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Synthesis and Properties of Bis(N-methyl-, N-phenyl-β-mercaptothiocinnamamido)palladium(II)

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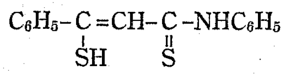
A new dithio chelate, bis(N-methyl-, N-phenyl-β-mercaptothiocinnamamido)palladium-(II) was prepared by the novel simultaneous sulfurization reaction of the carbonyl- and amide-group of N-methylbenzoylacetamide with phosphorus pentasulfide. The obtained complex was studied by infrared and mass spectral procedures. The complex did not produce pyridine clathrate unlike the cases of the palladium complexes of the N-dimethylated ligands. This is likely because the N-methylated palladium complex lacks the thioamide protons with which pyridine molecules are able to interact by forming hydrogen bonds.

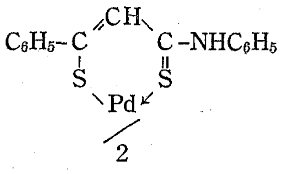
Keywords——dithio palladium(II) complex; sulfurization reaction of carbonyl- and amido-group; infrared spectra; mass spectrum; meta stable peaks; phosphorus pentasulfide

In the series of this study, we reported synthesis of a novel dithio ligand, N-phenyl-β-mercaptothiocinnamamide[2] (LH), synthesis and properties of its palladium complex[3] (PdL_2) and nickel complex[4] (NiL_2).

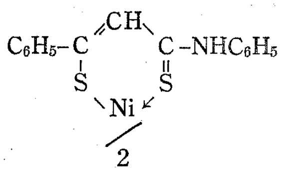


$C_6H_5{-}\underset{SH}{\underset{|}{C}}{=}CH{-}\underset{S}{\underset{\|}{C}}{-}NHC_6H_5$

LH

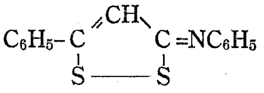


PdL_2

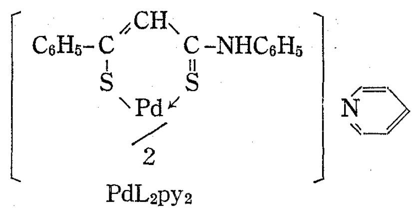


NiL_2

The obtained metal complexes were slightly soluble usual organic solvents except pyridine, and it was observed that NiL_2 decomposed gradually in pyridine resulting in the formation of 3-phenyl-5-phenylimino-1,2-dithiole (I), but that PdL_2 was very stable in pyridine and was able to include two pyridine molecules when it was recrystallized from pyridine. These pyridine molecules were not coordinated to the palladium ion, but were supposed as clathrate (PdL_2py_2), in which pyridine seemed to interact with the thioamido protons of PdL_2 forming hydrogen bonding. We also reported[5] how the steric hindrance around the thioamido protons influence clathrate formation, and it was observed that even after the introduction of one or two methyl groups to the ordo positions of the phenyl group attaching



I



PdL_2py_2

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[1] Location: *Yoshida, Shimoadachi-cho, Sakyo-ku, Kyoto, 606, Japan.*

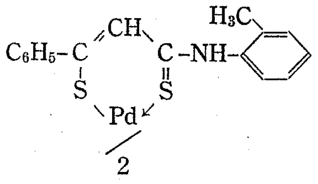
[2] S. Kitagawa and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **26**, 1021 (1978).

[3] S. Kitagawa and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **26**, 1026 (1978).

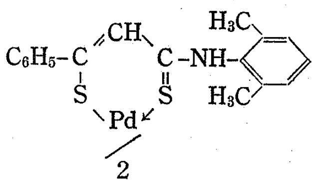
[4] S. Kitagawa and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **26**, 1629 (1978).

[5] S. Kitagawa and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **26**, 2793 (1978).

