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Studies on the Sulfur-containing Chelating Agents. XXXII.[1] The Reaction of Palladium(II) Ion with Monothio-β-diketones and Their Disulfides

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Infrared and nuclear magnetic resonance spectra of palladium (II) monothio-β-diketonates were studied in comparison with those of palladium (II) β-diketonates. The following novel reactions have been found. Namely, palladium dithioacetylacetonate was obtained in the reaction of monothioacetylacetone and palladium ion in acid solution by the reaction which may be called as "ligand atom replacement reaction" and palladium monothio-β-diketonates were obtained from disulfides of monothio-β-diketones and palladium ion. The reason for the occurance of this reaction may be reasonably explained by the high affinity between palladium and sulfur and the high stability of the palladium chelates formed.

In recent years, thio derivatives of β-diketones and their metal chelates have been actively investigated.[3] We have conducted the study of some metal chelates of monothio-β-diketones with the interest of their quasiaromaticity and the character of sulfur atom as a ligand atom, and have reported the results on cobalt(III) monothio-β-diketonates.[4]

The present paper deals with the chelate formations of some monothio-β-diketones and their disulfides with palladium ion. We have found some novel reactions in addition to the ordinary chelate formation. Namely, the reaction of monothioacetylacetone (4-mercapto-3-penten-2-one, abbreviated as SAA hereafter) with palladium ion yielded palladium dithioacetylacetonate together with palladium monothioacetylacetonate, and palladium monothio-β-diketonates were obtained from disulfide of monothio-β-diketones and palladium ion. The mechanism of these reactions is discussed in this paper.

Palladium Monothio-β-diketonates

Wave numbers and the possible assignments of the main absorption bands in infrared spectra of the palladium chelates of monothio-β-diketones and those of β-diketones[4a] are listed in Table I. The ligands, 3-mercapto-1-phenyl-2-buten-1-one, 4-mercapto-4-phenyl-3-buten-2-one and 3-mercapto-1,3-diphenyl-2-propen-1-one are abbreviated as SAB, SBA, and SBB respectively hereafter. The assignments were made by reference to the case of Co(III) chelates of monothio-β-diketones in the previous reports.[4b] The absorption band of ν(C=C) in palladium monothio-β-diketonates was observed at lower wave number than in the case of palladium β-diketonates. In addition, the influence of phenyl group in the ligands was observed similarly to cobalt(III) chelates.[4b]

In Table II, the results of the measurements of nuclear magnetic resonance spectra of palladium monothio-β-diketonates and β-diketonates are summarized. The chemical shifts of the protons of methine and methyl groups were found in lower field in monothio-β-diketonates than those of the corresponding β-diketonates. In the cases of the chelates obtained from the ligands involving phenyl group, the signals of methine and methyl groups were

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[1] Part XXXI: H. Sakurai, A. Yokoyama and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **19**, 1416 (1971).

[2] Location: *Yoshida, Shimoadachi-cho, Sakyo-ku, Kyoto.*

[3] *a*) L.P. Eddy, J.W. Hayes, S.E. Livingstone and H.L. Nigam, *Australian J. Chem.*, **24**, 1071 (1971); *b*) E. Uhlemann and H. Müller, *Anal. Chim. Acta*, **48**, 115 (1969).

[4] *a*) A. Yokoyama, S. Kawanishi and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **18**, 356 (1970); *b*) *Idem*, *ibid.*, **18**, 363 (1970).

Table I. Infrared Spectral Bands of Palladium Chelates of Thio-β-diketones and β-Diketones in KBr Disks

Ligand	Bands (cm^{-1})		Ligand	Bands (cm^{-1})	
	ν (C=O)	ν (C=O)		ν (C=O)	ν (C=O)
SAA	1570	1490 1470	AA	1565	1545 1520
SAB	1540	1470	AB	1530	1508
SBA	1563	1475			
SBB	1530	1463	BB	1520	1520

AA: acetylacetone AB: benzoylacetone BB: dibenzoylmethane

observed in lower field than the case of the chelate of SAA. As to the reason of this observation, the deshielding and mesomeric effects of the phenyl group can be taken into account similarly to the cobalt(III) chelates.[4b)] Judging from these data, in the comparison of palladium chelates of monothio-β-diketones with those of β-diketones, the quasiaromaticity may be more supportable in monothio-β-diketonates than in β-diketonates.

