

ring, resulting in a greater mesomeric electron release to the sulphur of  $-\text{SCH}_3$ . Indeed the expected steric inhibition of resonance is found in  $\text{trans-PdCl}_2(3,5\text{-di-CH}_3\text{-4-OCH}_3\text{C}_6\text{H}_2\text{SCH}_3)_2$ . The  $\nu(\text{Pd-S})$  stretching frequency is at  $312\text{ cm}^{-1}$  which is higher due to the inhibition of resonance caused by two methyl groups adjacent to the methoxy group.

In the electronic spectral data (table 1), the band at 277 is due to  $L(\pi) \rightarrow L(\pi)^*$  transition. The other intense one is of ligand to metal charge transfer band. The large bathochromic shift of the charge transfer band (332 nm to 365 nm) in the complex  $\text{trans-PdCl}_2(p\text{-OCH}_3\text{C}_6\text{H}_4\text{SCH}_3)_2$  is due to the presence of electron repelling  $-\text{OCH}_3$  in p-position. The  $\lambda_{\text{max}}$  value still increases to 372 nm in the complex  $\text{trans-PdCl}_2(3\text{-CH}_3\text{-4-OCH}_3\text{C}_6\text{H}_3\text{SCH}_3)_2$  which is due to steric enhancement of resonance.

This phenomenon also gains support from proton magnetic resonance studies (table 1). The proton signals of  $-\text{SCH}_3$ ,  $-\text{CH}_3$  and  $-\text{OCH}_3$  are in the ratio 1 : 1 for 3- $\text{CH}_3$ , 1 : 1 for 4- $\text{OCH}_3$ , 1 : 1 : 1 for 3- $\text{CH}_3$ -4- $\text{OCH}_3$  and 1 : 2 : 1 for 3,5-di- $\text{CH}_3$ -4- $\text{OCH}_3$  respectively as expected. The phenyl protons in the complex  $\text{trans-PdCl}_2(\text{C}_6\text{H}_5\text{SCH}_3)_2$  are in the range  $\delta$  7.2 to 7.86. In the complexes  $\text{trans-PdCl}_2(m\text{-CH}_3\text{C}_6\text{H}_4\text{SCH}_3)_2$  and  $\text{trans-PdCl}_2(p\text{-OCH}_3\text{C}_6\text{H}_4\text{SCH}_3)_2$  the phenyl protons are in the range  $\delta$  7.09 to 7.49 and  $\delta$  6.69 to 7.67 respectively. The shift to up field in these complexes is due to the electron-releasing nature of 3- $\text{CH}_3$  and 4- $\text{OCH}_3$  groups present in the phenyl ring. In the complex  $\text{trans-PdCl}_2(4\text{-OCH}_3\text{-3-CH}_3\text{C}_6\text{H}_3\text{SCH}_3)_2$  phenyl protons range still decreases ( $\delta$  6.66 to 7.66) which is due to steric enhancement.

The  $-\text{OCH}_3$  signal in  $\text{trans-PdCl}_2(p\text{-OCH}_3\text{C}_6\text{H}_4\text{SCH}_3)_2$ ,  $\delta$  3.69 is shifted to  $\delta$  3.80 in the complex  $\text{trans-PdCl}_2(4\text{-OCH}_3\text{-3-CH}_3\text{-C}_6\text{H}_3\text{SCH}_3)_2$ . This large shift is due to the steric effect of 3- $\text{CH}_3$  group, which restricts the free rotation of the methoxy group, thereby increasing the probability of the latter to attain the planarity with the benzene ring. It is also of interest to note that signal for  $-\text{OCH}_3$  in the complex  $\text{trans-PdCl}_2(3,5\text{-di-CH}_3\text{-4-OCH}_3\text{C}_6\text{H}_2\text{SCH}_3)_2$  is shifted to  $\delta$  3.60 because of the steric inhibition caused by two ortho methyl substituents.

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## SYNTHESIS AND CHARACTERIZATION OF TRISULPHURTRINITRIDE BIS (TRIPHENYLPHOSPHINE) NICKEL(I), $\text{Ni}(\text{S}_3\text{N}_3)(\text{PPh}_3)_2$

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IN continuation of our work on small ligands of sulphur and nitrogen such as  $\text{NS}^{1-5}$ ,  $\text{NSO}^{6-8}$ ,  $\text{NSO}_2^{9}$ ,  $\text{NS}_2^{10}$  and  $\text{NS}_3^{11}$ , we report here the formation of  $\text{Ni}(\text{S}_3\text{N}_3)(\text{PPh}_3)_2$  from the reaction of  $\text{S}_4\text{N}_4$  with  $\text{NiCl}_2(\text{PPh}_3)_2$ . The synthesis and characterization of  $\text{S}_3\text{N}_3^-$  anion from the reaction of azide ion and  $\text{S}_4\text{N}_4$  in ethanol have been reported earlier<sup>12, 13</sup>.