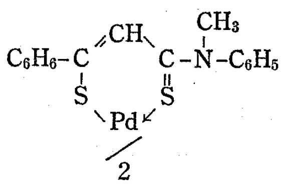
to the nitrogen atom, these palladium complexes, PdL'_2 and PdL''_2, still formed their pyridine clathrates.



PdL'_2



PdL''_2



$Pd(MeL)_2$

From the observation and assumption mentioned above we consider whether the pyridine clathrate formation is yet possible after methylation of the thioamido protons of PdL_2. Hence we studied on the synthesis and properties of bis(N-methyl-, N-phenyl-β-mercaptothiocinnamamido) palladium (II) ($Pd(MeL)_2$).

Experimental

Materials——Bis(N-methyl-, N-phenyl-β-mercaptothiocinnamamido)palladium(II): To 150 ml of pyridine were added 3 g of N-methylbenzoylacetanilide and 3 g of phosphorus pentasulfide. The mixture was heated to 65° in a round-bottom flask with stirring. After the temperature reached 65°, the mixture was heated for 10 more minutes keeping the temperature constant. The color turned scarlet and the mixture was cooled with ice. To this was added 200 ml of 10% NaOH aqueous solution slowly with stirring after which 1 g of palladium ammonium chloride in 200 ml of water was added to the solution. Orange substance was precipitated, collected and washed with ethanol. The compound was recrystallized from pyridine, mp over 280°. Yield 43%. *Anal.* Calcd. for $C_{32}H_{28}N_2PdS_4$: C, 56.97; H, 4.15; N, 4.15; Pd, 15.73; S, 18.99. Found: C, 56.81; H, 4.24; N, 4.33; Pd, 18.33; S, 19.00.

N-Methylbenzoylacetanilide: N-Methylbenzoylacetanilide was prepared by the method reported before.[6]

Apparatus——Mass spectrum was recorded with a Hitachi RMU-6C mass spectrometer at 70 eV. The sample heating temperature was 210°. Infrared measurements were carried out as potassium bromide disks with a Hitachi Infrared Spectrophotometer Model EPI-S2.

Results and Discussion

With respect to such an interest mentioned above, many attempts have been done so as to isolate N-methylated palladium complex, but almost all of these were found to be unsuccessful except the following method.

Sulfurization reaction of amide with phosphorus pentasulfide, first reported in 1878 by Hofmann,[7] has been widely utilized to prepare a variety of thioamides,[8] whose generalized reaction is presented by the reaction (1). We used N-methylbenzoylacetanilide (II) as a starting

$$5RCONR'R'' + P_2S_5 —— 5RCSNR'R'' + P_2O_5 \qquad (1)$$

material and two reactions, (2) and (3) were expected to occur by heating the amide with P_2S_5 in pyridine, although such a reaction as (3) where an

$$\underset{(\mathrm{II})}{C_6H_5COCH_2CON(CH_3)C_6H_5} \longrightarrow \underset{(\mathrm{III})}{C_6H_5COCH_2CSN(CH_3)C_6H_5} \qquad (2)$$

$$C_6H_5COCH_2CON(CH_3)C_6H_5 \longrightarrow \underset{(\mathrm{IV})}{C_6H_5CSCH_2CSN(CH_3)C_6H_5} \qquad (3)$$

amido- and carbonyl-group are sulfurized simultaneously has never been reported before. The results showed that the reaction (2) yielded not (III) but a dimer (V), whereas the

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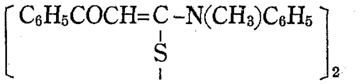
6) C.F. Koelsch and J.W. Britain, *J. Org. Chem.*, **24**, 1551 (1959).

7) A.W. Hofmann, *Chem. Ber.*, **11**, 340 (1878).

