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Synthesis and Characterization of Mixed Carbamato Complexes of Palladium(II) and Related Compounds

N. SONODA and T. TANAKA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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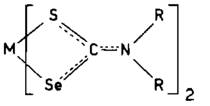
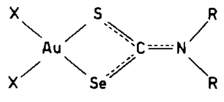
Thioselenocarbamato complexes of palladium(II) with formula $Pd(PR_3)Cl(SSeCNR'_2)$ (PR_3 = PPh_3, $PMePh_2$, or PMe_2Ph; R′ = Me, Et) have been prepared. These complexes react with dithio-, monothio-, or monoselenocarbamato ligand, with or without an elimination of PR_3 to give mixed carbamato complexes, $Pd(SSeCNR_2)(S_2CNR_2)$ (R = Me and Et) or $Pd(PR_3)Cl(SSeCNMe_2)(YC(O)NMe_2)$ (PR_3 = PPh_3, $PMePh_2$; Y = S or Se). Properties and configurations of these complexes are described on the basis of the conductivity measurements, infrared and pmr spectra.

Introduction

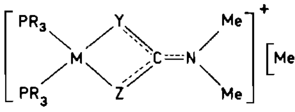
In the previous papers,[1–3] we have reported the synthesis and spectroscopic studies of some square planar d^8 metal complexes of N,N-dialkylthioselenocarbamate (*A, B,* and *C*):



A: M = Ni(II), Pd(II), and Pt(II);
R = Me and Et



B: X = Cl, Br, I, Me, and Et;
R = Me or Et



C: M = Pd(II) and Pt(II)
PR_3 = PPh_3 and $PMePh_2$
Y, Z = S or Se

Proton or ^{31}P nmr spectra of these complexes have shown that the coordination ability of the sulfur and selenium atoms to the d^8 metal resembles closely each other.[1–3]

This paper reports the preparation of some (N,N-dialkylthioselenocarbamato) (*tert*-phosphine)chloropalladium(II), $Pd(PR_3)Cl(SSeCNR'_2)$ (PR_3 = PPh_3, $PMePh_2$, PMe_2Ph; R′ = Me or Et) and the reactions with other carbamato ligands, *i.e.* S_2CNR_2, SC(O)NR_2, and SeC(O)NR_2, to give mixed carbamato complexes. In addition, some dithiocarbamato analogs were prepared to discuss the pmr spectra of these thioselenocarbamato complexes.

Experimental

Materials

Bis(*tert*-phosphine)dichloro-μ,μ-dichloropalladium(II), $[Pd(PR_3)Cl_2]_2$ (PR_3 = PPh_3, $PMePh_2$, PMe_2Ph), was prepared by the literature methods.[4] (N,N-Dialkylthioseleno- and -dithiocarbamato)dimethylchlorotin (IV), Me_2SnCl(dmtsc) (dmtsc = $SSeCNMe_2$),[5] Me_2SnCl(detsc) (detsc = $SSeCNEt_2$),[1] and Me_2SnCl(dmdtc) (dmdtc = S_2CNMe_2)[6] were prepared as described elsewhere. Bis(N,N-dimethylmonothio- and -monoselenocarbamato)dimethyltin(IV), $Me_2Sn(dmmtc)_2$ (dmmtc = SC(O)NMe_2)[7] and $Me_2Sn(dmmsc)_2$ (dmmsc = SeC(O)NMe_2)[8] were recently synthesized in our laboratory.

(N,N-Dialkyldicalcogenocarbamato)(tert-phosphine)chloropalladium(II)

A solution of Me_2SnCl(dmtsc) (0.40 g, 1.14 mmol) in dichloromethane was dropped slowly with stirring to a suspension of $[Pd(PPh_3)Cl_2]_2$ (0.50 g, 0.57 mmol) in the same solvent. The reddish brown suspension changed to a reddish orange solution, which was evaporated to dryness under reduced pressure. The resulting product was washed with diethylether several times to remove Me_2SnCl_2 and recrystallized from a benzene-diethylether mixture to give crystals of $Pd(PPh_3)Cl$(dmtsc) (0.45 g, 0.79 mmol). Other complexes of this type, $Pd(PMePh_2)Cl$(dmtsc), $Pd(PMe_2Ph)Cl$(dmtsc), $Pd(PPh_3)Cl$(detsc), $Pd(PPh_3)Cl$(dmdtc), and $Pd(PMePh_2)Cl$(dmdtc) were similary synthesized by reactions of $[Pd(PR_3)Cl_2]_2$ (PR_3 = PPh_3, $PMePh_2$, or PMe_2Ph) with $Me_2SnCl(XYCNR'_2)$ (X,Y = S or Se; R′ = Me or Et) at the mole ratio of 1:2 in dichloromethane, 70–85% yields. $Pd(PPh_3)Cl$(dedtc) (dedtc = S_2CNEt_2)

was obtained by reaction of [Pd(PPh$_3$)Cl$_2$]$_2$ in dichloromethane with Na(dedtc)·3H$_2$O in ethanol.

