Synthesis of Stable *cis*-Dichloro- and *cis*-Dimethylplatinum(II) Complexes Bearing Bulky Primary Phosphines and Introduction of an Alkyl Group on the Primary Phosphine Ligand

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Stable *cis*-dichloro- and *cis*-dimethylplatinum(II) complexes bearing bulky primary phosphines, such as BbtPH₂ (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl) and TbtPH₂ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl), were synthesized and isolated as stable compounds. The treatment of *cis*-[PtMe₂(PH₂Bbt)₂] with lithium diisopropylamide (LDA) followed by the addition of an alkyl halide afforded the corresponding alkylated complexes, *cis*-[PtMe₂(PHRBbt)(PH₂Bbt)] (R = Me, Et, Bu, etc.). The spectroscopic observation of the intermediacy of the lithiated complex, *cis*-[PtMe₂(PHLiBbt)(PH₂Bbt)], has been accomplished.

Several types of phosphines are frequently used as ligands toward transition metals and play important roles in catalytic chemistry.1 While the ligand chemistry of tertiary phosphines (R₃P) has been well established,¹ that of secondary phosphines (R_2PH) has attracted much attention from the viewpoints of their lower steric hindrance as compared with tertiary phosphines and unique reactivity of the P-H bond, which can potentially undergo deprotonation followed by introduction of another functional group or oligomerization leading to novel multinuclear complexes.² Although primary phosphines (RPH₂) should exhibit reactivities characteristic of the PH2 moiety and work as a unique ligand as well as secondary phosphines, primary phosphines have been less studied as a ligand toward transition-metal complexes most probably owing to their inherent instability under ambient conditions and their extremely high reactivity toward transition-metal complexes.³ Attempted synthesis of *cis*-dichloroplatinum complex, cis-[PtCl₂(MesPH₂)₂], by the reaction of [PtCl₂(cod)] with MesPH₂ resulted in the formation of a bridged dimer, $[PtCl(PH_2Mes)(\mu-PHMes)]_2$, generated by the intermolecular dehydrochlorination reaction of the intermediary cis-[PtCl₂(PH₂Mes)₂].⁴ On the other hand, the isolation of Mes*PH₂ $(Mes^* = 2,4,6-tri-t-butylphenyl)$ demonstrated that a primary phosphine bearing a bulky aryl substituent can be easily handled as a stable compound even in the open air.⁵ We have already reported the synthesis and isolation of new, stable primary phosphines, BbtPH₂ and TbtPH₂, which have the effective steric protection groups, Bbt and Tbt, respectively.⁶ We describe here the synthesis of the stable *cis*-dichloro- and *cis*-dimethylplatinum(II) complexes bearing $ArPH_2$ (Ar = Tbt and Bbt) ligands and the alkylation of the PH moiety of the cis-dimethylplatinum(II) complexes leading to the formation of novel platinum(II) complexes bearing both primary and secondary phosphines.

The reaction of *cis*-[PtCl₂(cod)] with ArPH₂ (Ar = Tbt and Bbt) in CHCl₃ at 72 °C gave the corresponding *cis*-dichloroplatinum(II) complexes **1a** and **1b** bearing bulky primary phosphines in high yields (**1a**, Ar = Tbt, 90%; **1b**, Ar = Bbt, 81%, Scheme 1).⁷ Of particular note is that *cis*-dichloroplatinum com-

plexes 1a and 1b are stable even under reflux conditions in CHCl₃ in contrast to the case of cis-[PtCl₂(PH₂Mes)₂],^{4a} which undergoes facile dimerization at room temperature, reflecting the steric protection ability of Tbt and Bbt groups. X-ray crystallographic analysis of $1a^7$ (Figure 1) showed that the P-Pt [2.3329(12)-2.3503(12) Å] and Pt-Cl [2.2155(11)-2.2194(12) Å] bonds of **1a** were somewhat longer and shorter than those of the known dichloroplatinum(II) complex bearing secondary phosphines, *cis*-[PtCl₂(PHMes₂)₂] (**3**)⁸ [P-Pt: 2.2315(9)-2.2481(9) Å, Pt-Cl: 2.3385(9)-2.3445(10) Å]. Although one can guess that such structural features should be due to the electronic properties of a primary phosphine, the longer P-Pt bonds of 1a, which make the Pt-Cl bonds of 1a shorter for electronic reasons (such as trans influence),¹ should be due to the steric bulkiness of the Tbt group. Indeed, the theoretical calculations showed that the optimized structure of dichloroplatinum(II) complex bearing less hindered primary phosphines, cis-[PtCl₂(PH₂Ph)₂], is similar to that of *cis*-[PtCl₂(PHPh₂)₂] bearing secondary phosphines with respect to the Pt-P and Pt-Cl bond lengths (Table S1).⁷ That is, the inherent coordinating ability of a primary phosphine should be similar to that of a secondary phosphine from the viewpoint of electronic properties. The NMR data (Table S2, $\delta_{\rm P}$, $\delta_{\rm H}$ (ArPH₂), $\delta_{\rm Pt}$, ${}^{1}J_{\rm PPt}$, ${}^{1}J_{\rm HP}$) of **1a** and 1b were in good agreement with those of the previously reported cis-[PtCl₂(PH₂Mes)₂] (4),⁸ indicating that the perturbation based



Figure 1. Molecular structures of (a) 1a and (b) 2. Thermal ellipsoids are drawn at 50% (for 1a) and 30% (for 2) probability levels. Hydrogen atoms other than those on the P atoms are omitted for clarity. One of the two independent molecules of 1a in the unit cell was shown.

on the steric bulkiness of Tbt and Bbt groups in **1a** and **1b** should be negligible in solution.