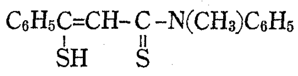
8) R.N. Hund and G. Delameter, *Chem. Rev.* **61**, 45 (1961).

compound (IV) was unable to be isolated in the reaction (3). A certain palladium complex, however, was obtained by making the reaction mixture of (3) alkaline with aqueous NaOH solution and then by adding aqueous solution of palladium ammonium chloride. The complex was bright orange in color and showed a high melting point and very low solubility in usual organic solvents. These properties are very similar to those of PdL_2. Furthermore, the elemental analysis indicated that no oxygen is contained in the complex and the found data agreed with the theoretical values for $Pd(MeL)_2$ only with some error for that of palladium.[9] Therefore, a novel simultaneous sulfurization reaction (3) apparently seems to proceed producing (IV) or its sulfhydryl tautomer (VI), although it is too unstable to isolate.



$$\left[C_6H_5COCH{=}\underset{\underset{|}{S}}{\underset{|}{C}}{-}N(CH_3)C_6H_5\right]_2$$

V



$$C_6H_5\underset{SH}{\underset{|}{C}}{=}CH{-}\underset{S}{\underset{\|}{C}}{-}N(CH_3)C_6H_5$$

VI

The infrared spectrum of $Pd(MeL)_2$ is shown in Fig. 1 in comparison with those of PdL_2 and the original amide (II). The spectrum of $Pd(MeL)_2$ gave a good accordance with that of PdL_2 except the former lacked a band at 3250 cm^{-1}, whereas it showed a strong new band at 1110 cm^{-1}. The band at 3250 cm^{-1} of PdL_2 is obviously a stretching vibration of the NH group, so it is natural that the band at 3250 cm^{-1} disappeared in $Pd(MeL)_2$ which has no NH group. The new band at 1110 cm^{-1} which PdL_2 lacked appeared in the original amide at 1120 cm^{-1}. Therefore, this is a band related not to PdL_2, but to both $Pd(MeL)_2$ and amide, probably a CN stretching vibration between the nitrogen atom and the carbon atom of the methyl group.

Randall[10] and Rao *et al.*[11] denoted that the compounds with $-\underset{S}{\underset{\|}{C}}-NH-$ or $-\underset{S}{\underset{\|}{C}}-N<$ group showed a strong absorption called thioureid band at 1615—

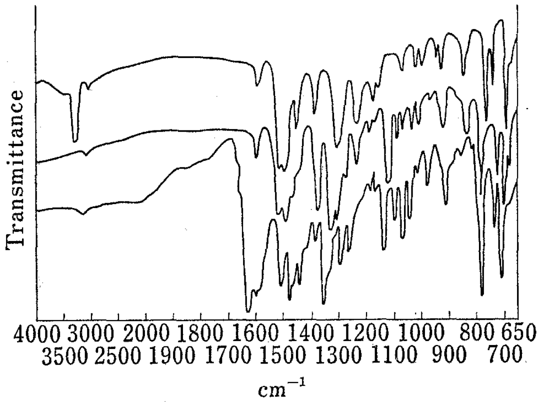


Fig. 1. Infrared Spectra of PdL_2 (Above), $Pd(MeL)_2$ (Middle) and the Original Amide (Below)

TABLE I. Relative Intensities of Major Ions in the Mass Spectrum ofthe Palladium Complex $Pd(MeL)_2$

Ion	m/e	Relative intensities (%)
M	674	*a*)
M-S	642	*a*)
M-L	390	*a*)
M-L-S+2H	360	*a*)
M-L-S	358	*a*)
M-L-S-H	357	*a*)
M-320	354	*a*)
L+S	316	*a*)
L+S-H	315	*a*)
L+H	285	19.9
L	284	100.0
L-S	252	8.3
M-424	250	10.1
C_6H_5CS	121	20.6
$C_6H_5NHCH_3$	107	12.6
$C_6H_5NCH_3$	106	16.0
$C_6H_5C{\equiv}CH$	102	23.3
C_6H_5	77	27.3

M: $Pd(MeL)_2$, L: MeL.
a) Relative intensities are less than 1.0%.

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9) Some metal complexes containing sulfur sometimes give analytical error for metal partly because of the formation of metal sulfide.