(N,N-Dialkylthioselenocarbamato)(N,N-dialkyldithiocarbamato)palladium(II)

To a dichloromethane solution of Pd(PPh$_3$)Cl(dmtsc) (0.30 g, 0.53 mmol) was added a small excess of Me$_2$SnCl(dmdtc) (0.21 g, 0.69 mmol) in the same solvent, and the solution was stirred for 5 hr. A precipitate formed was collected, washed repeatedly with ethanol and then dichloromethane, and dried *in vacuo* to yield Pd(dmtsc)(dmdtc) (0.19 g, 0.48 mmol). The N,N-diethyl analog, Pd(detsc)(dedtc), was similarly prepared by reaction of Pd(PPh$_3$)Cl(detsc) (0.30 g, 0.50 mmol) with a small excess amount of Na(dedtc)·3H$_2$O (0.15 g, 0.67 mmol) in ethanol, and recrystallized from dichloromethane (0.18 g, 0.40 mmol).

(N,N-Dimethylthioselenocarbamato)(N,N-dimethylmonoselenocarbamato)(tert-phosphine)palladium(II) and Related Compounds

A dichloromethane solution of Me$_2$Sn(dmmsc)$_2$ (0.20 g, 0.44 mmol) was dropped to a solution of Pd(PPh$_3$)Cl(dmtsc) (0.50 g, 0.88 mmol) in dichloromethane, and followed by stirring for 3 hr, during which time the solution turned from reddish orange to red. The solution was filtered and most of the solvent were evaporated under reduced pressure to produce a precipitate, which was collected by filtration, washed by diethylether several times, and recrystallized from acetone. The ir spectrum indicates that the crystals obtained include a small amount of acetone molecule. To remove the solvent molecule, this product was recrystallized from a dichloromethane–diethylether mixture to give solvent free Pd(PPh$_3$)(dmtsc)(dmmsc) (0.27 g, 0.39 mmol).

Pd(PPh$_3$)(dmtsc)(dmmtc) and Pd(PMePh$_2$)(dmtsc)(dmmsc) were analogously prepared by reactions of Pd(PR$_3$)Cl(dmtsc) (PR$_3$ = PPh$_3$ or PMePh$_2$) with Me$_2$Sn(dmmtc)$_2$ or Me$_2$Sn(dmmsc)$_2$ in dichloromethane. Pd(PPh$_3$)(dmdtc)(dmmsc) was obtained from Pd(PPh$_3$)Cl(dmdtc) and Me$_2$Sn(dmmsc)$_2$. Properties and analytical data for the newly prepared complexes are collected in Table I.

Physical Measurements

Infrared and proton magnetic resonance spectra were measured as described elsewhere.[2]

TABLE I. Properties, Analytical and IR Data of the Complexes.

