Fast Cis-Trans Isomerization of Square-Planar Bis(diethyl sulfide)platinum(II) Complexes. Reaction of *cis*-Dichlorobis(diethyl sulfide)platinum(II) with Mesityllithium

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Synopsis. Reaction of *cis*-[$PtCl_2(SEt_2)_2$] with a slight excess of mesityllithium in benzene-ether mixture afforded *trans*-[PtCl(Mes)(SEt_2)$_2$] (Mes=2,4,6-trimethylphenyl; SEt_2= diethyl sulfide) as a major product. When mesityllithium reagent containing lithium bromide was used, *trans*-[PtBr(Mes)(SEt_2)$_2$] was obtained. Acceleration of cis-trans isomerization in the presence of mesityllithium was observed.

Arylplatinum(II) complexes having sulfide ligands are useful precursors of various organoplatinum complexes, since the sulfide ligands can be replaced easily by phosphine, pyridine, carbonyl, etc.[1] The reaction of *trans*-[PtX_2L_2] (X=Cl, Br, or I; L=SEt_2 or $SeEt_2$) with phenyl, *o*-tolyl, or mesityllithium has been reported by Sergi et al.[2,3] who found that the trans isomers of [$PtXArL_2$] and/or [$PtAr_2L_2$] were the exclusive products with the exception of the reaction of *trans*-[$PtCl_2(SEt_2)_2$] with phenyllithium. In the latter reaction, the major product was *cis*-[$PtPh_2(SEt_2)_2$] (60%) with 20% of the trans isomer.

The reaction of *cis*-[$PtCl_2(SR_2)_2$] (R=Et, *n*-Pr, or *i*-Pr) with excess phenyl or *p*-tolyllithium has been reported by Steele and Vrieze to give the dimeric [$PtAr_2(SR_2)]_2$ (Ar=Ph or *p*-tolyl).[1] Exceptionally, the reaction of *cis*-[$PtCl_2(SEt_2)_2$] with C_6F_5Li afforded monomeric *cis*-[$Pt(C_6F_5)_2(SEt_2)_2$] in high yield.[1] They also carried out the reaction of *trans*-[$PtCl_2(SEt_2)_2$] with phenyllithium and obtained products which were different from Sergi's, i.e., a dimer [$PtPh_2(SEt_2)]_2$ (55%) and a monomer *cis*-[$PtPh_2(SEt_2)_2$] (20%).

This paper deals with the reaction of *cis*-[$PtCl_2(SEt_2)_2$] with bulky mesityllithium which has not been examined before. When *cis*-[$PtCl_2(SEt_2)_2$] was allowed to react with mesityllithium reagent containing lithium bromide, *trans*-[PtBr(Mes)(SEt_2)$_2$] was obtained. A possible mechanism is proposed for the reaction.

Experimental

Apparatus. ^{1}H NMR spectra were recorded on JEOL FX-90Q and Varian EM-390 spectrometers, and ^{13}C NMR spectra on a JEOL FX-90Q spectrometer. Electronic spectra were measured on a Hitachi 330 spectrophotometer. Mass spectra were obtained on a Hitachi M-52 spectrometer.

Reaction of *cis*-[$PtCl_2(SEt_2)_2$] with Mesityllithium. Reactions were carried out under nitrogen using dried solvents. *cis*-[$PtCl_2(SEt_2)_2$] was prepared according to a literature procedure.[4]