Table II. Chemical Shifts of Palladium Chelates of Thio-β-diketones and β-Diketones in $CDCl_3$

Liqnd	τ-Values		Ligand	τ-Values	
	=CH-	$-CH_3$		=CH-	$-CH_3$
SAA	3.72	7.70 7.80	AA	4.58	7.93
SAB	2.92	7.51	AB	3.93	7.78
SBA	3.30	7.63			
SBB	~2.62	—	BB	3.23	—

AA: acetylacetone AB: benzoylacetone BB: dibenzoylmethane

Formation of Palladium Dithioacetylacetonate

In the reaction of SAA with palladium ion, the formation of two kinds of chelate (yellow and red) was observed in acidic medium, whereas only yellow chelate was obtained when the reaction medium was neutral. Dry column chromatography[5)] with silica gel was found to be very effective for the separation of these chelates. From the results of elemental analyses, molecular weight measurement, and infrared, nuclear magnetic resonance and electronic spectra, the yellow chelate was found to be identical to palladium monothioacetylacetonate which was reported previously, whereas the red chelate was considered to be palladium dithioacetylacetonate, which was reported by Martin.[6)] Both chelates were found to be monomer from the molecular weight determination in benzene. The data from elemental analyses, molecular weight measurement, infrared (IR) and nuclear magnetic resonance (NMR) spectra of both chelates, are presented in Table III. The fact that in NMR spectra, the signal of methyl groups was a doublet in palladium monothioacetylacetonate and a singlet in palladium dithioacetylacetonate may be considered as a support for the structure shown in Table III.

In addition, the protons of the chelate ring and the methyl groups of palladium dithioacetylacetonate showed the chemical shifts at 2.80 ppm and 7.49 ppm respectively. These

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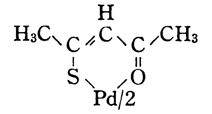
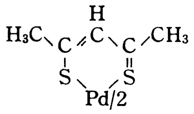
5) B. Loev and K.M. Snader, *Chem. Ind.* (London), **1965**, 15.

6) *a*) R.L. Martin and I.M. Stewart, *Nature*, **210**, 522 (1966); *b*) O. Sümann and J. Fresco, *Inorg. Chem.*, **8**, 1846 (1969).

Table III. Two Kinds of Palladium Chelates obtained from Monothioacetylacetone with Palladium Ion

									
Color		yellow				bright red			
mp (°C)		181				240 (sublim.)			
		C	H	S	Pd	C	H	S	Pd
Anal.	Calcd.	35.67	4.16	19.02	31.62	32.57	3.80	34.72	28.84
	Found	35.40	4.16	18.81	31.69	32.67	4.12	33.67	28.48
Mol. Wt.	Calcd.	336.4				372.4			
	Found	332.0				365.2			
NMR (τ)		=CH-		$-CH_3$		=CH-		$-CH_3$	
		3.72		7.70		2.80		7.49	
				7.80					
IR (cm^{-1})		ν (C=O)		ν (C=C)		ν (C=O)		ν (C=C)	
		1570		1470		—		1485	
				1490					

chemical shifts are very close to those of benzene and toluene. The delocalization of π-electons and the long range deshielding effect due to the presence of the sulfur containing group⁷⁾ may be taken into account for these observations on the NMR spectra. On the basis of these considerations, it may be presumed that palladium dithioacetylacetonate possesses quasiaromaticity to a considerable extent.

