(23.96); N ,2.80(2.82); S, 6.50(6.46)

IR(cm^{-1}) : ν C=N 1620; ν Sn-C/Sn-O 550/480

^{1}H NMR (δ ppm) : 6.1-7.6,m, 8H (Ph); 0.8-1.6, m, 18H (n-Bu); 0.3-0.9, t, 6H (terminal methyl of butyl), 3.24, S, 1H (=CH)

Compound 8. $Me_2Sn(SC_6H_4N{=}C(H)C_6H_4O)$

Physical and Analytical data : yield, 70%; brown solid; M.P. 168°C;
Analysis (% F(C)) : Sn, 31.51(31.59); N ,3.68(3.72); S, 8.59(8.51)
IR(cm^{-1}) : ν C=N 1595; ν Sn-C/Sn-O 510/450
^1H NMR (δ ppm) : 6.5-7.3,m, 8H (Ph); 1.0, S, 6H (CH_3); J(^{119}Sn-^1H)=72Hz; 2.95, S, 1H(=CH)
(F : Found; C; Calculated; m : complex pattern; S : Singlet; t : triplet)

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REFERENCES

1. S.K.Mishra and D.K Awasthi, *J. Inst. Chem.*, **58**, 46(1986).
2. P.R. Shukla, M. Mishra and A.K.Pathak, *J. Indian Chem.Soc.*, **67**, 678 (1990).
3. A. Syamal and M.R,Mourya, *Synth. React. Inorg. Met. org. Chem.*, **16**, 39 (1986).
4. S.Vatsala and G. Parmeshwaran, *Indian J. Chem.*, **25 A**, 1158(1986)
5. N.S.Biradar and A.L. Locker, *Indian J. Chem.*, **11**, 833 (1973).
6. J. Chacko and G. Parmeshwaran, *Indian J. Chem.*, **28 A**, 77 (1989).
7. N.S. Biradar and A.L. Locker, *J. Inorg. Nucl. Chem.*, **37**, 1308 (1979).
8. R.K. Sharma, R.V.Singh and J.P. Tandon, *Curr. Sci.*, **48**, 886 (1979(.
9. A. Syamal and D. Kumar, *Indian J. Chem.*, **32A**, 625 (1993).
10. R.J. Rao and H.B. Wankhade, *Synth. React. Inorg. Met. Org. Chem.*, In press (1995)
11. P.S. Prabhu and S.S. Dodwad, *J Indian Chem. Soc.*, **60**, 546 (1983).
12. V.J. Raju, V. Ranabaore, B.B.Kumar and M.C. Ganorker, *J.Indian Chem. Soc.*, **60**, 724 (1983).
13. S.Bhardawaj. M.N. Ansari and M.C.Jain, *Indian J. Chem.*, **28 A**, 81 (1989).
14. L. Birladeanu, *Infrared Spectroscopy Organic Sulphur compounds (Wiley Interscience, New York)* **291**,(1966)
15. K. Kawakani and R. Okawara, *J. Organometal Chem.*, **6**, 249 (1966).
16. J.R. Holmes and H.D.Kaesz, *J. Am. Chem. Soc.*, **83**, 3903 (1961).
17. M.L.Maddox, N. Flitctoft and H.D.Kaesz, *J Organomet. chem.*, **4**, 50 (1965).
18. K.L. Richie and G. End., *Inorg. Chim. Acta*, **31**, L417 (1978)
19. Y. Kawakami and T. Sasaki, *Chem. Lett.*, **279** (1979).
20. W.D. Honnick, M.C.Hughes, C.D.Schafter and J.J Zuckerman., *Inorg. Chem.*, **15**, 1931 (1976).
21. S.W. Ng and J.J Zuckerman, *J. Organometal chem.*, **249**,81 (1983).
22. A.K. Gupta, S. Sharma, H.P.S. Chauhan and R.J. Rao, *Synth. React.Inorg. Met. Org.Chem.*, **21**, 497(1991).
23. M. Boualam, R. Willim, M. Biesemans, B. Mahieu, J. Meunier-Piret and M.Gielen, *Main group met. Chem.*, **14**, 41 (1991).
24. A. Saxena and J.P.Tandon, *Polyhedron*, **2**, 443 (1983).
25. T.N. Mitchell, *J. Organometal Chem.*, **59**, 189(1973).
26. H.O Kalinowaski, S. Berger and S. Braun, *Carbon NMR spectroscopy*, J. Wiley, Chichester, 313(1988).
27. B.S.Saraswat and J. Mason, *Polyhedron*, **5**, 1449(1986).
28. J. Holecek, M. Nadvornik, K. Handler and A. Lycka, *J. Organometal Chem.*, **315**,299 (1986).
29. P.J. Smith and T.P.Tupciauskar, *Ann. NMR Rep. Spect.*, **8**, 305 (1978).
30. J. Otera, *J. Organometal Chem.*, **221**, 57(1981).
31. N.A.Davies, K.B. Dillon, R.K. Harris, G.F. Hewitson and L. Toms, *Polyhedron*, **13**, 19 (1994).
32. F. Huber, M. Vornefeld, G. Ruisi and R. Barbieri, *App. Organometal Chem.*, **7**, 243(1993).

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