***trans*-[PtBr(Mes)(SEt_2)$_2$] and *trans*-[$PtBr_2(SEt_2)_2$].** A suspension of mesityllithium was prepared by adding 1.5 mol dm^{-3} butyllithium in hexane (10 ml) to an ether solution (40 ml) of bromomesitylene (2.00 g, 10.0 mmol) at room temperature. A 3 ml portion of this suspension (ca. 0.60 mmol) was added to a benzene (20 ml) solution of *cis*-[$PtCl_2(SEt_2)_2$] (200 mg, 0.448 mmol) at 0 °C. After stirring for 15 min, the reaction mixture was allowed to warm to room temperature and stirred for 17 h. The turbid reaction mixture was filtered through a Celite 545 column and the filtrate was evaporated to give a brown crystalline residue. It was then placed on an alumina column (200 mesh) and eluted with benzene. Evaporation of the eluates afforded *trans*-[$PtBr_2(SEt_2)_2$][5] as yellow crystals (12.0 mg, 5%): mp 117—118 °C (lit, mp 129, 124, 118 °C)[5] and *trans*-[PtBr(Mes)(SEt_2)$_2$] as colorless crystals (104 mg, 40%): mp 130—131 °C. Found: C, 35.90; H, 5.57; Br, 14.35%. Calcd for $C_{17}H_{31}BrPtS_2$: C, 35.54; H, 5.44; Br, 13.91%. ^{1}H NMR (90 MHz, C_6D_6) δ=0.95 (12H, t, J_H=7.3 Hz, CH_3 of Et), 2.22 (3H, s, J_{Pt}=5.2 Hz, *p*-CH_3), 2.63 (8H, q, J_H=7.1 Hz, J_{Pt}=42.7 Hz, CH_2 of Et), 2.74 (6H, s, J_{Pt}=8.1 Hz, *o*-CH_3), 6.78 (2H, s, J_{Pt}=8.9 Hz, *m*-H);[6] ^{13}C NMR (22.6 MHz, C_6D_6) δ=13.0 (q, J_{Pt}=42.7 Hz, CH_3 of Et), 20.8 (q, *p*-CH_3), 26.4 (q, J_{Pt}=52.9 Hz, *o*-CH_3), 30.2 (t, J_{Pt}=13.2 Hz, CH_2 of Et), 133.2, 133.4, and 141.3 (aromatic ring carbons);[6] MS *m*/*z* 572 (M^+, based on ^{194}Pt; 6), 482 (1), 403 (10), 392 (1), 374 (42), 362 (7), 346 (21), 281 (9), 120 (96), 105 (83), 90 (100), 75 (73).

***trans*-[PtCl(Mes)(SEt_2)$_2$].** Lithium bromide-free mesityllithium was prepared by removing the supernatant of the reaction mixture by decantation and washing the white, fine crystals of mesityllithium with dry ether several times. This suspension of mesityllithium (0.45 mmol) in ether was added to a solution of *cis*-[$PtCl_2(SEt_2)_2$] (200 mg, 0.448 mmol) in benzene (20 ml) and the mixture was stirred for 2.5 h at room temperature. After removal of the solvent, purification by column chromatography (200 mesh alumina, benzene) followed by recrystallization from hexane gave *trans*-[PtCl(Mes)(SEt_2)$_2$] as colorless crystals (94 mg, 36%): mp 119 °C. Found: C, 38.81; H, 5.95; S, 12.05; Cl, 7.05%. Calcd for $C_{17}H_{31}ClPtS_2$: C, 38.52; H, 5.89; S, 12.10; Cl, 6.69%. ^{1}H NMR (90 MHz, C_6D_6) δ=0.97 (12H, t, J_H=7.6 Hz, CH_3 of Et), 2.23 (3H, bs, *p*-CH_3), 2.60 (8H, q, J_H=7.9 Hz, J_{Pt}=44.0 Hz, CH_2 of Et), 2.78 (6H, s, J_{Pt}=7.9 Hz, *o*-CH_3), 6.80 (2H, s, J_{Pt}=8.0 Hz, *m*-H);[6] ^{13}C NMR (22.6 MHz, C_6D_6) δ=12.8 (q, J_{Pt}=41.2 Hz, CH_3 of Et), 20.8 (q, *p*-CH_3), 28.8 (q, J_{Pt}=50.9 Hz, *o*-CH_3), 29.1 (t, J_{Pt}=13.4 Hz, CH_2 of Et), 133.1 and 141.6 (aromatic ring carbons);[6] MS *m*/*z* 528 (M^+, based on ^{194}Pt; 6), 438 (1), 403 (2), 374 (41), 346 (24), 318 (8), 282 (6), 120 (81), 105 (77), 90 (100), 75 (97).

***trans*-[Pt(Mes)$_2$(SEt_2)$_2$].** To a solution of *cis*-[$PtCl_2(SEt_2)_2$] (200 mg, 0.448 mmol) in ether (20 ml) was added a suspension of mesityllithium (1.2 mmol) in ether. After stirring for 14 h at room temperature, the solvent was removed in vacuo. The ^{1}H NMR spectrum of the residue in $CDCl_3$ showed both signals of *trans*-[PtBr(Mes)(SEt_2)$_2$] and *trans*-[Pt(Mes)$_2$(SEt_2)$_2$]. The molar ratio of these two products was nearly 1 : 1. Ether and water were added to the residue to remove salt and the ether layer was concentrated. Recrystallization of the residue from methanol yielded *trans*-[Pt(Mes)$_2$(SEt_2)$_2$][3] as colorless crystals (24 mg, 18%): Mp 175—178 °C (decomp) (lit, mp 180 °C (decomp)).[3]

