Table 1. Direct Conversion of Carboxylic Acids into 1,3-Dithiolanes[a]

R	Method[b]	time, h	isolated yield of 1,3-dithiolanes	R	Method[b]	time, h	isolated yield of 1,3-dithiolanes
$CH_3(CH_2)_6$	A	3	83	$p\text{-}CH_3C_6H_4$	A	12	63(27)[c]
	B	3	88		B	18	73
$C_6H_5CH_2$	A	4	83	$p\text{-}CH_3OC_6H_4$	B	20	71
	B	3	92	$BrCH_2(CH_2)_9$	A	6	98
$(CH_3)_2CH$	A	3	85		B	4	92
	B	4	86	$MeOOCCH_2(CH_2)_3$	A	6	87
cyclohexyl	A	5	87		B	3.5	87
	B	4	85	$Et_2NCOCH_2(CH_2)_3$	A	6	75
$(CH_3)_3C$	A	6	81		B	4	75
	B	4.5	84	$CH_2=CH(CH_2)_8$	A	17	25
1-adamantanyl	A	7	90		B	7	78
	B	3	91	$CH_2=CHCH_2CH_2$	B	20	71
C_6H_5	B	5	79	$CH_2=CHCH_2$	B	24	82
$m\text{-}BrC_6H_4$	B	18	78	$C_6H_5CH=CH$	B	24	75

[a] The reaction was carried out in THF at room temperature. [b] Method A : Reacted with 1.5 equiv of the reagent in the presence of 1.0 equiv of boron trifluoride etherate. Method B : Reacted with 1.7 equiv of the reagent for aliphatic acids and 2.0 equiv for aromatic acids in the presence of 1.0 equiv of stannous chloride. [c] The yield of p-methylbenzyl alcohol.

responding thioacetals, as shown in Table 1. However, selective reduction of acids in the presence of olefins failed under the present conditions. Thus, reaction of 11-undecylenic acid with 1.5 equiv of the reagent in the presence of 1.0 equiv of boron trifluoride etherate gave the desired thioacetal in 25% yield along with 30% of the starting material, 35% of the hydroxy-acid, and 10% of the hydroxy thioacetal. Apparently, the hydroxy compounds are resulted from hydroboration reaction. Also, the present method does not work well with aromatic acids. Under the present condition, p-toluic acid gave a 70:30 mixture of the desired thioacetal and p-methylbenzyl alcohol.[30] These problems were solved by the use of stannous chloride.

Clean reaction of aromatic acids and selective reaction with acids in the presence of olefins become possible in the presence of stannous chloride. The yields, the reaction conditions, and the scope of the present method were very similar with those of the previously reported one using 1,3,2-dithiaborinane.[1] Thus, 1.5 equiv of the reagent and 1.0 equiv of stanous chloride for aliphatic carboxylic acids and 2 equiv of the reagent and stannous chloride for aromatic acids (Method B) are recommended to obtain maximum yields. As shown in Table 1, Method B works well with both aliphatic and aromatic acids. Of synthetic significance of Method B is selective reduction of acids without attacking isolated ole-

finic double bonds. The result are smmarized in Table 1.

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5. To a stirred solution of borane-dimethyl sulfide in tetrahydrofuran (5.0 ml, 10 M, 50 mmol) at 0 °C under nitrogen was added freshly distilled 1,2-ethanedithiol (4.71 g, 50 mmol) dropwise over a period of 30 min. The reaction mixture, from which gas evolved slowly, was stirred at room temperature for 24 h. The concentration of 1,3,2-dithiaborolane-dimethyl sulfide in tetrahydrofuran was adjusted to 1.0 M solution by adding tetrahydrofuran.
6. The preparation of 1,3,2-dithiaborinane required much longer reaction times (7 days).
7. The use of boron trifluoride etherate as a catalyst (0.1 equiv) did not improve the reaction.

Syntheses and Spectral Properties of Pd(II)-and Pt(II)-bis(diphenylphosphino)methane Complexes

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The binuclear complexes of palladium and platinum bridged by bis(diphenylphosphino)methane(dppm) ligand are ex-

tensively investigated, especially relevance to the catalytic effects[1,2] and the structural properties.[3,4] It is known that the
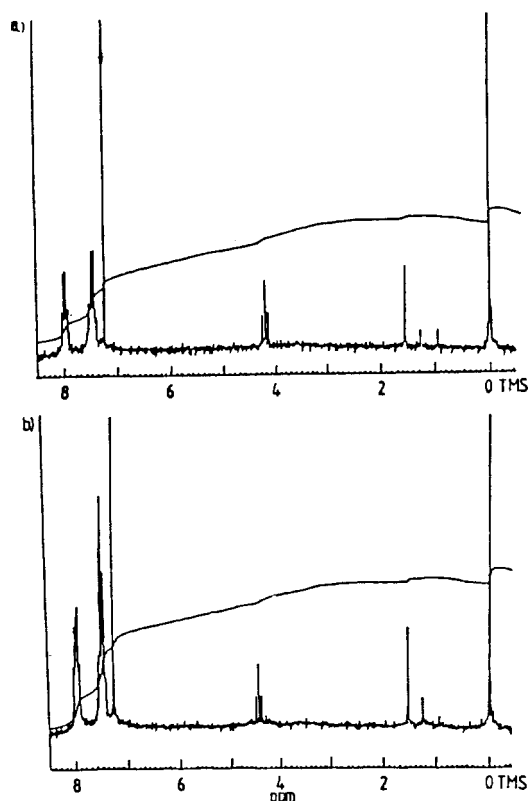
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Figure 1. ^{1}Hnmr spectra of PdCl$_2$dppm(a) PtCl$_2$dppm(b) in CDCl$_3$ in acetonitrile solution.