Compound	Color	M.p. °C	C % Found (Calcd)	H % Found (Calcd)	N % Found (Calcd)	M.W.[a] Found (Calcd)	ν(C=N) cm^{-1}	ν(Pd–Cl) cm^{-1}	ν(C=O) cm^{-1}
Pd(PPh$_3$)Cl(dmtsc)	Red orange	238–240	44.32 (44.15)	3.92 (3.71)	2.55 (2.45)	576 (571)	1553	306, 315	
Pd(PMePh$_2$)Cl(dmtsc)	Red orange	209–212	37.54 (37.74)	3.51 (3.77)	2.94 (2.75)	497 (509)	1550	305, 313	
Pd(PMe$_2$Ph)Cl(dmtsc)	Red orange	170–172	29.55 (29.55)	3.89 (3.84)	3.28 (3.13)	442 (447)	1545	306 br	
Pd(PPh$_3$)Cl(dmdtc)	Orange	215 dec.	47.87 (48.10)	4.07 (4.04)	2.75 (2.67)	521 (524)	1553	303	
Pd(PMePh$_2$)Cl(dmdtc)	Yellow	194–197	41.80 (41.57)	4.08 (4.15)	3.05 (3.03)	469 (462)	1546	302	
Pd(PPh$_3$)Cl(detsc)	Red	203–204	46.30 (46.09)	4.18 (4.21)	2.58 (2.34)	588 (599)	1529	304, 315	
Pd(PPh$_3$)Cl(dedtc)	Orange	207–208	49.92 (50.00)	4.55 (4.57)	2.74 (2.54)	554 (552)	1527	304	
Pd(dmtsc)(dmdtc)	Yellow	>250	18.08 (18.30)	3.04 (3.08)	7.17 (7.12)	b (394)	1536		
Pd(detsc)(dedtc)	Red orange	246–247	27.06 (26.70)	4.67 (4.49)	6.31 (6.23)	419 (450)	1517		
Pd(PPh$_3$)(dmtsc)(dmmsc)	Red	199–202	42.24 (41.96)	4.15 (3.97)	4.28 (4.08)	644 (687)	1545		1609
Pd(PPh$_3$)(dmtsc)(dmmtc)	Orange	202–204	44.98 (45.04)	4.32 (4.26)	4.45 (4.38)	613 (640)	1537		1593
Pd(PMePh$_2$)(dmtsc)(dmmsc)	Red	198–200	36.37 (36.52)	4.04 (4.04)	4.50 (4.48)	570 (625)	1541		1612
Pd(PPh$_3$)(dmdtc)(dmmsc)	Red	161–163	44.90 (45.04)	4.40 (4.26)	4.39 (4.38)	572 (640)	1539		1613

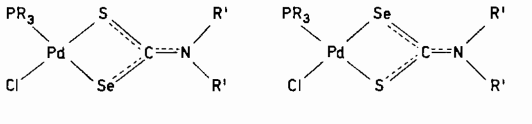
[a] VPO in CHCl$_3$ at 37° C. [b] Insoluble in CHCl$_3$.

Results and Discussion

(Carbamato)(tert-phosphine)chloropalladium(II): Pd(PR$_3$)ClL (PR$_3$ = PPh$_3$, PMePh$_2$, or PMe$_2$Ph; L = thioseleno- or dithiocarbamate)

The complexes of this type in the solid state are fairly stable to air and moisture, but somewhat unstable in solution. They are soluble in polar organic solvent, while less soluble in non-polar ones.

Infrared spectra of these complexes in the solid state show a strong ν(C$\overset{...}{=}$N) band around 1550 cm^{-1} (Table I), suggesting that the thioseleno- and dithiocarbamato ligands act in a bidentate manner. The complexes exhibit an absorption band assigned to the ν(Pd–Cl) mode in the 302–315 cm^{-1} range. Molecular weight determinations indicate that these complexes are essentially monomeric in chloroform (Table I). Moreover, the molar conductance of Pd(PPh$_3$)Cl (dmtsc) in dichloromethane (1.05 × 10^{-3} *M*) is 0.041 ohm^{-1} cm^2 mol^{-1} at 25° C, indicating that this complex is non-electrolyte. In view of these results, the complexes are suggested to take an essentially rigid planar configuration both in the solid state and in solution, which involves two possible isomers, *D* and *E*.



D E

PR$_3$ = PPh$_3$, PMePh$_2$, or PMe$_2$Ph
R' = Me or Et

There are four kinds of N–CH$_3$ groups located in different environments in Pd(PPh$_3$)Cl(dmtsc). The pmr spectrum of this complex, however, shows only two N-CH$_3$ signals (Figure 1a), whose chemical shifts are very close to those of the dmdtc analog (Figure 1b). From this result as well as the similarity in coordination ability to palladium(II) between sulfur and selenium,[1–3] the separation of the N-CH$_3$ signals in the dmtsc complex is most likely to result from a magnetic anisotropy effect of PPh$_3$. This is evidenced from the fact that in (PR$_3$)$_2$Pt(Cl)C(O)NMe$_2$ (PR$_3$ = PPh$_3$, PMePh$_2$, and PMe$_2$Ph) the phosphorus ligands move the N-CH$_3$ signals nearby to a higher field.[9] Thus, the higher field signal of Pd(PPh$_3$)Cl(dmtsc) is assigned to the N-CH$_3$ protons located in the same side as PPh$_3$ with respect to a direction involving the carbamato C$\overset{...}{=}$N bond, and *vice versa*. The present observation is in contrast with the pmr spectrum of Ni(PPh$_3$)Cl(dmdtc), which was reported to exhibit only one N-CH$_3$ signal even at low temperature.[10]

