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The Structure and Properties of (η-Cyclopentadienyl)(*O*-methyl dithiocarbonato)(triphenylphosphine)nickel(II)

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The title complex was synthesized, and the structure was determined by means of the X-ray diffraction technique. The crystal is triclinic; space group $P\bar{1}$, $a=9.944(1)$, $b=14.336(2)$, $c=9.759(1)$ Å, $\alpha=107.00(1)$, $\beta=117.35(1)$, $\gamma=76.55(1)°$, $Z=2$, $D_x=1.40$, $D_m=1.36(3)$ g cm^{-3}, μ(Mo $K\alpha$)$=1.08$ mm^{-1}. The *O*-methyl dithiocarbonato ion acts as a unidentate ligand, and it is coordinated with the metal through one sulfur atom. The coordination number of the metal is 3 if the cyclopentadienyl is regarded as a unidentate ligand. A series of [(η-cyclopentadienyl)(*O*-alkyl dithiocarbonato)(trialkyl- or triarylphosphine)nickel(II)], [Ni(C_5H_5)(S_2COR)(PR'_3)], where R=CH_3, C_2H_5, $CH_3(CH_2)_2$, $(CH_3)_2CH$, or $CH_3(CH_2)_3$; R'=C_6H_5, $C_6H_5CH_2$, or $CH_3(CH_2)_3$, were also obtained. The dissociation of the phosphine ligand of the complexes in solution was studied spectrophotometrically, and it was found that the more electron-donative the alkyl group of the *O*-alkyl dithiocarbonato ligand is, the weaker the phosphorus-nickel bond is.

The title complex is unique in that three different ligands are coordinated to the metal, also as will be shown in the later part of this paper, the *O*-alkyl dithiocarbonate ion acts as a unidentate in it. 1,1-Dithioacid ions, including *O*-alkyl dithiocarbonate ions, commonly act as bidentate ligands with their sulfur atoms; however, exceptionally, the ligand acts as a unidentate in the case of [Sn($S_2COC_2H_5$)$_4$],[1] [Sn{$S_2CN(C_2H_5)_2$}$_4$],[2] [Ru(NO){$S_2CN(C_2H_5)_2$}$_3$],[3] [As(C_6H_5)$_4$][Pt($S_2COC_2H_5$)$_3$],[4] [Sn(C_6H_5)$_3$\{$S_2P(OC_2H_5)_2$\}],[5] [Sb(CH_3)$_3$\{$S_2CN(CH_3)_2$\}$_2$],[6] and [(C_2H_5)$_4$N]-[Cd($S_2COC_2H_5$)$_3$].[7]

Therefore, the present authors started to investigate this type of complex. In the course of the study, the crystal and molecular structure of the title complex was clarified by the X-ray diffraction technique; a part of the results have already been published.[8]

Recently, Tsipis and his collaborators have reported the crystal and molecular structure as well as the NMR results of the analoguous [Ni(η-C_5H_5)($S_2COC_2H_5$)\{$P(C_6H_5)_3$\}].[9] They gave a qualitative interpretation of the equilibrium between two non-equivalent conformations as well as the phosphine dissociation. Their work prompted us to investigate quantitatively the effect of the alkyl group in the *O*-alkyl dithiocarbonato ligand on the dissociation of phosphine in the complex. As a result, the dissociation constants, as well as some thermodynamic data of the equilibrium were obtained.

Experimental

Synthesis of (η-Cyclopentadienyl)(O-methyl dithiocarbonato)-(triphenylphosphine)nickel(II). The chemicals used were all GR-grade reagents: they were purified further by distillation or recrystallization, if necessary. The starting materials, dicyclopentadienylnickel(II) and chlorobis(triaryl or trialkylphosphine)nickel(II), were synthesized by the methods of Cordes[10] and of Venanzi[11] respectivelly. The chloro-(η-cyclopentadienyl)(triphenyl-, tribenzyl-, or tributylphosphine)nickel(II) (0.84 g, 2 mmol), obtained by the method of Yamazaki *et al.*,[12] was dissolved in 25 cm^3 of dichloromethane. To the solution, solid potassium *O*-methyl dithiocarbonate (0.29 g, 2 mmol) was then added, and the mixture was stirred at room temperature. The dithiocarbonate, initially insoluble, started to react, and the color of the solution changed from dark red to deep brown due to the product dissolved in it. The reaction was completed in several minutes. The precipitated potassium chloride was filtered off, and a 30 cm^3 portion of hexane was added to the filtrate. The solution was then concentrated to about 10 cm^3 using a rotary vacuum evaporator at room temperature, and finally was left standing. The precipitated crystals were filtered off and washed with hexane; yield, 0.69 g (70%). (Recrystallized from petroleum benzine.)