For the investigation of the above-mentioned rather anomalous reaction, change in the electronic spectra with time was followed. Fig. 1 shows electronic spectra of isolated palladium chelates of acetylacetone, and thio and dithio derivatives. Fig. 2 shows the spectral change in the reaction of palladium ion with SAA. The absorption maxima at 356 mμ, 400 mμ and 510 mμ were ascribed to excess ligand SAA, palladium monothioacetylacetonate and palladium dithioacetylacetonate respectively. From Fig. 2, it is obviously observed that excess SAA was consumed for the formation of palladium dithioacetylacetonate from palladium monothioacetylacetonate. Monothioactylacetone was found to be hydrolyzed to acetylacetone and hydrogen sulfide in acidic medium. It may be presumed that the formation of palladium monothioacetylacetonate takes place rapidly and the succeeding reactions take place slowly to yield palladium dithioacetylacetonate finally. A mechanism shown in Chart 1 seems to be reasonable for this reaction, from the following experimental results. The existence of acetylacetone was confirmed by the formation of iron(III) chelate. Palladium monothioacetylacetonate isolated could be converted into palladium dithioacetylacetonate in the presence of excess SAA in acid medium, but palladium monothioacetylacetonate was found to be stable in acid medium in the absence of SAA. Palladium dithioacetylacetonate was also prepared from palladium monothioacetylacetonate with hydrogen sulfide or sodium sulfide in acid solution.

These facts may suggest that SAA is hydrolyzed in acid solution to liberate hydrogen sulfide which has very high affinity to palladium. Significant decrease in absorbance of SAA at 356 mμ in Fig. 2 in the course of the reaction may be due to the hydrolysis of SAA. The detailed investigation on the hydrolysis of SAA and other thio-β-diketones is now under way.

Eventually, the above-mentioned reaction may be expediently called as "ligand atom replacement reaction" which is caused by the apparently anomalous behaviors of SAA and

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7) M. Tomoeda, M. Inuzuka and T. Furuta, *Tetrahedron Letters*, **1964**, 1233.

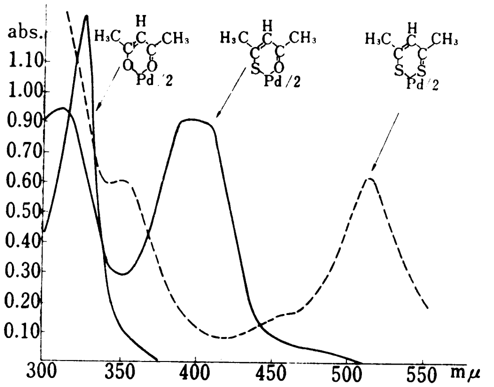

Fig. 1. Electronic Spectra of Palladium Chelates of Acetylacetone, Monothioacetylacetone and Dithioacetylacetone in Chloroform Solution

concentration: 10^{-4}M

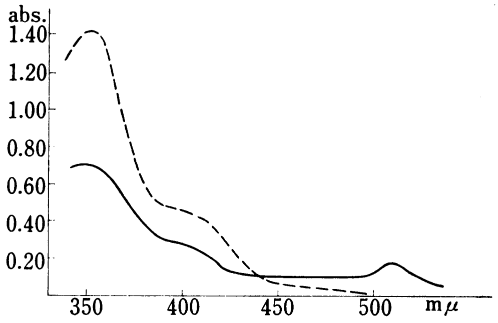

Fig. 2. Change in Electronic Spectra with Time in Reaction of Thioacetylacetone with Palladium (II) Ion

——: immediately after reaction
——: 24 hours after reaction

50% EtOH		
EtOH		4 ml
NaAc-HAc pH 4.4		4 ml
SAA	5×10^{-3}M	1 ml
$PdCl_2$	5×10^{-4}M	1 ml

palladium ion in the chelate formation. The formation of palladium dithioacetylacetonate may be attributed to the high affinity of palladium to sulfur, namely b-character of palladium, and also the extremely high stability of palladium dithioacetylacetonate due to its quasiaromaticity.