Although no pmr evidence has been obtained for the existence of the two isomers, *D* and *E*, of Pd(PPh$_3$) Cl(dmtsc), the pmr spectra of Pd(PMePh$_2$)Cl(dmtsc) and Pd(PMe$_2$Ph)Cl(dmtsc) show two doublets of P-CH$_3$ signals with different intensities and small separations (Figure 2), indicating the existence of the two isomers. No separation of the N-CH$_3$ signal owing

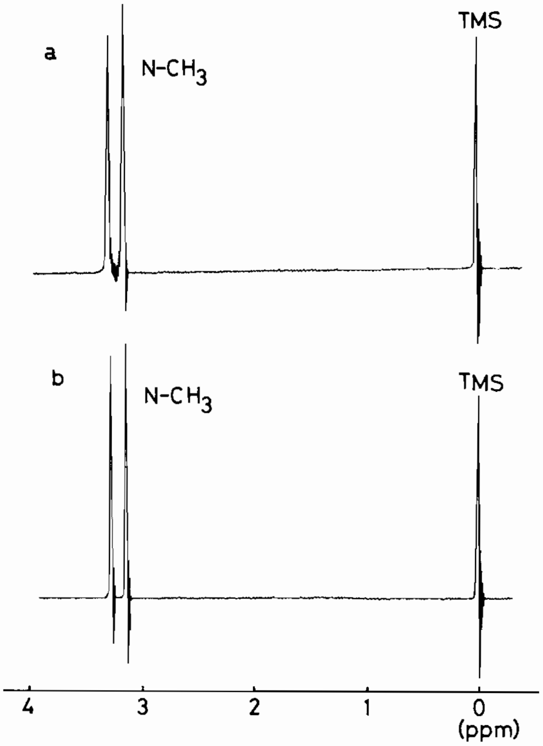


Figure 1. Pmr spectra of Pd(PPh$_3$)Cl(dmtsc) (a) and Pd (PPh$_3$)Cl(dmdtc) (b) in CH$_2$Cl$_2$.

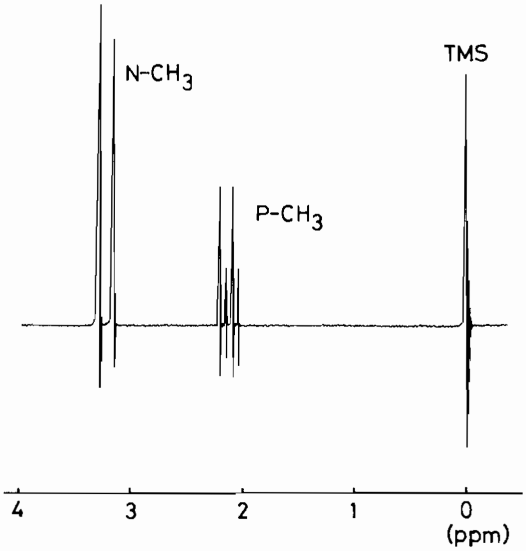


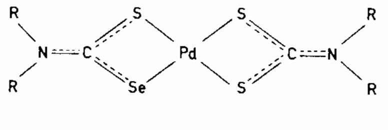
Figure 2. Pmr spectrum of Pd(PMePh$_2$)Cl(dmtsc) in CH$_2$Cl$_2$.

to the isomers is still found in these complexes. The existence of two isomers of Pd(PPh_3)Cl(dmtsc) may be suggested from the infrared spectrum in the solid state, which shows two ν(Pd–Cl) bands. This is the case of the $PMePh_2$ complex, while the PMe_2Ph analog exhibits only a broad ν(Pd–Cl) band (Table I).

The pmr spectrum of Pd(PPh_3)Cl(detsc) shows two quartets of N-CH_2 signals. From the comparison with the spectrum of Pd(PPh_3)Cl(dedtc), the separation of N-CH_2 signals is similarly attributed to the anisotropic effect of the phosphorus ligand, although the C-CH_3 proton signals are very complicated. The pmr data are summarized in Table II.

Mixed Carbamato Complexes: Pd(SSeCNR$_2$)(S$_2$CNR$_2$) (R = Me and Et) and Pd(PR$_3$)(SSeCNMe$_2$)(YC(O)NMe$_2$) (PR$_3$ = PPh$_3$, PMePh$_2$; Y = S or Se)

Pd(PPh_3)ClL (L = dmtsc and detsc) reacts with Me_2SnCl(dmdtc) or Na(dedtc)·$3H_2O$ to give mixed chelate complexes, *F*, with elimination of PPh_3.