Synthesis of (η-Cyclopentadienyl)(O-alkyl dithiocarbonate)-(triaryl- or trialkylphosphine)nickel(II), [Ni(C_5H_5)(S_2COR)-(PR'_3)] (Where R=CH_3, C_2H_5, $CH_3(CH_2)_2$, $(CH_3)_2CH$, or $CH_3(CH_2)_3$; R'=C_6H_5, $C_6H_5CH_2$, or $CH_3(CH_2)_3$). These complexes were obtained by a technique similar to that used in the synthesis of [Ni(C_5H_5)(S_2COCH_3)\{$P(C_6H_5)_3$\}] described above. Yield: 60—85%. Since the tribenzylphosphine derivatives are relatively sensitive to air-oxidation in solution, care had to be taken not to raise the temperature higher than 50 °C during the recrystallization.

The other alkyldithiocarbamato complexes, [Ni(η-C_5H_5)-(S_2CNHR)\{$P(C_4H_9)_3$\}] (where R=CH_3, C_2H_5, C_6H_5, $C_6H_5CH_2$), were also obtained by the same technique; however, no triphenylphosphine derivatives of this type were obtained.

The dialkyldithiocarbamato derivatives could not be synthesized. From the reaction between [NiCl(η-C_5H_5)\{$P(C_6H_5)_3$\}] and dimethylammonium dimethyldithiocarbamate, [Ni(η-C_5H_5)\{$S_2CN(CH_3)_2$\}] was obtained; it was stable only below 10 °C. An attempt was made to synthesize the complexes of this type by using a ligand containing an alkyl group longer than methyl, but no stable products were obtained.

Infrared, Visible, and NMR Spectra Measurements. The infrared spectra of samples were recorded by means of a JASCO infrared spectrophotometer (type 403G), using Nujol and hexachloro-1,3-butadiene mull.

The visible spectra of the samples in a benzene solution were measured by means of a Hitachi 124 spectrophotometer

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the temperature of the cell chamber kept at 15, 20, 25, or 30 °C by means of thermostatted circulating water.

The proton NMR spectra were obtained by the use of a JNM-MH-100 type NMR spectrometer, by using chloroform-*d* as the solvent and TMS as the internal standard.

X-Ray Measurement. The single crystals of $[Ni(C_5H_5)(S_2COCH_3)\{P(C_6H_5)_3\}]$ had grown in a dichloromethane-hexane solution kept in hexane vapor for several days at the ambient temperature. The crystal used was shaped into a sphere ($\phi=0.43$ mm). Crystallographic data: $C_{25}H_{23}NiOPS_2$, F.W.=493.25, triclinic, space group $P\bar{1}$, $a=9.944(1)$, $b=14.336(2)$, $c=9.759(1)$ Å, $\alpha=107.00(1)$, $\beta=117.35(1)$, $\gamma=76.55(1)°$, $Z=2$, $D_x=1.40$, $D_m=1.36(3)$ g cm^{-3}, $\mu=1.08$ mm^{-1} for Mo $K\alpha$(0.7107 Å). The reflections with 2θ less than 60° (Mo $K\alpha$ radiation) were collected on a Rigaku automated four-circle diffractometer, the θ-2θ scan technique being employed. The 5768 independent reflections with $|F_o|>3\sigma(|F_o|)$ were used for the structure refinement. The intensities were corrected for Lorentz and polarization factors, but no correction was made for absorption and extinction. The calculations were carried out mainly by means of the FACOM 230-48 computer at The Institute for Solid State Physics, The University of Tokyo, and partially by means of the HITAC 8700/8800 computer at The Computer Center of The University of Tokyo, using the local version of the UNICS program.[13] The atomic scattering factors were taken from Ref. 14.[14]