complexes, MCl$_2$dppm(M = Pd^{II} and Pt^{II}) are very important to prepare the complexes M$_2$(dppm)$_3$ which have the catalytic activities for the hydrogenation of olefines and the reaction of gas molecules. Conventionally, MCl$_2$dppm have been prepared by the reaction of anhydrous metal chlorides[1,5] or dichlorocyclooctadiene-metal complexes[4a,b] with dppm and PdCl$_2$dppm is only characterized analytically, while PtCl$_2$-dppm both analytically and by nmr spectroscopy but not full spectrum.

The practical syntheses and the spectral properties (^{1}Hnmr and uv-visible) of the compounds MCl$_2$dppm are reported in this report. The palladium-dppm complex was prepared by adding dppm to a suspension of K$_2$PdCl$_4$ in the distilled n-propanol as shown in reaction (1). The equimolar solution of K$_2$PdCl$_4$ and dppm was stirred for ca.15 min and then the solution was refluxed for 50 min.

$$K_2PdCl_4 + dppm \xrightarrow{\text{in n-PrOH}} PdCl_2dppm + 2KCl \qquad (1)$$
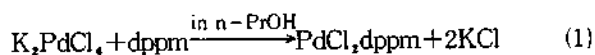
The pale yellow PdCl$_2$dppm formed was collected by vacuum filteration. The solid was washed with ice-water and ether, and dried in vacuo for 24 h. The white solid PtCl$_2$dppm was prepared by the same procedure as above. The elemental analyses were carried out at the Laboratory of Chemistry, N. Illinois University, U.S.A.

For PdCl$_2$dppm
Calcd: Pd, 18.77; C, 53.45; H, 3.96%. Found: Pd, 18.95; C, 53.26; H, 3.97%. Yield: 92%

For PtCl$_2$dppm
Calcd: Pt, 30.00; C, 46.16; H, 3.42%. Found: Pt, 30.42; C, 46.18; H, 3.52%. Yield: 93%

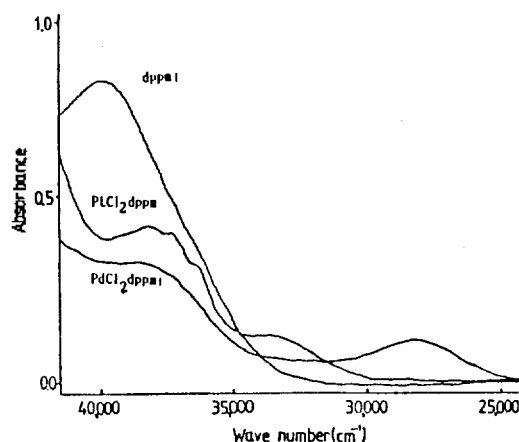**Figure 2.** Uv-visible spectra of dppm, PtCl$_2$dppm and PdCl$_2$dppm in acetonitrile solution.

The ^{1}Hnmr spectra of the CH$_2$ groups of MX$_2$dppm were used as the other criterion for identifying the compounds (Figure 1). The ^{1}Hnmr(200 MHZ) and uv-visible spectra were obtained on IBM WP200 SY and Cary 1510 spectrometers, respectively.

The syntheses of the complexes, PdCl$_2$dppm and PtCl$_2$-dppm according to reaction(1) could be carried out under mild conditions and the yields were very high. The ^{1}Hnmr spectra of the complexes in CDCl$_3$ were represented in Figure 1. The ^{1}Hnmr spectrum of PdCl$_2$dppm in Figure 1a. showed a triplet due to the methylene protons at 4.2 ppm, a multiplet due to the o-protons of phenyl rings at 7.95 ppm and a multiplet due to m-and p-protons of phenyl rings at 7.5 ppm. The ^{1}Hnmr spectrum of PtCl$_2$dppm in Figure 1b showed a triplet due to the methylene protons at 4.4 ppm (4.6 ppm in C$_2$D$_2$Cl$_4$)[8] a multiplet due to the o-protons of phenyl rings at 7.95 ppm and a multiplet due to the m-and p-protons of phenyl rings at 7.5 ppm. The chemical shift of the methylene group in PdCl$_2$dppm was appeared in higher field than in PtCl$_2$dppm. The difference of chemical shift between PdCl$_2$-dppm and PtCl$_2$dppm is explained by considering the size effect of metal d-orbitals: that is the strong back bonding of the phosphorous with the d-orbital of platinum.

The uv-visible spectra of PdCl$_2$dppm and PtCl$_2$dppm were measured in the range of 24000-41000 cm^{-1}. The spectra in Figure 2 showed the ligand field bands at 28350 cm^{-1} (ϵ_{max} = 580 M^{-1}cm^{-1}) for PdCl$_2$dppm and at 3350 cm^{-1} (ϵ_{max} = 390 M^{-1}cm^{-1}) for PtCl$_2$dppm, which are probably due to the transition $^1A_1' - ^1E'(d_{x^2-y^2} - p_z)$. The details of electronic structures of the complexes will be analyzed using the magnetic circular dichroism method[7] in the next.

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