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PREPARATION AND PROPERTIES OF NEW THIOLATO- AND MERCAPTO-TRANSITION METAL COMPLEXES, $MR(SR')(PR''_3)_2$ (M = Ni, Pd; R = H, Ar; R' = H, Ar). EVOLUTION OF R-R' FROM THE COMPLEXES THROUGH CLEAVAGE OF THE S-R' BOND

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New nickel(II) and palladium(II) complexes having both hydrido and arylthiolato ligands, $MH(SAr)(PCy_3)_2$, and complexes with aryl and mercapto ligands, $Ni(Ar)(SH)(PEt_3)_2$ (M = Ni, Pd; Ar = C_6H_5-, p-$CH_3C_6H_4$-, p-$CH_3OC_6H_4$-), were prepared. Thermolysis of these complexes caused cleavage of the S-C or S-H bond to evolve Ar-H.

Elucidation of chemical reactivities of transition metal compounds containing metal to sulfur bond is the subject of recent interest.1) The study on the reactivities of SH or SR groups bonded to transition metals is valuable to understand the fundamental reactions involved in metal-catalyzed desulfurization of organic sulfur compounds,2) reactions at the metal center of some enzymes containing metal to sulfur bonds,3) and metal-organic chemical vapor deposition (MOCVD) process which often proceeds through formation of a metal to SH or SR bond.4) In this paper we wish to report preparation of new nickel and palladium complexes having an arylthiolato (SAr) or mercapto (SH) ligand and occurrence of facile cleavage of the S-C and S-H bond in the ligands at elevated temperatures. The cleavage of the S-C and S-H bond is deemed relevant to the metal catalyzed desulfurization and formation of metal sulfide in the MOCVD process.

The reaction of trans-$Ni(Ar)(Me)(PEt_3)_2$5) with H_2S occurs selectively at the Ni-Me bond to afford methane and trans-$Ni(Ar)(SH)(PEt_3)_2$ (Eq. 1, Yield = 41-93%). Oxidative addition of ArSH to $Ni_2(N_2)(PCy_3)_4$6) or $Pd(PCy_3)_2$7) proceeds smoothly at room temperature to give trans-$NiH(SAr)(PCy_3)_2$ (Eq. 2, Yield = 65-66%) or $PdH(SAr)(PCy_3)_2$ (Eq. 3, Yield = 44-82%), respectively.

$$Ni(Ar)(Me)(PEt_3)_2 + H_2S \longrightarrow \underset{\mathbf{1}}{\underline{\text{trans}}\text{-}Ni(Ar)(SH)(PEt_3)_2} + CH_4 \qquad (1)$$

($\mathbf{1a}$, Ar = C_6H_5-; $\mathbf{1b}$, Ar = p-$CH_3C_6H_4$-;
$\mathbf{1c}$, Ar = p-$CH_3OC_6H_4$-)

$$Ni_2(N_2)(PCy_3)_4 + 2\ ArSH \longrightarrow 2\ \underset{\mathbf{2}}{\underline{\text{trans}}\text{-}NiH(SAr)(PCy_3)_2} + N_2 \qquad (2)$$

($\mathbf{2a}$, Ar = C_6H_5-; $\mathbf{2b}$, Ar = p-$CH_3C_6H_4$-)

$$\mathrm{Pd(PCy_3)_2} + \mathrm{ArSH} \longrightarrow \underset{\underset{\sim}{3}}{\mathrm{PdH(SAr)(PCy_3)_2}} \qquad (3)$$

($\underset{\sim}{3a}$, Ar = C_6H_5-; $\underset{\sim}{3b}$, Ar = p-$CH_3C_6H_4$-;
$\underset{\sim}{3c}$, Ar = p-$CH_3OC_6H_4$-)

IR and NMR (^1H and $^{31}P\{^1H\}$) spectra as well as elemental analysis of the complexes agree well with the proposed formulations of the complexes. The spectroscopic data are summarized in Table 1. Nickel complexes 1 and 2 have trans structures as confirmed by NMR spectra where the proton signals of Ni-H and SH appear as triplets due to ^{31}P-^1H coupling. Signals of Pd-H protons of 3a-3c appear as singlets presumably due to small J_{PH} value, which obstructs the unequivocal determination of the configuration by NMR spectroscopy.