On the other hand, the treatment of *cis*-[PtMe₂(cod)] with BbtPH₂ in benzene at room temperature afforded *cis*-[PtMe₂-(PH₂Bbt)₂] (2) as stable colorless crystals in 73% yield. Dimethylplatinum(II) complex 2 is stable under ambient conditions in the solid and even in solution, though it underwent decomposition at 60 °C in CHCl₃ to afford a complicated mixture. To the best of our knowledge, no report has appeared on the synthesis and generation of a dimethylplatinum(II) complex bearing primary phosphines,⁹ and hence the spectroscopic properties of 2 should be of great importance. In the NMR spectra, characteristic signals corresponding to BbtPH₂ units were observed at δ_P -73.7, $\delta_{\rm H}$ 5.10, and $\delta_{\rm Pt}$ -4504 with coupling constants of ${}^{1}J_{\rm HP} = 323 \,{\rm Hz}$ and the satellite of ${}^{1}J_{\rm PPt} = 1472$, where the $\delta_{\rm P}$ and $\delta_{\rm H}$ values were shifted to a lower field region than those of the free ligand (BbtPH₂, $\delta_{\rm P}$ -145.2, $\delta_{\rm H}$ 3.62, ${}^{1}J_{\rm PH}$ = 203). Xray crystallographic analysis of 2 showed that 2 possesses a C2 axis passing through the central Pt atom in the crystalline state and its Pt-P bond length is 2.272(4) Å, the value of which is similar to those of $[PtMe_2(PR_3)_2]$ (PR₃ = PEt₃, PMe₂Ph, etc.).¹⁰

We have examined the modification of the P-H moiety of 2. The treatment of 2 with an excess amount of LDA in THF at 0 °C followed by the addition of an alkyl halide (RX) as an electrophile afforded the corresponding dimethylplatinum(II) complexes 5a-5e bearing BbtPH₂ and BbtPHR in moderate yields (Scheme 2 and Table 1). The formation of 5a-5e in these reactions should be most likely interpreted in terms of the intermediacy of cis-[PtMe₂(PH₂Bbt)(PHLiBbt)] (6), the formation of which was evidenced by the ³¹P NMR spectral data reasonably assignable to those of **6** [in THF, δ_P -71.0 (${}^1J_{PPt} = 642 \text{ Hz}$, ${}^{2}J_{\text{PP}} = 18.5 \text{ Hz}, {}^{1}J_{\text{PH}} = 183 \text{ Hz}), -63.4 ({}^{1}J_{\text{PPt}} = 1675 \text{ Hz}, {}^{2}J_{\text{PP}} = 18.5 \text{ Hz}, {}^{1}J_{\text{PH}} = 311 \text{ Hz})].^{11}$ Lithiated compound **6** was found to be stable in THF at 0 °C, though the complicated mixture was obtained on warming up of the reaction mixture to room temperature in the sealed tube. When BuCl was used as an electrophile, not the expected complex, 5d, but a complicated mixture was obtained. However, 5d was obtained by using BuBr as an electrophile, implying the electron-transfer process in the reaction of 6 with electrophiles.



Table 1. Lithiation of 2 followed by the addition of electrophiles

Electrophile	Product	2		1	
		Yield/%	$\delta_{ m P}$	$\delta_{ m Pt}$	$^{1}J_{\rm PPt}/{\rm Hz}$
MeI	5a	69	-57.9	-4498	1540
	$(\mathbf{R} = \mathbf{M}\mathbf{e})$		-79.5		1556
EtBr	5b	83	-33.8	-4520	1483
	$(\mathbf{R} = \mathbf{Et})$		-71.0		1554
PrBr	5c	81	-33.8	-4479	1482
	$(\mathbf{R} = \mathbf{Pr})$		-71.9		1537
BuCl	C.M.	_	_	_	_
BuBr	5d	78	-39.4	-4490	1495
	$(\mathbf{R} = \mathbf{B}\mathbf{u})$		-70.8		1553
OctBr	5e	63	-39.5	-4515	1493
	(R = Oct)		-70.9		1551

In summary, a variety of *cis*-dichloro- and *cis*-dimethylplatinum(II) complexes bearing primary phosphine ligands have been successfully synthesized as stable compounds. It was found that *cis*-[PtMe₂(PH₂Bbt)₂] (**2**) could be deprotonated by the addition of an excess amount of LDA to give *cis*-[PtMe₂(PH₂Bbt)(PHLiBbt)] (**6**), which was trapped by alkyl halides to afford the corresponding alkylated complexes **5**, *cis*-[PtMe₂(PH₂Bbt)(PHRBbt)].

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References and Notes

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