Structure Determination. The structure was solved by the heavy-atom method. The positions of the nickel, phosphorus, and sulfur atoms were deduced from a three-dimensional Patterson map; all the other non-hydrogen atoms successively located by means of Fourier syntheses. The positional and thermal parameters were refined by the use of the block-diagonal least-squares method. The positions of hydrogen atoms were obtained from a difference Fourier synthesis, and were also refined. In the final cycle of the refinement with anisotropic temperature factors for all the non-hydrogen atoms, all the parameter shifts were less than one-third of the corresponding standard deviations. The final R value was 0.030.[15]

Results and Discussion

The chemical formulae and the analytical data of the complexes, together with their melting points (or decomposition temperature), are shown in Table 1. The ir data are shown in Table 2. As the wave numbers of these peaks of the complexes are not very different from each other, the structure and the coordination mode of the ligands in them are also likely to be similar.

The final atomic parameters of [(η-cyclopentadienyl)(*O*-methyl dithiocarbonato)(triphenylphosphine)-nickel(II)] are listed in Table 3.[16] The interatomic distances and bond angles are tabulated in Table 4. A perspective drawing of the complex and the numbering scheme are shown in Fig. 1. Figure 2 gives a projection of the structure along c.

The crystal consists of discrete molecules. As may be seen from Fig. 1, the coordination number of the nickel atom is 3 if the cyclopentadienyl group is regarded as a unidentate. The dihedral angle between the cyclopentadienyl plane (the maximum deviation from the mean plane is 0.3 Å) and the plane formed by Ni, P, and S (coordinated) atoms is almost rectangluar (89.1°). The ∠P–Ni–S (coordinated) angle was close to a right angle (92.3°). All the non-hydrogen atoms of the *O*-methyl dithiocarbonato ligand and the central nickel atom are coplanar. The C(6) and O atoms of the ligand are likely to have sp^2 hybridization. The C(6)–O, C(6)–S (non coordinated), and to a lesser extent, C(6)–S (coordinated) bonds have

Table 1. Analyses and melting points of the $[Ni(\eta\text{-}C_5H_5)(S_2COR)(PR'_3)]$ complexes

R	R′	Ni(%) Found	Ni(%) Calcd	C(%) Found	C(%) Calcd	H(%) Found	H(%) Calcd	Mp θ_m/°C
Me	Ph[a]	11.62	(11.90)	60.61	(60.88)	4.85	(4.70)	98.0 (decomp)
Et	Ph[b]	11.56	(11.57)	61.53	(61.56)	4.93	(4.97)	90.0 (decomp)
Pr	Ph	11.11	(11.26)	62.36	(62.21)	5.30	(5.22)	93.5 (decomp)
i-Pr	Ph	11.16	(11.26)	62.44	(62.21)	5.33	(5.22)	92.0 (decomp)
Bu	Ph[c]	10.74	(10.97)	62.87	(62.82)	5.45	(5.46)	90.0 (decomp)
Me	Bu	13.39	(13.55)	52.84	(52.67)	8.18	(8.14)	87.0—88.0
Et	Bu	13.06	(13.12)	53.88	(53.70)	8.28	(8.34)	110.0—110.5
Pr	Bu	12.65	(12.72)	54.79	(54.67)	8.32	(8.52)	106.0—107.5
i-Pr	Bu	12.58	(12.72)	54.85	(54.67)	8.40	(8.52)	94.5— 95.0
Bu	Bu	12.26	(12.35)	55.63	(55.59)	8.69	(8.69)	84.0— 85.0
Me	Bz[d]	10.59	(10.96)	62.70	(62.82)	5.54	(5.46)	101.5—103.0
Et	Bz	10.46	(10.69)	63.07	(63.48)	5.69	(5.69)	103.0 (decomp)
Pr	Bz	10.34	(10.42)	64.56	(63.96)	6.18	(5.90)	117.0 (decomp)
i-Pr	Bz	10.09	(10.42)	63.74	(63.96)	5.93	(5.90)	118.0 (decomp)
Bu	Bz	9.89	(10.10)	64.65	(64.48)	6.17	(6.11)	114.0 (decomp)

Sulfur analyses: a), Found 12.74, Calcd 13.00; b), Found 12.46, Calcd 12.64; c), Found 11.71, Calcd 11.98; d), Found 11.26, Calcd 11.98%.

