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Preliminary communication

NOVEL PALLADIUM COMPOUNDS CONTAINING A THIOMETHOXYMETHYL GROUP

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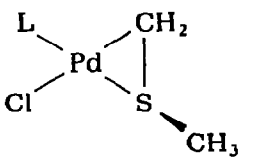
Summary

A novel palladium compound, $(Ph_3P)Pd(Cl)(CH_2SCH_3)$, was prepared in which the CH_3SCH_2 group acts as a chelate ligand, the stereochemically non-rigid property of $(Ph_3P)Pd(CH_2SCH_3)[S_2CN(CH_3)_2]$ was also discussed in terms of the ligating effect of sulfur in this group

The study of transition metal compounds containing the CH_3SCH_2 group is of interest in that this ligand may behave in either a mono or bidentate fashion [1], resulting in novel structural and chemical features In this paper, we report the preparation and properties of two palladium compounds containing the CH_3SCH_2 group

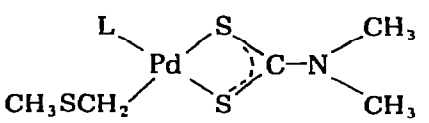
$$L_4Pd \xrightarrow{ClCH_2SCH_3} L_2Pd(Cl)CH_2SCH_3 \underset{+L}{\overset{-L}{\rightleftharpoons}}$$

(I)



(II)

$$\xrightarrow{NaSSCN(CH_3)_2}$$



(III)

L = $P(C_6H_5)_3$

Compound I was obtained in good yield by the addition of chloromethyl methyl sulfide to a suspension of $Pd(Ph_3P)_4$ in benzene at room temperature Molecular weight studies in CH_2Cl_2 at 25 °C show that I partially dissociates with liberation of triphenylphosphine The triphenylphosphine set free in the solvents on each crystallization of the mixture of I and II from CH_2Cl_2/Et_2O

was removed repeatedly by filtration to give finally a monomeric complex II* A preliminary X ray structural determination showed II to be an approximately square-planar complex as depicted above with the $(H_2)C-S$ bond length (1 76 Å) [2] practically the same as that found in the complex $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\ CH_2SCH_3)$ (1.78 Å) [3] In the ^1H NMR spectrum** of II in $CDCl_3$ at −30 °C, the CH_3 and CH_2 protons appear as doublets at δ 2 34 (J(HP) 4 Hz) and δ 2 68 ppm (J(HP) 2 Hz), respectively However, each signal coalesces to a singlet at elevated temperatures The fact that the methylene protons are magnetically equivalent even at −30 °C is best attributed to rapid inversion at the sulfur atom Both coalescenses are probably induced by rapid phosphine exchange at higher temperatures

Treatment of II in CH_2Cl_2 with $NaS_2CN(CH_3)_2$ in EtOH at room temperature gave a monomeric complex III As shown in Fig 1, the $(N)CH_3$ proton resonance of III appears as a singlet at 25 °C, but is split upon cooling

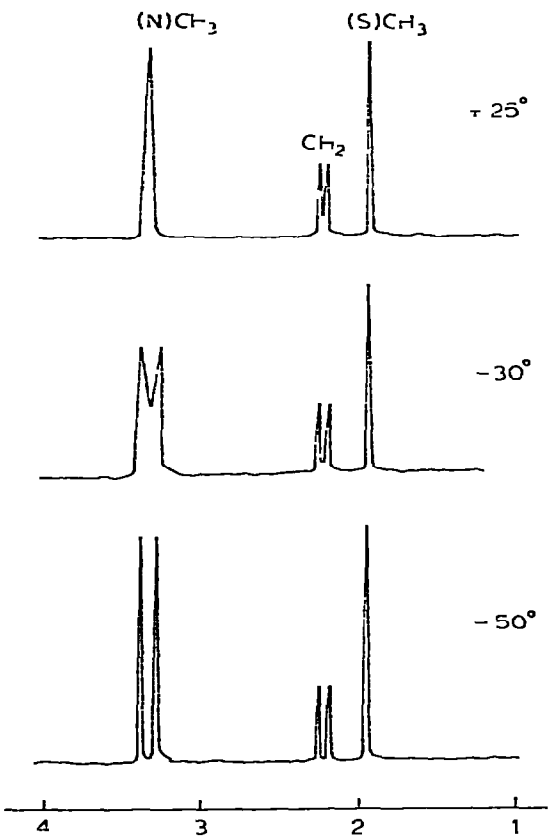


Fig.1 ^1H NMR spectra of $(Ph_3P)Pd(CH_2SCH_3)[S_2CN(CH_3)_2]$ (III) in $CDCl_3$

*The corresponding platinum analog of II could not be obtained from *trans* $[(Ph_3P)_2Pt(Cl)\text{-}CH_2SCH_3]$

**The spectra were recorded at both 60 and 100 MHz

On the other hand, the $(N)CH_3$ protons of $(Ph_3P)PdMe[S_2CN(CH_3)_2]$ obtained by treatment of *trans*-$[(Ph_3P)_2PdMeI]$ with $NaS_2CN(CH_3)_2$ exhibited singlets at δ 3.36 and δ 3.27 ppm in $CDCl_3$ up to 50 °C. The magnetic equivalence of the $(N)CH_3$ protons of III at 25 °C is possibly associated with the ligating effect of the sulfur atom in the CH_3SCH_2 group in the transition state*

References

1 R B King and M B Bisnette Inorg. Chem 4 (1965) 486
2 N Kasai et al to be published
3 E. Rodulfo de Gil and L F Dahl J Amer Chem Soc 91 (1969) 3751

*We believe that in the ground state there is no significant interaction between sulfur in the CH_3SCH group and palladium since the $(S)CH_3$ proton signals are not coupled to the ^{31}P nucleus even at −50 °C (Fig 1)