

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-CH ₃ C ₆ H ₄	A	12	63(27) ^c
	B	3	88		B	18	73
C ₆ H ₅ CH ₂	A	4	83	p-CH ₃ OC ₆ H ₄	B	20	71
	B	3	92	BrCH ₂ (CH ₂) ₉	A	6	98
(CH ₃) ₂ CH	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 ₂ NCOCH ₂ (CH ₂) ₃	A	6	75
(CH ₃) ₃ C	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 ₂ CH ₂	B	20	71
C ₆ H ₅	B	5	79	CH ₂ = CHCH ₂	B	24	82
m-BrC ₆ H ₄	B	18	78	C ₆ H ₅ CH = CH	B	24	75

^aThe reaction was carried out in THF at room temperature. ^bMethod 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. ^cThe 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-dithiabborinane.¹ Thus, 1.5 equiv of the reagent and 1.0 equiv of stannous 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 summarized 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-dithiabborolane-dimethyl sulfide in tetrahydrofuran was adjusted to 1.0 M solution by adding tetrahydrofuran.
6. The preparation of 1,3,2-dithiabborinane 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

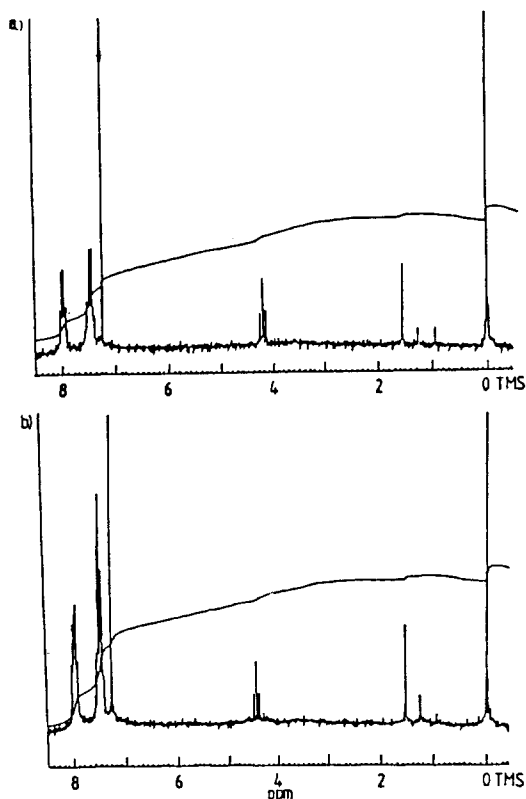
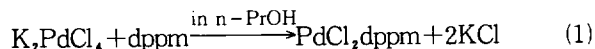


Figure 1. ^1H nmr spectra of PdCl_2dppm (a) PtCl_2dppm (b) in CDCl_3 in acetonitrile solution.

complexes, MCl_2dppm ($\text{M} = \text{Pd}^{\text{II}}$ and Pt^{II}) are very important to prepare the complexes $\text{M}_2(\text{dppm})_3$ which have the catalytic activities for the hydrogenation of olefins and the reaction of gas molecules. Conventionally, MCl_2dppm have been prepared by the reaction of anhydrous metal chlorides^{1,5} or dichlorocyclooctadiene-metal complexes^{4a,b} with dppm and PdCl_2dppm is only characterized analytically, while PtCl_2dppm both analytically and by nmr spectroscopy but not full spectrum.

The practical syntheses and the spectral properties (^1H nmr and uv-visible) of the compounds MCl_2dppm are reported in this report. The palladium-dppm complex was prepared by adding dppm to a suspension of K_2PdCl_4 in the distilled n-propanol as shown in reaction (1). The equimolar solution of K_2PdCl_4 and dppm was stirred for ca. 15 min and then the solution was refluxed for 50 min.



The pale yellow PdCl_2dppm formed was collected by vacuum filtration. The solid was washed with ice-water and ether, and dried in vacuo for 24 h. The white solid PtCl_2dppm 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_2dppm

Calcd: Pd, 18.77; C, 53.45; H, 3.96%. Found: Pd, 18.95; C, 53.26; H, 3.97%. Yield: 92%

For PtCl_2dppm

Calcd: Pt, 30.00; C, 46.16; H, 3.42%. Found: Pt, 30.42; C, 46.18; H, 3.52%. Yield: 93%

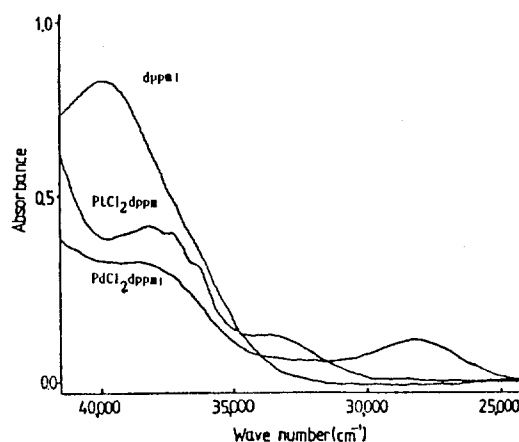


Figure 2. Uv-visible spectra of dppm, PtCl_2dppm and PdCl_2dppm in acetonitrile solution.

The ^1H nmr spectra of the CH_2 groups of MX_2dppm were used as the other criterion for identifying the compounds (Figure 1). The ^1H nmr (200 MHz) and uv-visible spectra were obtained on IBM WP200 SY and Cary 1510 spectrometers, respectively.

The syntheses of the complexes, PdCl_2dppm and PtCl_2dppm according to reaction (1) could be carried out under mild conditions and the yields were very high. The ^1H nmr spectra of the complexes in CDCl_3 were represented in Figure 1. The ^1H nmr spectrum of PdCl_2dppm 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 ^1H nmr spectrum of PtCl_2dppm in Figure 1b showed a triplet due to the methylene protons at 4.4 ppm (4.6 ppm in $\text{C}_2\text{D}_2\text{Cl}_4$), 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_2dppm was appeared in higher field than in PtCl_2dppm . The difference of chemical shift between PdCl_2dppm and PtCl_2dppm 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_2dppm and PtCl_2dppm were measured in the range of 24000–41000 cm^{-1} . The spectra in Figure 2 showed the ligand field bands at 28350 cm^{-1} ($\epsilon_{\text{max}} = 580 \text{ M}^{-1}\text{cm}^{-1}$) for PdCl_2dppm and at 3350 cm^{-1} ($\epsilon_{\text{max}} = 390 \text{ M}^{-1}\text{cm}^{-1}$) for PtCl_2dppm , 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 method⁷ in the next.

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