Analysis of $[Ni(C_5H_5)\{S_2CN(CH_3)_2\}]$: Found Ni, 23.76; C, 39.71; H, 4.40; S, 25.94; N, 5.55%. Calcd Ni, 24.06; C, 39.38; H, 4.54; S, 26.28; N, 5.74%.

Me=CH_3, Et=C_2H_5, Pr=$CH_3(CH_2)_2$, *i*-Pr=$(CH_3)_2CH$, Bu=$CH_3(CH_2)_3$, Ph=C_6H_5, Bz=$C_6H_5CH_2$, decomp=decomposed.

Table 2. Infrared spectra (cm^{-1}) of $[Ni(\eta\text{-}C_5H_5)(S_2COR)(PR'_3)]$ complexes (abbreviations in the table are the same as those in Table 1)

R	R′	ν(C=S)[b]			
Me	Ph	1198	1147	1050,	1038
Et	Ph	1179	1111	1029	
Pr	Ph	a)	1119	1034	
i-Pr	Ph	1203	1091	1026	
Bu	Ph	1178	1120	1037	
Me	Bu	1192	1145	1058,	1045
Et	Bu	1173	1109	1037	
Pr	Bu	1178	1123	1047	(broad)
i-Pr	Bu	1192	1095	1030	
Bu	Bu	1157	1126	1040	
Me	Bz	1192	1135, 1126	1056	
Et	Bz	1196	1110	1037	
Pr	Bz	1180 (broad)		1030	
i-Pr	Bz	1195	1088	1025	
Bu	Bz	1186	1121	1036	

a) Superimposed by the absorption of the phenyl group.
b) Some modes of vibrations caused by the C-O-C bond, such as ν(C-O), may be mixed.

a multiple-bond character.

The structural data indicate that the C–S (non coordinated) is shorter than the C–S (coordinated) in the case of unidentate 1,1-dithioacid ion. The steric conformations concerned with C–O are always E, except for $[M(S_2COC_2H_5)_3]$ (M=As or Sb), where the ligands are in an intermediate state between the

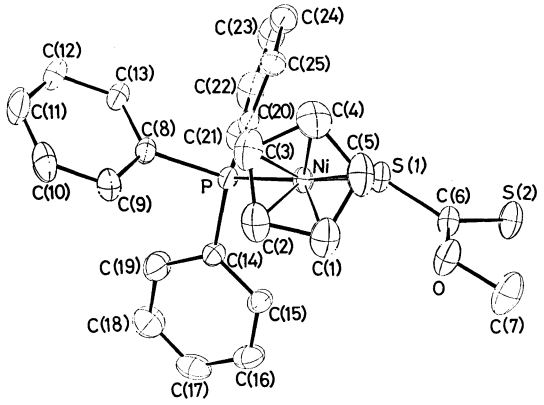

Fig. 1. A perspective drawing of the title complex with the numbering scheme of atoms.