F : R = Me and Et

This is in contrast with the reaction of Pd(PR_3)Cl(dmtsc) (PR_3 = PPh_3 and $PMePh_2$) with Me_2Sn$(dmmtc)_2$ or $Me_2Sn(dmmsc)_2$, in which the phosphorus ligands were not removed from the palladium, because of a weak chelating ability of dmmtc or dmmsc.

Pd(detsc)(dedtc) is soluble in polar organic solvents, and Pd(dmtsc)(dmdtc) is slightly soluble in polar ones.

TABLE II. Proton Chemical Shifts of the Complexes, δ(ppm).

Compound	N-CH_3	P-CH_3
Pd(PPh_3)Cl(dmtsc)	3.13, 3.29	
Pd($PMePh_2$)Cl(dmtsc)	3.15, 3.28	2.12, 2.16
Pd(PMe_2Ph)Cl(dmtsc)	3.22, 3.30	1.78, 1.82
Pd(PPh_3)Cl(dmdtc)	3.11, 3.24	
Pd($PMePh_2$)Cl(dmdtc)	3.13, 3.23	2.09
Pd(PPh_3)(dmtsc)(dmmsc)	2.92(br), 3.14, 3.16, 3.30	
Pd(PPh_3)(dmtsc)(dmmtc)	2.88(br), 3.17, 3.18, 3.32	
Pd($PMePh_2$)(dmtsc)(dmmsc)	2.94(br), 3.16, 3.29	2.07, 2.17
Pd(PPh_3)(dmdtc)(dmmsc)	2.93(br) 3.14, 3.28	
	N-CH_2	C-CH_3
Pd(PPh_3)Cl(detsc)	3.55, 3.76	Complicated
Pd(PPh_3)Cl(dedtc)	3.57, 3.71	1.15, 1.22
Pd(detsc)(dedtc)	3.71, 3.76	1.28, 1.31

On the other hand, the mixed carbamato complexes with tertiary phosphine are fairly soluble in common organic solvents. All the complexes are stable to air and humidity both in the solid state and in solution.

The pmr spectrum of Pd(detsc)(dedtc) (Figure 3) shows two kinds of triplet and quartet both with the intensity ratios of 1:3. It was previously reported that in $M(detsc)_2$ (M = Ni(II), Pd(II), and Pt(II)) the pmr signals of N-C_2H_5 group *trans* to sulfur with respect to the carbamato $C\overset{\cdots}{-}N$ bond occur in a slightly higher magnetic field than those *trans* to selenium, and are almost identical in chemical shift with those of $M(dedtc)_2$.[1] In view of this fact, the triplet and quartet signals with smaller intensities may be assigned to the N-C_2H_5 protons *trans* to the selenium atom with respect to the $C\overset{\cdots}{-}N$ bond, and those with larger intensities may be due to the N-C_2H_5 protons *trans* to the sulfur of detsc as well as dedtc protons.

Ir spectra of the mixed carbamato complexes with *tert*-phosphine in the solid state show a strong $\nu(C\overset{\cdots}{-}N)$ band around 1530 cm^{-1}, which is characteristic of a bidentate thioseleno- or dithiocarbamate. They also exhibit the ν(C=O) band about 1600 cm^{-1}, which confirms that the monothio- or monoselenocarbamato ligand coordinates to the palladium through the sulfur or selenium with a free carbonyl in the solid state.

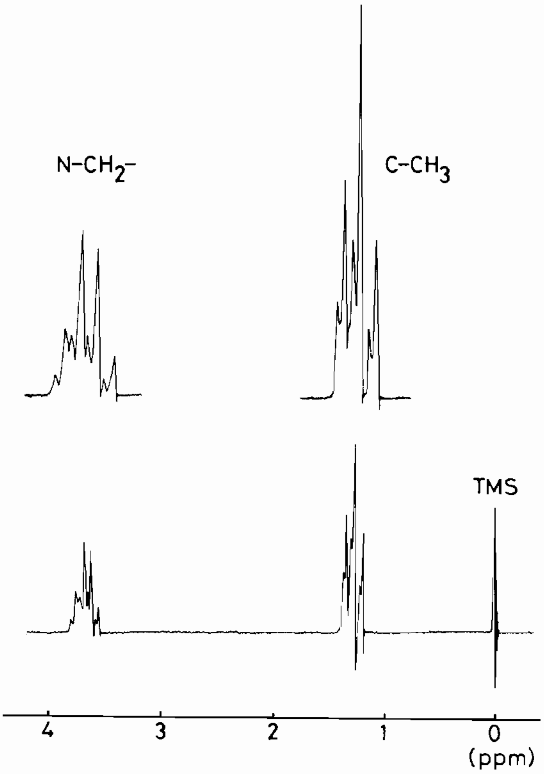


Figure 3. Pmr spectrum of Pd(detsc)(dedtc) in CH_2Cl_2.