10) H.M. Randall, R.G. Fowler, N. Fuson, and J.R. Dangle, "Infrared Determination of Organic Structures," Van Nostrand, New York, 1949.

11) C.N.R. Rao and R. Venkataraghavan, *Spectrochim. Acta*, 18, 541 (1962).

1470 cm^{-1} which seems to be due to ν_{CN}. Thus PdL_2 and $Pd(MeL)_2$ displayed such a band at 1490 and 1480 cm^{-1}, respectively.

Among the spectral changes between the starting amide and $Pd(MeL)_2$, the most prominent one is that of the bands around 1600 cm^{-1}. The amide showed strong absorptions at 1630 and 1570 cm^{-1} which seem to be that of so-called amide I band and that of carbonyl group, respectively. On the other hand, $Pd(MeL)_2$ lacked such bands around 1600 cm^{-1}, which proves that both carbonyl- and amido-group of the starting amide completely sulfurized in the reaction (3).

Ouchi *et al.*[12] reported that some dithio-β-diketonato metal complexes showed strong $\nu_{C=S}$ around 1200 and 840 cm^{-1}, although the former may be the mixture of $\nu_{C=S}$, ν_{C-C} and δ_{C-H}. Further thioamides usually show a strong band at about 1200 cm^{-1}, which is called thioamide I band, namely $\nu_{C=S}$. PdL_2 and $Pd(MeL)_2$ showed strong bands at 1240 and 840 cm^{-1}, and at 1240 and 840 cm^{-1}, respectively, both of which disappeared in the starting amide. Therefore, these bands are probably those due to $\nu_{C=S}$.