Table 3. Final atomic coordinates ($\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms) and isotropic temperature factors (B/Å^2) with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}/Å^2 [a]	Atom	x	y	z	B_{eq}/Å^2 [a]
Ni	3355.5(2)	1505.7(1)	2969.1(2)	3.16	C(11)	−3179(2)	2868(2)	1030(3)	7.50
S(1)	5392.0(4)	1864.7(3)	5168.4(5)	4.02	C(12)	−2479(2)	3036(2)	2641(4)	7.87
S(2)	8735.5(5)	1629.9(4)	6536.3(7)	5.55	C(13)	−906(2)	3052(2)	3430(3)	5.51
P	2039.5(4)	2853.3(3)	3580.0(4)	2.99	C(14)	2394(2)	3931(1)	3227(2)	3.63
O	6951(2)	1085(1)	3515(2)	5.70	C(15)	3744(2)	3943(1)	3161(2)	4.46
C(1)	3768(3)	710(2)	961(2)	5.78	C(16)	4026(3)	4770(2)	2922(3)	5.98
C(2)	2236(2)	1062(2)	492(2)	5.39	C(17)	2980(3)	5579(2)	2736(3)	6.35
C(3)	1636(2)	655(2)	1224(3)	5.80	C(18)	1639(3)	5573(2)	2796(4)	7.89
C(4)	2785(3)	15(2)	2108(3)	7.01	C(19)	1335(3)	4763(2)	3036(3)	7.03
C(5)	4120(2)	100(1)	2013(3)	5.83	C(20)	2407(2)	3131(1)	5658(2)	3.60
C(6)	7084(2)	1487(1)	4982(2)	4.09	C(21)	2535(2)	4068(2)	6604(2)	4.92
C(7)	8307(3)	658(2)	3253(3)	7.72	C(22)	2691(3)	4217(2)	8141(3)	6.76
C(8)	−42(2)	2895(1)	2587(2)	3.66	C(23)	2699(3)	3448(2)	8717(2)	7.31
C(9)	−776(2)	2750(2)	950(2)	4.97	C(24)	2062(3)	2529(2)	7806(3)	6.81
C(10)	−2341(2)	2725(2)	174(3)	6.10	C(25)	2467(2)	2357(2)	6277(2)	5.00
Atom	x	y	z	B_{iso}/Å^2	Atom	x	y	z	B_{iso}/Å^2
H(1)	456(3)	91(2)	67(3)	7.6(6)	H(13)	−42(2)	313(1)	456(2)	5.4(5)
H(2)	166(3)	148(2)	−30(3)	7.7(6)	H(15)	447(2)	339(1)	330(2)	5.1(5)
H(3)	71(3)	77(2)	120(3)	8.0(7)	H(16)	491(3)	471(2)	286(3)	6.7(6)
H(4)	277(3)	−28(2)	279(3)	7.8(6)	H(17)	323(3)	609(2)	256(3)	7.3(6)
H(5)	507(3)	−15(2)	259(3)	6.7(6)	H(18)	88(4)	607(2)	258(4)	10.7(9)
H(7-1)	804(3)	56(2)	218(3)	7.8(7)	H(19)	33(3)	480(2)	319(3)	8.3(7)
H(7-2)	860(3)	5(2)	364(3)	6.9(6)	H(21)	252(2)	457(1)	620(2)	5.1(5)
H(7-3)	911(3)	114(2)	386(3)	8.5(7)	H(22)	279(3)	484(2)	872(3)	7.3(6)
H(9)	−12(2)	269(2)	42(2)	5.9(5)	H(23)	280(3)	357(2)	978(3)	8.9(7)
H(10)	−284(3)	257(2)	−87(3)	8.1(7)	H(24)	269(3)	202(2)	831(3)	7.9(7)
H(11)	−427(4)	286(2)	52(4)	11.5(9)	H(25)	237(2)	177(1)	568(2)	5.0(4)
H(12)	−309(3)	324(2)	338(3)	9.7(8)					

a) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha)$. The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

Table 4. Interatomic distance and bond angles with their estimated standard deviations in parentheses