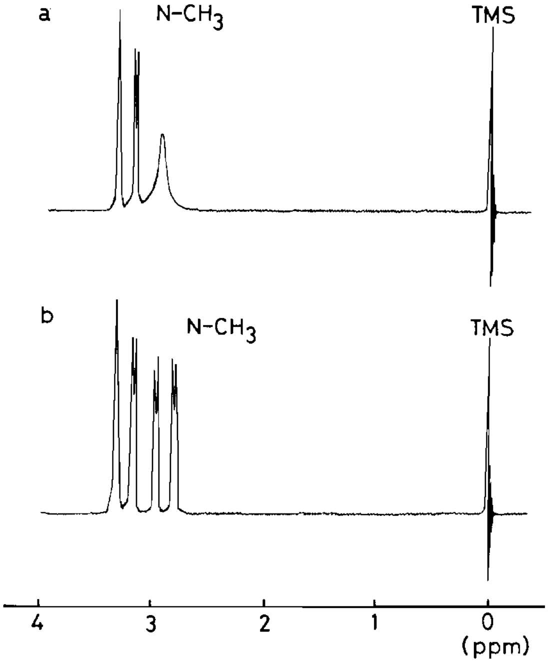
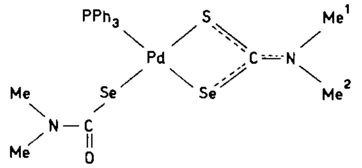


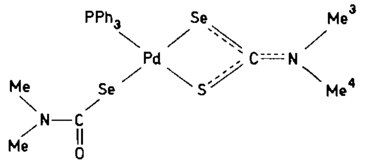
Figure 4. Pmr spectra of $Pd(PPh_3)(dmtsc)(dmmsc)$ in CH_2Cl_2 at room temperature (a) and at −32° C (b).

Conductivity measurements in dichloromethane at 25° C indicate that $Pd(PPh_3)(dmtsc)(dmmsc)$ is non-electrolyte (Λ at 1.05×10^{-3} *M*: 0.291 ohm^{-1} cm^2 mol^{-1}), but the complexes of this type in chloroform gave somewhat smaller molecular weights than the calculated ones. These results seem to indicate that the carbonyl oxygen of monothio- or monoselenocarbamate weakly coordinates to palladium(II) to dissociate slightly *tert*-phosphine in a dilute solution, as in the case of $M(PPh_3)_2(SeC(O)N(n\text{-}Bu)_2)_2$ (M = Pd(II) and Pt(II)).[11]

Figure 4 shows the pmr spectrum of $Pd(PPh_3)$(dmtsc)(dmmsc) in dichloromethane. The broad $N\text{-}CH_3$ signal observed at room temperature is characteristic of the monodentate dmmsc[11] and three sharp $N\text{-}CH_3$ signals are due to the bidentate dmtsc. Comparison with the pmr spectrum of the dmdtc analog, $Pd(PPh_3)(dmdtc)(dmmsc)$, (Table II) reveals that two signals with a small separation around 3.15δ are assigned to the Me^1 and Me^3 protons, and the lowest field signal, though the separation was not observed, to the Me^2 and Me^4 protons in the following isomers, *G* and *H*.



G



H

The existence of two isomers in the complexes of this type is also confirmed by the spectrum of $Pd(PMePh_2)$(dmtsc)(dmmsc), which exhibits two doublets of $P\text{-}CH_3$ signals with the intensity ratio of about 1:1 (Table II).

With decreasing temperature for $Pd(PPh_3)$(dmtsc)(dmmsc) in dichloromethane, the broad $N\text{-}CH_3$ signal splits into four lines (Figure 4b). Again, the comparison with the pmr spectrum of the dmdtc analog, $Pd(PPh_3)$(dmdtc)(dmmsc), at low temperature reveals that the phosphorus ligand causes the main splitting of the signals and small separations are due to the nature of atoms (S and Se) *trans* to dmmsc with respect to palladium. Similar temperature dependent spectra were also observed in $Pd(PPh_3)$(dmtsc)(dmmtc).

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