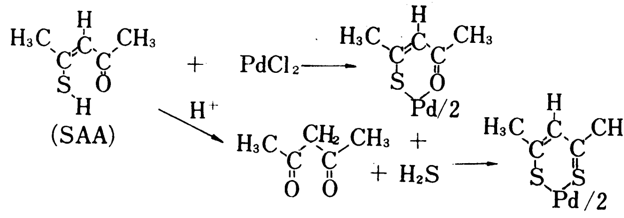

Chart 1

Reaction of Disulfide with Palladium(II) Ion

It was found that palladium chelate of SBB is obtained when disulfide of SBB was mixed with palladium ion in ethanol or dioxane solution, and similar reactions were observed with disulfides of other monothio-β-diketones. In order to find the best condition for the reaction, the optical absorbance of the palladium chelates of SAA, SAB, and SBB which were produced by the reactions of their disulfides with palladium(II) ion were measured in the solutions of various pH. The results are shown in Fig. 3. In all cases, palladium monothio-β-diketonates were obtained with high yield from the solution of pH 5—6. In order to discuss the mechanism of the reaction, the electronic spectra were measured in the reactions with various ratios of disulfide to palladium ion. The results are shown in Fig. 4. It was assumed from Fig. 4 that 4 moles of disulfide react with 3 moles of palladium chloride to give 3 moles of palladium chelate of monothio-β-diketone. This chelate formation is considered to be accompanied by the cleavage of disulfide and may be described as shown in Chart 2. In the case of the cleavage of disulfide bond of oxidized glutathione in alkaline medium by *p*-hydroxymercuribenzoate, the existence of sulfinic acid has been reported.[8]

Livingstone, *et al.* have mentioned briefly the occurance of the similar reaction in ethanol solution and presumed that ethanol acts as a reducing agent for disulfide.[9] However, the similar reaction was observed also in dioxane solution as mentioned above. Accordingly the

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[8] L.O. Andersson and G. Berg, *Biochim. Biophys. Acta*, **192**, 534 (1969).

[9] S.H.H. Chaston, S.E. Livingstone, T.N. Lockyer, V.A. Pickles and J.S. Shannon, *Australian J. Chem.*, **18**, 673 (1965).

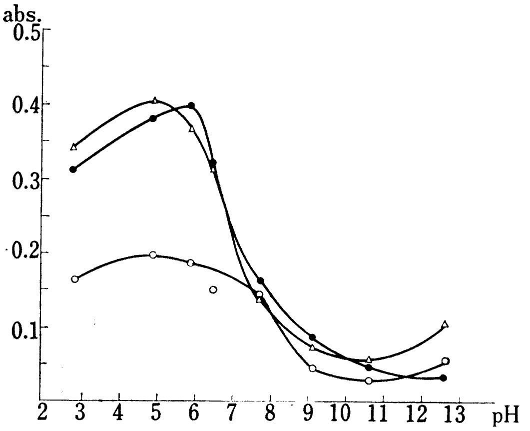

Fig. 3. Reaction of Disulfides of Thio-β-diketones with Palladium (II) Ion in the Solutions of Various pH

disulfide	8×10^{-4} M	1 ml
EtOH		4 ml
buffer		4 ml
$PdCl_2$-HCl	6×10^{-4} M	1 ml

reaction time: 1 hour

$(SAA)_2$	395 mμ
$(SAB)_2$	435 mμ
$(SBB)_2$	445 mμ

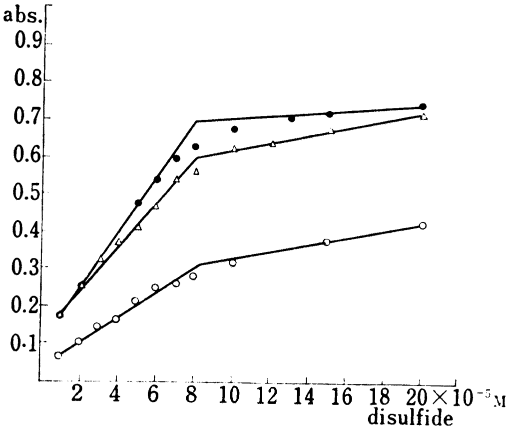

Fig. 4. Change in Absorbance with Ratio of Disulfide to Pd Ion concentration of $PdCl_2$ 6.0×10^{-5}M