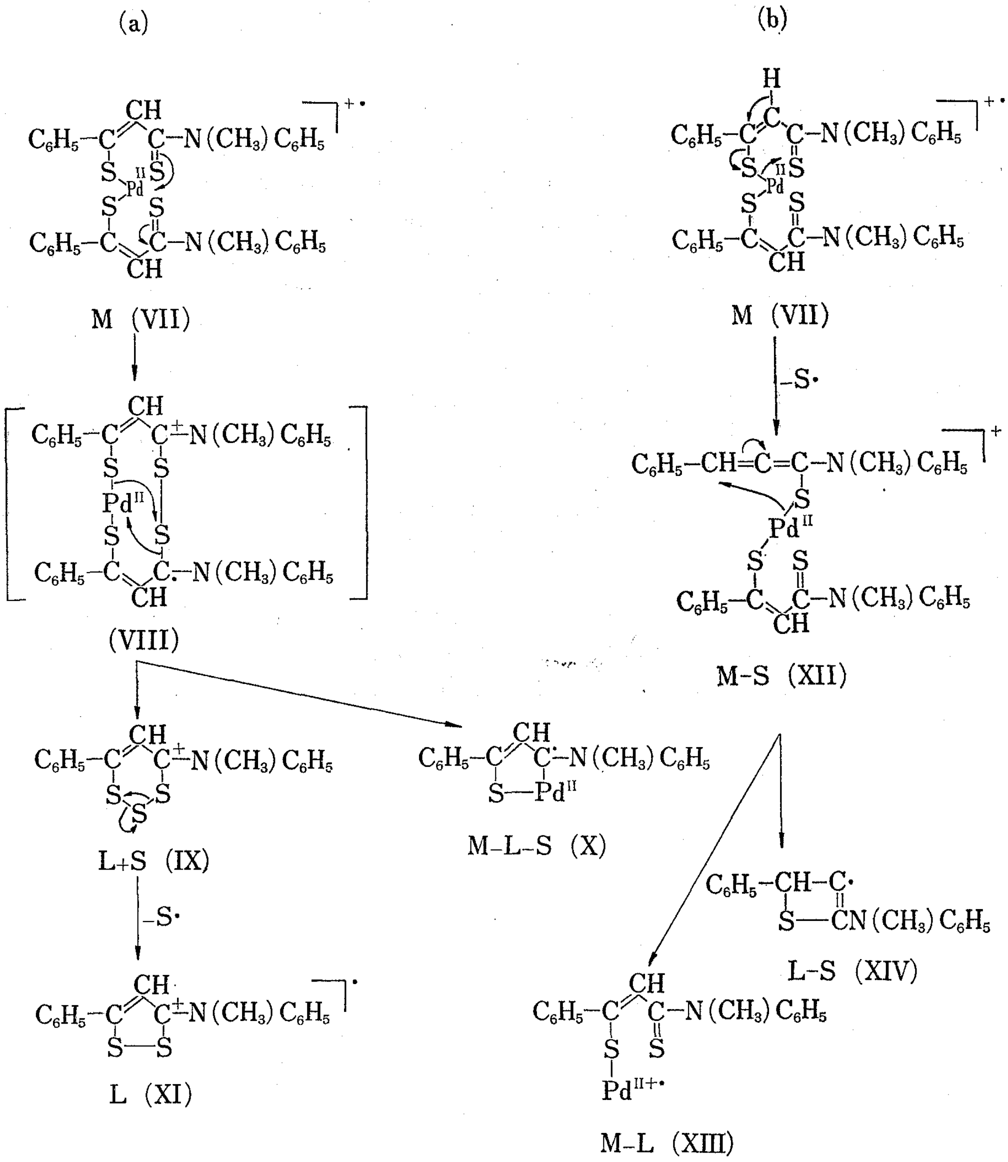

Chart 1. Proposed Mechanisms for the Fragmentation of $Pd(MeL)_2$

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[12] A. Ouchi, M. Nakatani, and Y. Takahashi, *Bull. Chem. Soc. Jpn.*, 41, 2044 (1968).

The relative intensities of the major ions in the mass spectrum of $Pd(MeL)_2$ is listed in Table I. The mechanisms for the ion reactions are supposed as shown in Chart 1 and the metastable peaks are presented in Table II.

TABLE II. Metastable Peaks in the Mass Spectrum of the Palladium Complex $Pd(MeL)_2$

Reaction	Metastable peak m^* $(m_2)^2/m_1$ $(m_1 \rightarrow m_2)$ Calcd.	Found
M → M-S	611.5 (674→642)	611.0
M → M-L-S	190.2 (674→358)	190.5
M → L+S	148.2 (674→316)	149.3
M-S → M-L	236.9 (642→390)	237.0
L+S → L	255.2 (316→284)	255.2

The parent ion M seems to decompose by taking two routes, (a) and (b), as shown in Chart 1. In the route (a), M formed intermediate of intramolecular disulfide (VIII) which then decomposed into two ions, trisulfide (IX) and palladium-containing fragment (X). The trisulfide (IX) lost sulfur radical producing the most abundant fragment (XI) which is supposed to be very stable by its resonance. Actually, such disulfides of dithioacetylacetones appear in the literatures as "the resonance stabilized dithiolium cation."[13,14] In the pathway (b), M changed into a complex (XII) both by the loss of sulfur radical from the β-position and by the rearrangement of the hydrogen atom from the α-carbon to the β-carbon, after which the fragment (XII) caused the bond rupture between sulfur- and palladium-atom producing two radicals, (XIII) and (XIV). All these ion reactions supposed above were confirmed by the existence of their metastable peaks as shown in Table II.

Pyridine clathrate of $Pd(MeL)_2$ was not obtained as supposed when it was recrystallized from pyridine, not similarly to the cases of PdL_2, PdL'_2 and PdL''_2 which readily gave their pyridine clathrates.

These facts strongly confirm our assumption that in these clathrates pyridine molecules probably interact with the thioamide protons of the ligands forming hydrogen bonds, while clathrate formation is impossible in $Pd(MeL)_2$ which lacks thioamide protons.

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13) R.L. Martin and I.M. Stewart, *Nature*, **210**, 522 (1966).
14) A.R. Hendrickson and R.L. Martin, *Aust. J. Chem.*, **25**, 257 (1972).