Interatomic distance (l/Å)			
Ni-S(1)	2.195(1)	C(8)-C(9)	1.390(3)
Ni-P	2.160(1)	C(9)-C(10)	1.388(3)
Ni-C(1)	2.126(2)	C(10)-C(11)	1.376(5)
Ni-C(2)	2.108(2)	C(11)-C(12)	1.365(4)
Ni-C(3)	2.096(2)	C(12)-C(13)	1.392(3)
Ni-C(4)	2.161(2)	C(13)-C(8)	1.384(3)
Ni-C(5)	2.085(2)	C(14)-C(15)	1.377(3)
S(1)-C(6)	1.719(2)	C(15)-C(16)	1.384(4)
S(2)-C(6)	1.651(1)	C(16)-C(17)	1.360(3)
C(6)-O	1.334(2)	C(17)-C(18)	1.362(5)
O-C(7)	1.449(3)	C(18)-C(19)	1.372(4)
C(1)-C(2)	1.386(3)	C(19)-C(14)	1.390(2)
C(2)-C(3)	1.416(4)	C(20)-C(21)	1.386(2)
C(3)-C(4)	1.400(3)	C(21)-C(22)	1.391(3)
C(4)-C(5)	1.407(4)	C(22)-C(23)	1.373(5)
C(5)-C(1)	1.412(4)	C(23)-C(24)	1.353(4)
P-C(8)	1.833(1)	C(24)-C(25)	1.385(3)
P-C(14)	1.818(2)	C(25)-C(20)	1.388(3)
P-C(20)	1.822(2)		
Bond angle (ϕ/°)			
S(1)-Ni-P	92.29(1)	C(11)-C(12)-C(13)	120.2(3)
C(5)-C(1)-C(2)	107.0(2)	C(12)-C(13)-C(8)	120.3(2)
C(1)-C(2)-C(3)	108.3(2)	C(19)-C(14)-C(15)	118.2(2)
C(2)-C(3)-C(4)	108.9(2)	C(14)-C(15)-C(16)	120.2(2)
C(3)-C(4)-C(5)	106.0(3)	C(15)-C(16)-C(17)	121.0(2)
C(4)-C(5)-C(1)	109.6(2)	C(16)-C(17)-C(18)	119.2(3)
S(1)-C(6)-S(2)	121.1(1)	C(17)-C(18)-C(19)	120.9(3)
S(1)-C(6)-O	115.3(1)	C(18)-C(19)-C(14)	120.5(3)
S(2)-C(6)-O	123.6(1)	C(25)-C(20)-C(21)	119.2(2)
C(6)-O-C(7)	119.5(2)	C(20)-C(21)-C(22)	119.4(2)
Ni-P-C(8)	117.35(5)	C(21)-C(22)-C(23)	120.6(3)
Ni-P-C(14)	114.47(7)	C(22)-C(23)-C(24)	120.2(3)
Ni-P-C(20)	111.56(6)	C(23)-C(24)-C(25)	120.5(3)
Ni-S(1)-C(6)	114.44(7)	C(24)-C(25)-C(20)	120.2(2)
C(8)-P-C(14)	103.35(8)	P-C(8)-C(9)	119.6(2)
C(14)-P-C(20)	106.46(8)	P-C(8)-C(13)	121.5(1)
C(20)-P-C(8)	102.36(7)	P-C(14)-C(15)	120.2(1)
C(13)-C(8)-C(9)	118.9(2)	P-C(14)-C(19)	121.6(2)
C(8)-C(9)-C(10)	120.4(2)	P-C(20)-C(21)	123.7(2)
C(9)-C(10)-C(11)	119.9(2)	P-C(20)-C(25)	117.0(1)
C(10)-C(11)-C(12)	120.4(2)		

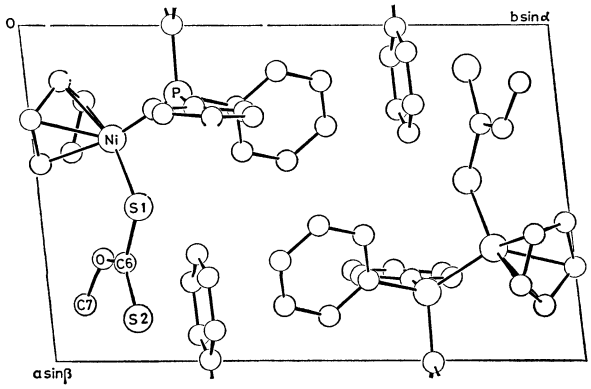

Fig. 2. Crystal packing diagram projected along c.

chelate and unidentate types of coordination.[17,18] The conformation of the ligand in the title complex is also E.

Of the present complexes, the bond distances between nickel and ligating sulfur atoms as well as between nickel and cyclopentadienyl are almost equal to the respective values of the *O*-ethyl dithiocarbonato complexes. On the other hand, the Ni–P distances of both the complexes are slightly, but significantly, different from each other (2,160(1) *vs.* 2.184(1) Å). This fact will be discussed later.