### Preparation of $\text{Ni}(\text{S}_3\text{N}_3)(\text{PPh}_3)_2$

To a solution of  $\text{NiCl}_2(\text{PPh}_3)_2$ <sup>14</sup> (1.21 g, 2 mmol) in 60 ml acetonitrile-dichloromethane (1:1), solid  $\text{S}_4\text{N}_4$ <sup>15</sup> (0.37 g, 2 mmol) was added. The reaction

Table 1 Mass spectrum of  $Ni(S_3N_3)(PPh_3)_2$ 

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
294	75.4	$S=P(C_6H_5)_3^+$	139	21.0	$(C_{11}H_7)^+$
293	50.9	$HS-P(C_6H_4)_2(C_6H_5)^+$	133	5.2	$Ni(N_3S)^+$
262	21.0	$P(C_6H_5)_3^+$	123	7.0	$NiS_2^+$
217	7.0	$S=P(C_6H_5)_2^+$	108	15.8	$P(C_6H_5)^+$
215	10.5	$S=P(C_6H_4)_2^+$	107	21.0	$P(C_6H_4)^+$
197	2.6	$Ni(S_3N_3)^+$	105	32.4	$Ni(NS)^+$
185	51.7	$P(C_6H_5)_2^+$	77	49.0	$C_6H_5^+$
183	100.0	$P(C_6H_4)_2^+$	63	15.7	$C_5H_3^+$
165	7.9	$Ni(S_2N_3)^+$	59	14.9	$Ni^+$
152	19.3	$(C_6H_4)_2^+$	51	47.3	$C_4H_3^+$
			46	22.8	$NS^+$

mixture, which turned brown within 5 min, was stirred for 2 hr. It was concentrated at reduced pressure to about 20 ml whereby the brown crystals of  $Ni(S_3N_3)(PPh_3)_2$  separated out which were filtered, washed several times with *n*-hexane and dried under vacuum. The yield was 1.16 g (87%). Anal. Calcd for  $C_{36}H_{30}N_3P_2S_3Ni$ : C, 59.94; H, 4.16; N, 5.82; S, 13.32%. Found: C, 59.8; H, 4.1; N, 6.0; S, 13.5%. IR spectrum, 3045, 1585, 1570, 1480, 1435, 1310, 1180, 1160, 1150, 1098, 1074, 1032, 1000, 925, 850, 745, 720, 695, 680, 655, 645, 530, 510, 490, 410, 384 and  $320\text{ cm}^{-1}$ . Magnetic moment  $\mu = 1.85$  B.M. at  $295^\circ\text{K}$ .

Carbon, hydrogen, nitrogen and sulphur analysis were performed at the Microanalytical Laboratory, Göttingen, FRG. IR spectrum was recorded as KBr pellets on a Perkin Elmer Model 511 Spectrophotometer in the range  $4000\text{--}300\text{ cm}^{-1}$ . Magnetic moment was measured by Gouy balance.

Reaction of tetrasulphurtetranitride with dichlorobis(triphenylphosphine)nickel(II) results in the formation of a brown complex which is analyzed satisfactorily for the formula  $Ni(S_3N_3)(PPh_3)_2$ . It decomposes slowly in air. The magnetic moment for  $Ni(S_3N_3)(PPh_3)_2$  at  $295^\circ\text{K}$  is 1.85 B.M. IR spectrum shows absorption bands at 1032 S, 925 VW, 655 S, 645 S and  $384\text{ S cm}^{-1}$  due to  $S_3N_3^-$  ligand which shift slightly towards higher wavenumber from free  $S_3N_3^-$  ion<sup>13</sup>  $320\text{ cm}^{-1}$  due to  $\nu(Ni-N)$  and bands due to triphenylphosphine. The mass spectrum shows decomposition of  $Ni(S_3N_3)(PPh_3)_2$  (table 1) and fragments due to  $SPPH_3$  and  $Ni(S_3N_3)$ . The magnetic behaviour shows the oxidation state of nickel ion as +1 and  $S_3N_3$  moiety is bonded as  $S_3N_3^-$  in this complex.

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