Thermolysis of the Ni and Pd complexes causes the cleavage of S-H and S-Ar bond. Coupling of the H atom released from the SH ligand with Ar group in 1 and coupling of the Ar group released from the SAr ligand with the hydrido ligand in 3, respectively, give arenes. The remaining sulfur atom is trapped mainly by the PR''_3 ligand to form $S=PR''_3$ and partly by the metal to form metal sulfide.

$$\underset{\underset{\sim}{1b}}{\mathrm{H{\wr}S\text{-}Ni(C_6H_4CH_3)(PEt_3)_2}} \longrightarrow \underset{70\%}{\mathrm{CH_3C_6H_5}} + \underset{72\%}{\mathrm{S{=}PEt_3}} + \underset{15\%}{\mathrm{CH_3C_6H_4SC_6H_4CH_3}} + \mathrm{H_2} \qquad (4)$$

$$\underset{\underset{\sim}{3c}}{\mathrm{CH_3OC_6H_4{\wr}S\text{-}PdH(PCy_3)_2}} \longrightarrow \underset{61\%}{\mathrm{CH_3OC_6H_5}} + \underset{73\%}{\mathrm{S{=}PCy_3}} \qquad (5)$$

Table 1. IR and NMR data of the complexes

Complex	IR[a)]		NMR	
	ν(MH)	ν(SH)	^1H[b)]	$^{31}P\{^1H\}$[c)]
1a		2560	-2.0(SH, t, J_{PH} = 18 Hz)	19.4(s)
1b		2550	-2.0(SH, t, J_{PH} = 18 Hz) 2.2(CH_3, s)	19.3(s)
1c		2550	-2.0(SH, t, J_{PH} = 18 Hz) 3.4(OCH_3, s)	19.5(s)
2a	1939		-20.0(NiH, t, J_{PH} = 71 Hz)	41.4(s)
2b	1932		-20.1(NiH, t, J_{PH} = 69 Hz)	41.5(s)
3a	1947		-11.0(PdH)[d)]	47.3(s)
3b	1955		-11.0(PdH)[d)]	47.5(s)
3c	1958		-11.1(PdH)[d)]	47.7(s)

a) In cm^{-1} in KBr disks. b) 100 MHz in C_6D_6. c) Ppm downfield from external PPh_3; 40 MHz in C_6D_6. d) ^{31}P-^1H coupling was not observed. See text.

Table 2. Thermolysis of $MR(SR')(PR''_3)_2$

Complex	Condition[a)]		Products (Yield/%)[b)]			
	Solvent	Temp/°C	Ar-H	ArSAr	H_2	$S=PR''_3$
1a	$CH_3C_6H_5$	120	70	15	c)	72
1b	C_6H_6	120	54	15	c)	74
1c	C_6H_6	130	68	18	15	c)
2a	Ph_2CH_2	140	37	18	c)	44
2b	Ph_2CH_2	140	28	35	c)	28
3a	Ph_2CH_2	200	22	26	23	68
3b	Ph_2CH_2	200	24	7	21	75
3c	Ph_2CH_2	200	61	0	0	73

a) Reaction was carried out for 1-3 h under vacuum.

b) Yields by gaschromatography. c) Formation of the compound was confirmed by gaschromatography, but its amount was not measured.

The diaryl sulfide evolved in Eq. 4 is considered to be formed through the thermal isomerization of **1** to $NiH(SAr)(PEt_3)_2$ followed by disproportionation of it to $NiH_2(PEt_3)_2$ and $Ni(SAr)_2(PEt_3)_2$, the latter complex undergoing the cleavage of Ni-S and S-Ar bond. Thermolysis of $Ni(SPh)_2(PEt_3)_2$ at 200 °C actually affords PhSPh in 100% yield similarly to the result of thermolysis of <u>cis</u>-$Ni(SPh)_2(bpy)_2$ (bpy = 2,2'-bipyridine).[8)] In the case of the thermolysis of the hydrido-thiolato complexes, **2b** and **3a**, such type of disproportionation occurs easily, thus giving ArSAr as a main thermolysis product. Table 2 summarizes the results of the thermolysis of **1**-**3**.

$$\underset{\mathbf{2b}}{CH_3C_6H_4\text{-}S\text{-}NiH(PCy_3)_2} \longrightarrow \underset{28\%}{CH_3C_6H_5} + \underset{28\%}{S{=}PCy_3} + \underset{35\%}{CH_3C_6H_4SC_6H_4CH_3} + H_2 \qquad (6)$$

The reaction pathway for the thermolysis of **3** was estimated based on the reaction using a mixture of $PdD(SC_6H_4CH_3)(PCy_3)_2$ and $PdH(SC_6H_5)(PCy_3)_2$. It is revealed that Ar-H obtained in this reaction ($CH_3C_6H_4D$ and C_6H_6) is formed mainly through an intramolecular coupling of the hydrido ligand and the Ar group of SAr.

Related complexes, <u>trans</u>-$MoH(SR)(dpe)_2$ (dpe = 1,2-bis(diphenylphosphino)-ethane)[9)] and $IrH(SPh)Cl(CO)(PPh_3)_2$,[10)] was reported to lose corresponding thiols at room temperature in the presence or absence of CO. However, the corresponding reductive elimination of ArSH was not observed in thermolysis of these Ni and Pd complexes at all. Although formation of benzene from transition metal benzenethiolato complex with hydrido ligand has been reported in thermolysis of an osmium compound, $HOs_3(CO)_{10}(\mu\text{-}SPh)$,[11)] occurrence of such reactions as described in Eqs. 4 and 5 in a mononuclear complex has no precedent.

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