The visible spectra of the complex in benzene solution containing an excess of phosphine ligand are shown in Fig. 3. In the figure, two isosbestic points were found at 492 and 535 nm; they remained unchanged even when the concentration of the co-ex-

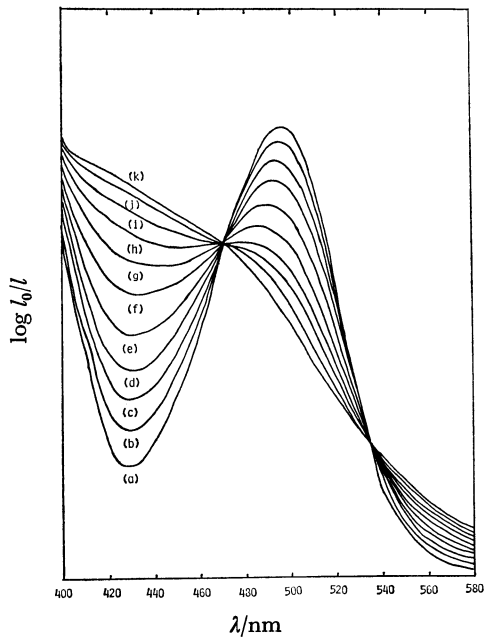

Fig. 3. Absorption spectra of the complex $[Ni(C_5H_5)(S_2COC_4H_9)\{P(C_6H_5)_3\}]$ in benzene solution containing excess of triphenylphosphine.
Concentration of Ni(II): 0.3285×10^{-3} mol dm^{-3}, total concentration of triphenylphosphine: a) 0.3285, b) 2.04, c) 4.33, d) 7.31, e) 11.8, f) 20.2, g) 32.3, h) 49.2, i) 76.8, j) 137.9, k) 197.5×10^{-3} mol dm^{-3}.

isting phosphine was varied from 1 to 600 times (mol/mol) to that of the original 1:1 complex adduct.

Tsipis proposed the following dissociation scheme of the phosphine from the complex in order to explain the temperature variation on the NMR spectra of the complex above 56 °C:[9] $[Ni(C_5H_5)(S_2COR)(PPh_3)] = PPh_3 + [Ni(C_5H_5)(S_2COR)]$ (where Ph=C_6H_5)

The equillibrium constant, K', of this reaction was obtained from the measured absorbance of the solutions at 430 nm containing the complex and the excess of the phosphine ligand at 15, 20, 25, and 30 °C. The procedure is as follows: The equilibrium constant, K', is given by $K'=[M][L]/[ML]$ (where M=$Ni(C_5H_5)(S_2COR)$, L=PPh_3, and ML=$Ni(C_5H_5)(S_2COR)(PPh_3)$.) The total amount of $PPh_3(l)$, and $Ni(m_0)$ are expressed by $l=[ML]+[L]$ and $m_0=[M]+[ML]$ respectively. The absorbance, $A_c=\varepsilon_2[ML]+\varepsilon_1[M]$, where ε_1 and ε_2 are the absorption coefficients of M and ML respectively. The equation becomes:

$$A_c = \varepsilon_2\frac{(m_0+l+K')-\sqrt{D}}{2} + \varepsilon_1\frac{(m_0-l-K')+\sqrt{D}}{2},$$

where $D=(m_0+l+K')^2-4m_0l$ by representing [ML] and [M] in terms of l,m_0, and K'. The values of ε_1, ε_2, and K' were obtained by using the least-squares method, which minimizes $\Sigma(A_o-A_c)^2$, where A_o is observed absorbance. The calculation was carried out on a HITAC M-200H computer at The Computer Center of The University of Tokyo, using the SALS program.[20]

The K''s were converted to the equilibrium constants in molar fraction units, K**. From the van't Hoff plots for each complex, the apparent standard enthalpy, entropy, and Gibb's free energy change of the reaction were obtained; the results are shown in Table 5. As is shown in the table, all of these dissociation reactions are endothermic, and their entropy changes are all positive. The relation between $\Delta H°$ or $\Delta S°$ and the aliphatic polar substituent constants, σ^*,[21] of the alkyl groups of the *O*-alkyl dithiocarbonato ligand is shown in Fig. 4. The complex involving the more electron-donative alkyl group shows lower ΔH and ΔS values. At room temperature, the complexes having the higher electron-donative alkyl group of the ligand dissociate more easily. From the equilibrium constants, it is shown that, at the ambient temperature, the complex in the solution of about 10^{-4} mol dm^{-3} dissociates almost completely (more than 99%) in the absence of an excess of ligands. The Ni–P distance in the *O*-methyl dithiocarbonato complex, which is shorter than that of the *O*-ethyl dithio-

Table 5. Standard enthalpy $\Delta H°$, entropy $\Delta S°$, and Gibb's free energy $\Delta G°$ of the reaction $[Ni(C_5H_5)(S_2COR)\{P(C_6H_5)_3\}]=[Ni(C_5H_5)(S_2COR)]+P(C_6H_5)_3$ at 25 °C.