Spectral Measurements. The reactions of *cis*-[$PtCl_2(SEt_2)_2$] with lithium bromide and mesityllithium were followed by monitoring the spectral changes. To a benzene solution of the complex placed in a quartz cell (optical path length=1 cm) was added a solution of slightly excess lithium bromide

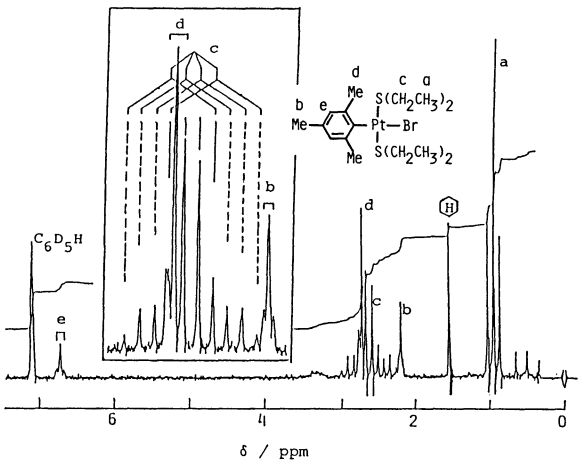

Fig. 1. ^{1}H NMR spectrum of *trans*-[PtBr(Mes)-$(SEt_2)_2$] in C_6D_6 (internal standard, cyclohexane). The inset shows an expanded spectrum in the region of about 2 to 3 ppm.

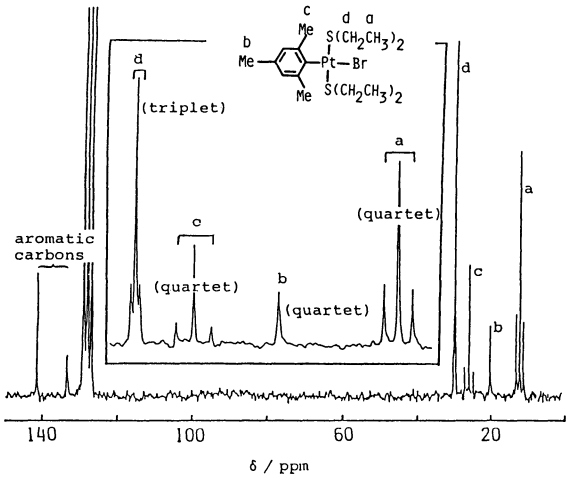

Fig. 2. ^{13}C NMR spectrum of *trans*-[PtBr(Mes)-$(SEt_2)_2$] in C_6D_6. The inset shows an expanded spectrum in the region of the signals of aliphatic carbons. Off resonance patterns are shown in parentheses.

or mesityllithium in ether. Absorption maxima of *cis*-$[PtCl_2(SEt_2)_2]$, *trans*-$[PtBr(Mes)(SEt_2)_2]$, *trans*-$[PtCl_2(SEt_2)_2]$, and *trans*-$[PtBr_2(SEt_2)_2]$ appear at 330, 306 (shoulder), 338, and 357 nm, respectively.

Results and Discussion

Reaction of *cis*-$[PtCl_2(SEt_2)_2]$ with Mesityllithium. When *cis*-$[PtCl_2(SEt_2)_2]$ in benzene was treated with an ether solution of slightly excess mesityllithium prepared from bromomesitylene and butyllithium, two products, *trans*-$[PtBr(Mes)(SEt_2)_2]$ and *trans*-$[PtBr_2(SEt_2)_2]$, were obtained in 40 and 5% yields, respectively, after purification with an alumina column.

$$cis\text{-}[PtCl_2(SEt_2)_2] + MesLi/LiBr \xrightarrow[0\ ^\circ C - r.t.]{\text{ether-benzene}} trans\text{-}[PtBr(Mes)(SEt_2)_2] + trans\text{-}[PtBr_2(SEt_2)_2]$$

The molecular formula of *trans*-$[PtBr(Mes)(SEt_2)_2]$ was determined by elemental analysis and mass spectroscopy. The ^{1}H NMR spectrum of *trans*-$[PtBr(Mes)(SEt_2)_2]$ shows only one set of signals assigned to ethyl groups (Fig. 1) that is consistent with the trans form. The configuration is further confirmed by the ^{13}C NMR spectrum which likewise exhibits a set of ethyl carbon signals (Fig. 2). The known compound *trans*-$[PtBr_2(SEt_2)_2]$ was identified by comparing its melting point (117—118 °C) to the literature value (129, 124, and 118 °C; cf. cis-isomer, mp 93—95 °C)[5] and by measuring mass, ^{1}H NMR, and ^{13}C NMR spectra.