—○—: $(SAA)_2$ 395 mμ
—●—: $(SAB)_2$ 435 mμ
—△—: $(SBB)_2$ 445 mμ
pH: 3.0

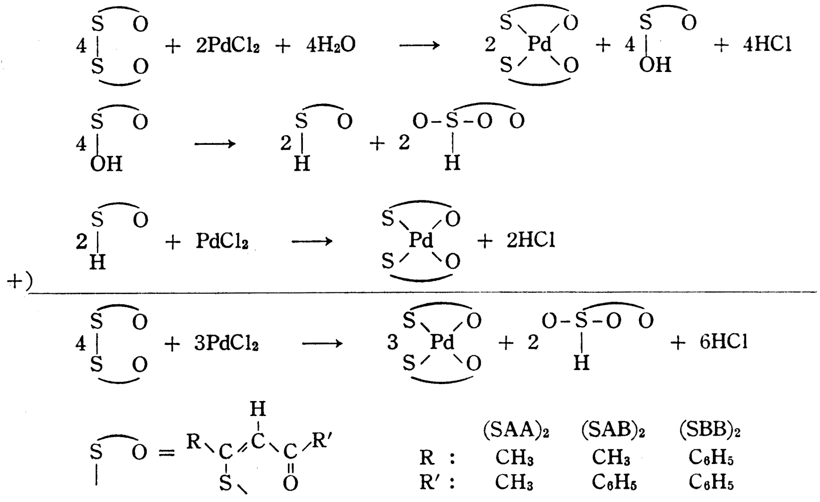

Chart 2

reason for the occurance of this reaction may be reasonably explained from the high affinity between palladium and sulfur, namely a nucleophilic attack on the palladium by a sulfur atom of the disulfide(10) and the high stability of the palladium monothio-β-diketonates.(11) The reaction may be considered as a similar type of the reaction to the scission of disulfide by mercuric chloride which has been already reported.(12) Metal ions are generally classified

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10) T. Boschi, B. Crociani, L. Toniolo and V. Belluco, *Inorg. Chem.*, **9**, 532 (1970).

11) P. Haake and P.A. Cronin, *Inorg. Chem.*, **2**, 879 (1963).

12) *a*) P.R. Brown and J.O. Edwards, *Biochemistry*, **8**, 1200 (1969); *b*) F. Challenger, "Aspects of the Organic Chemistry of Sulphur," Butterworths, London, 1959, p. 15; *c*) F. Challenger and A.A. Rawlings, *J. Chem. Soc.*, **1937**, 868; *d*) S. Blackburn and F. Challenger, *J. Chem. Soc.*, **1938**, 1872.

in their properties of coordination as a-character which has stronger affinity towards oxygen than sulfur, or b-character which has stronger affinity towards sulfur than oxygen.[13] In conclusion, the occurance of two kinds of interesting reactions mentioned above are attributed to b-character of palladium. The investigations of the reaction of these type with various metal ions, including typical b-character metal ions and those possess both a-character and b-character are now under way. The results of these investigations will give some contributions to the characterization of the affinity of metal ion to sulfur as a ligand atom.

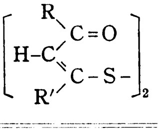
Experimental

Materials——Palladium chelates of SAA, SAB, SBA and SBB were prepared by the method reported previously.[4a]

Isolation of Two Kinds of Palladium Chelate——To a solution of excess of SAA (232 mg, 2×10^{-3} mole in 20 ml of EtOH), a solution of $PdCl_2$ (88.66 mg, 5×10^{-4} mole in 5 ml of 0.1N HCl) was added slowly. After the reaction mixture was allowed to stand overnight at room temperature, the precipitate which is the mixture of two kinds of chelate was collected. The mixture was chromatographed over nylon column packed with dry silica gel which was dipped in benzene, and the yellow and red colored bands on the column were cut off respectively. From the respective bands, yellow (21 mg, mp 181°) and red (22 mg, mp 240°) chelates were isolated by the extraction with benzene and the evaporation, and were recrystallized from acetone.