R	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}	ΔG/kJ mol^{-1}
CH_3	42.1 (8)	82 (2)	18 (1)
CH_3CH_2	40.7 (16)	82 (5)	16 (3)
$CH_3(CH_2)_2$	39.5 (4)	80 (2)	16 (1)
$CH_3(CH_2)_3$	39.6 (14)	80 (5)	16 (3)
$(CH_3)_2CH$	38.4 (12)	79 (4)	15 (2)

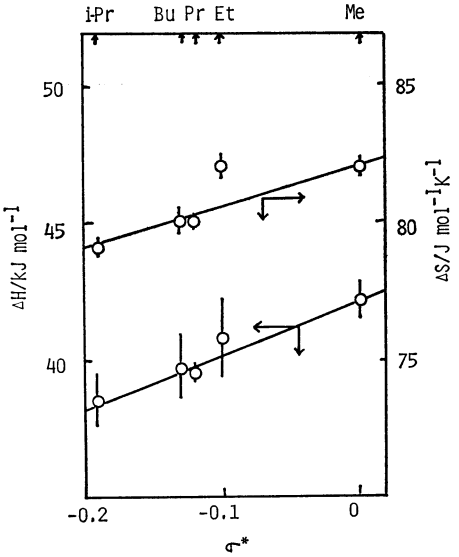

Fig. 4. Dependence of $\Delta H°$ and $\Delta S°$ of the reaction $[Ni(C_5H_5)(S_2COR)\{P(C_6H_5)_3\}]=[Ni(C_5H_5)(S_2COR)]+P(C_6H_5)_3$ on aliphatic polar substituent constants σ^* of R.

** The temperature variation of the specific gravity of the solvent was also taken into consideration. The standard changes in enthalpy, *etc.*, obtained from the new K's stand for those in which all components of the equation are in the unit molar fraction.

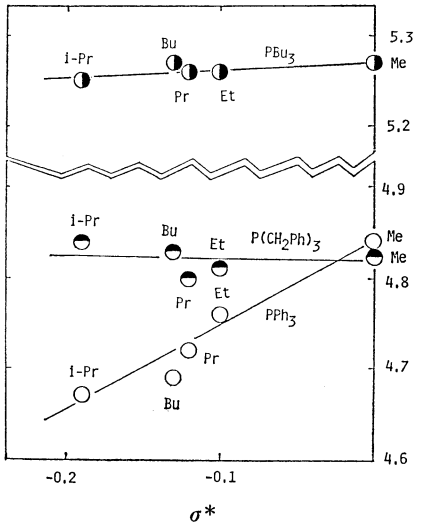

Fig. 5. Dependence of the chemical shifts of cyclopentadienyl protons on the aliphatic polar substitent constants σ^* of R in $[Ni(C_5H_5)(S_2COR)(PR'_3)]$. Abbreviations. For phosphines, Bu=$CH_3(CH_2)_3$, Ph=C_6H_5; for R of $(S_2COR)^-$, Me=CH_3, Et=CH_3CH_2, Pr=$CH_3(CH_2)_2$, *i*-Pr=$(CH_3)_2CH$, Bu=$CH_3(CH_2)_3$.

carbonato one, is explained by the fact that the methyl group is less electronegative than the ethyl group.

The relation between the chemical shifts of ^{1}H-NMR of the cyclopentadienyl proton of the complexes, and the aliphatic polar substituent constants, σ^*,[21] is shown in Fig. 5. The NMR study reveals that the dissociation of the complex in the solution is complete when the concentration of the solution is high (about 10^{-1} mol dm^{-3}), and that the cyclopentadienyl protons of complexes containing triphenylphosphine are more shielded when the alkyl group of the *O*-alkyl dithiocarbonato ligand is more electron-donative. However, this relation is not realized for the tributyl- and tribenzylphosphine complexes, as is shown in the figure. Therefore, in these cases some additional effects should be involved.

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