The origin of bromo ligands in *trans*-$[PtBr(Mes)(SEt_2)_2]$ and *trans*-$[PtBr_2(SEt_2)_2]$ is considered to be lithium bromide which was formed as a by-product when mesityllithium was prepared. In fact, when lithium bromide-free mesityllithium was used for the reaction, the major product was *trans*-$[PtCl(Mes)(SEt_2)_2]$ (36%). The reaction of *cis*-$[PtCl_2(SEt_2)_2]$ with ca. 2.5 equivalent of mesityllithium afforded a 1 : 1 mixture of *trans*-$[PtBr(Mes)(SEt_2)_2]$ and *trans*-$[Pt(Mes)_2(SEt_2)_2]$.

Reaction Mechanism. The mechanism of the conversion from *cis*-$[PtCl_2(SEt_2)_2]$ to *trans*-$[PtBr(Mes)(SEt_2)_2]$ should, at least, involve the following three reactions: (a) nucleophilic substitution of halide by mesityl anion, (b) cis-trans isomerization of a square-planar complex, and (c) substitution of chloro ligand by bromo ligand. The ligand substitution reaction of square-planar platinum(II) complexes usually occurs with the retention of geometrical configuration.[7] In other words, the reaction (b) (cis-trans isomerization) is normally much slower than the reactions (a) and (c) (ligand substitutions). However, this empirical rule seems not to apply to the present reaction, since only the isomerized products have been obtained.

The reaction of *cis*-$[PtCl_2(SEt_2)_2]$ in a benzene-ether mixture in the presence of lithium bromide was monitored at 21 °C by periodic measurements of UV-visible spectra, but only a slight change of the spectrum was observed even after two hours. In sharp contrast with this result, when mesityllithium was added to a benzene solution of *cis*-$[PtCl_2(SEt_2)_2]$, this compound disappeared within 30 min and *trans*-$[PtBr(Mes)(SEt_2)_2]$ was formed. These experimental results indicate that mesityllithium accelerates the geometrical isomerization. The formation of *trans*-$[PtBr_2(SEt_2)_2]$ shows that the geometrical isomerization of the platinum(II) complex occurs before the displacement of a coordinated halide ion by a mesityl anion. Low solubility of mesityllithium in ether as well as the bulkiness of mesityl group may significantly contribute to the slow substitution.

From these results, the following mechanism is suggested, where mesityllithium catalyzes the fast cis-trans isomerization followed by the relatively slow substitution by mesityl group (Scheme 1).

$$cis\text{-}[PtCl_2(SEt_2)_2] \xrightarrow{MesLi,\ LiX} trans\text{-}[PtX_2(SEt_2)_2] \quad X = Cl \text{ or } Br$$

$$trans\text{-}[PtX_2(SEt_2)_2] + MesLi \longrightarrow trans\text{-}[PtX(Mes)(SEt_2)_2]$$

Scheme 1.

^{13}C NMR Spectra. The ^{13}C NMR spectrum of *trans*-[PtBr(Mes)(SEt_2)$_2$] shows typical ^{195}Pt couplings on the signals of diethyl sulfide ligands (Fig. 2). A somewhat surprising result is that the methylene carbons show smaller coupling constant ($^2J_{Pt}$=13.2 Hz) than the methyl carbons ($^3J_{Pt}$=42.7 Hz). The spectrum of chloro complex exhibits the same phenomenon ($^2J_{Pt}$=13.4 Hz, $^3J_{Pt}$=41.2 Hz). To our knowledge, there is no report which mentions this phenomenon, but a similar reversal of ^{195}Pt coupling constants can be seen in the ^{13}C NMR spectra of aryl groups in many arylplatinum complexes, where the ^{195}Pt coupling constant on ortho carbon ($^2J_{Pt}$) is smaller than that on meta carbon ($^3J_{Pt}$).[1)]

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References

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2) Abbreviations used in this paper: Et=C_2H_5, Pr=C_3H_7, Ph=C_6H_5, Ar=aryl, Mes=mesityl (2,4,6-trimetylphenyl).
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6) J_{Pt} is a coupling constant of ^{195}Pt satellites (the natural abundance of ^{195}Pt=33.7%).
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