Oxidation of Monothio-β-diketones to Disulfides——A solution of iodine–potassium iodide in water (11 ml of 0.1N) was added dropwise to a solution of SBB (240 mg in 40 ml EtOH). When color of SBB disappeared and that of iodine appeared, H_2O (20 ml) was added into the reaction mixture. The product was collected and recrystallized from aqueous EtOH: yield 143 mg. The disulfide of SAA or SAB was prepared in a similar manner as that of SBB. The disulfides obtained are listed in Table IV.

TABLE IV. Disulfides of Monothio-β-diketones



	R	R′	Color	mp (°C)	Analysis (%)					
					Calcd.			Found		
					C	H	S	C	H	S
$(SAA)_2$	CH_3	CH_3	white	124	52.17	6.09	27.83	52.38	6.23	27.73
$(SAB)_2$	CH_3	C_6H_5	pale yellow	164 (144)[a]	67.80	5.08	18.08	68.15	5.02	17.58
$(SBB)_2$	C_6H_5	C_6H_5	yellow	137 (140)[a]	75.31	4.60	13.39	75.22	4.93	13.18

[a] Livingstone, *et al.* obtained these disulfides by air oxidation. Melting points of $(SAB)_2$ and $(SBB)_2$ were reported to be 144° and 140° respectively.[9]

Synthesis of Palladium Chelate from Disulfide of Monothio-β-diketone——To a solution of disulfide of SBB (60 mg, 1.25×10^{-4} mole) in 40 ml of acetone, $PdCl_2$ (22.13 mg, 1.25×10^{-4} mole) in 10 ml of 0.1N HCl was added. The reaction mixture was allowed to stand overnight at room temperature. The acetone was evaporated off and the precipitate (palladium chelate) was collected and recrystallized from acetone, mp 240°; yield 44 mg.

Measurement of Electronic Spectra in the Formation of Palladium Dithioacetylacetonate——Spectral change of the mixture of EtOH 4 ml, buffer (pH 4.4) 4 ml, SAA 5×10^{-3}M 1 ml, $PdCl_2$ 5×10^{-4}M 1 ml was measured in various time intervals. Similar experiments were carried out with palladium monothioacetylacetonate isolated in the presence of Na_2S, H_2S or SAA at pH 4.4.

Reaction of Disulfides of Monothio-β-diketones with Palladium Ion——i) The reaction mixture of EtOH 4 ml, disulfide 8×10^{-4}M 1 ml, $PdCl_2$ 6×10^{-4}M 1 ml, Britton–Robinson's buffer of various pH values 4 ml was allowed to stand for 1 hour at room temperature. The reaction mixture was extracted with 10 ml of benzene. The absorbance of the palladium chelates of SAA, SAB and SBB were measured at the wavelengthes at 395, 435 and 445 mμ respectively.

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[13] S. Ahrland, J. Chatt and N.R. Davies, *Quart. Rev.*, **12**, 265 (1958).

ii) Solutions of disulfide with various concentrations (ranging from 10^{-5}M to 2×10^{-4}M) were prepared and mixed with the solution of 6×10^{-5}M $PdCl_2$ in 50% dioxane which contains 6×10^{-4}M HCl and the reaction mixture was allowed to stand for several hours at room temperature. The absorbances of palladium chelates were measured at the wavelengthes at 395, 435 and 445 mμ respectively.

Apparatus——The electronic spectra were measured on a Hitachi recording spectrophotometer model EPS-2 and the absorbances were determined with a Shimadzu Spectrophotometer model QV 50. Nuclear magnetic resonance spectra in $CDCl_3$ with the concentration of 5×10^{-2}M were measured by a Varian A-60 spectrometer at 60 Mc. with tetramethylsilane as internal standard. The infrared absorption spectra were measured as potassium bromide disks in the range 4000—400 cm^{-1} on Koken DS 301 spectrophotometer. Molecular weight was measured by a Mechrolab osmometer model 301 A. Measurements of pH were made with a Hitachi–Horiba pH meter model F-5, with a combination glass electrode. The correction of pH value in 50% EtOH and dioxane solution was not carried out.

Acknowledgement The authers are indebted to Dr. T. Shingu and Miss M. Ohkawa of Kyoto University for NMR measurements, and the members of the Micro Analytical Center of Kyoto University for elemental analyses.