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

Takahiro Sasamori, Masahiro Kawai, Nobuhiro Takeda,[†] and Norihiro Tokitoh[*]
Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011

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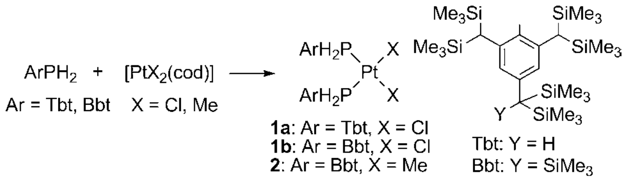
Stable *cis*-dichloro- and *cis*-dimethylplatinum(II) complexes bearing bulky primary phosphines, such as $BbtPH_2$ (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl) and $TbtPH_2$ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl), were synthesized and isolated as stable compounds. The treatment of *cis*-$[PtMe_2(PH_2Bbt)_2]$ with lithium diisopropylamide (LDA) followed by the addition of an alkyl halide afforded the corresponding alkylated complexes, *cis*-$[PtMe_2(PHRBbt)(PH_2Bbt)]$ (R = Me, Et, Bu, etc.). The spectroscopic observation of the intermediacy of the lithiated complex, *cis*-$[PtMe_2(PHLiBbt)(PH_2Bbt)]$, 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 (R_3P) 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 (RPH_2) should exhibit reactivities characteristic of the PH_2 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*-$[PtCl_2(MesPH_2)_2]$, by the reaction of $[PtCl_2(cod)]$ with $MesPH_2$ resulted in the formation of a bridged dimer, $[PtCl(PH_2Mes)(\mu\text{-}PHMes)]_2$, generated by the intermolecular dehydrochlorination reaction of the intermediary *cis*-$[PtCl_2(PH_2Mes)_2]$.[4] On the other hand, the isolation of Mes^*PH_2 (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, $BbtPH_2$ and $TbtPH_2$, 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*-$[PtCl_2(cod)]$ with $ArPH_2$ (Ar = Tbt and Bbt) in $CHCl_3$ 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 complexes **1a** and **1b** are stable even under reflux conditions in $CHCl_3$ in contrast to the case of *cis*-$[PtCl_2(PH_2Mes)_2]$,[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*-$[PtCl_2(PHMes_2)_2]$ (**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*-$[PtCl_2(PH_2Ph)_2]$, is similar to that of *cis*-$[PtCl_2(PHPh_2)_2]$ 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, δ_P, $\delta_H(ArPH_2)$, δ_{Pt}, $^1J_{PPt}$, $^1J_{HP}$) of **1a** and **1b** were in good agreement with those of the previously reported *cis*-$[PtCl_2(PH_2Mes)_2]$ (**4**),[8] indicating that the perturbation based



Scheme 1.

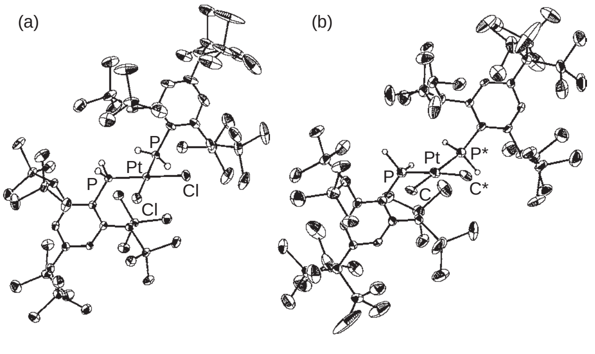
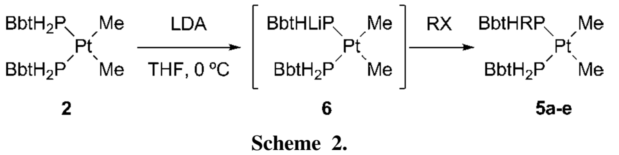


Figure 1. Molecular structures of (a) **1a** and (b) **2**. Thermal ellipsoids are drawn at 50% (for **1a**) and 30% (for **2**) probability levels. Hydrogen atoms other than those on the P atoms are omitted for clarity. One of the two independent molecules of **1a** in the unit cell was shown.

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*-[$PtMe_2$(cod)] with $BbtPH_2$ in benzene at room temperature afforded *cis*-[$PtMe_2$(PH_2Bbt)$_2$] (**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 $CHCl_3$ 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 $BbtPH_2$ units were observed at δ_P −73.7, δ_H 5.10, and δ_{Pt} −4504 with coupling constants of $^1J_{HP} = 323$ Hz and the satellite of $^1J_{PPt} = 1472$, where the δ_P and δ_H values were shifted to a lower field region than those of the free ligand ($BbtPH_2$, δ_P −145.2, δ_H 3.62, $^1J_{PH} = 203$). X-ray crystallographic analysis of **2** showed that **2** possesses a *C*2 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 [$PtMe_2(PR_3)_2$] ($PR_3 = PEt_3$, PMe_2Ph, 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 $BbtPH_2$ 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*-[$PtMe_2$(PH_2Bbt)(PHLiBbt)] (**6**), the formation of which was evidenced by the ^{31}P NMR spectral data reasonably assignable to those of **6** [in THF, δ_P −71.0 ($^1J_{PPt} = 642$ Hz, $^2J_{PP} = 18.5$ Hz, $^1J_{PH} = 183$ Hz), −63.4 ($^1J_{PPt} = 1675$ Hz, $^2J_{PP} = 18.5$ Hz, $^1J_{PH} = 311$ 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.



Scheme 2.

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

Electrophile	Product	Yield/%	δ_P	δ_{Pt}	$^1J_{PPt}$/Hz
MeI	**5a**	69	−57.9	−4498	1540
	(R = Me)		−79.5		1556
EtBr	**5b**	83	−33.8	−4520	1483
	(R = Et)		−71.0		1554
PrBr	**5c**	81	−33.8	−4479	1482
	(R = Pr)		−71.9		1537
BuCl	C.M.	—	—	—	—
BuBr	**5d**	78	−39.4	−4490	1495
	(R = Bu)		−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*-[$PtMe_2$(PH_2Bbt)$_2$] (**2**) could be deprotonated by the addition of an excess amount of LDA to give *cis*-[$PtMe_2$(PH_2Bbt)(PHLiBbt)] (**6**), which was trapped by alkyl halides to afford the corresponding alkylated complexes **5**, *cis*-[$PtMe_2$(PH_2Bbt)(PHRBbt)].

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† Present address: Department of Chemistry and Chemical Biology, Graduate School of Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu 376-8515.

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