Synthesis and X-ray Structural Analysis of Hydrido(thiolato) Platinum(II) Complexes

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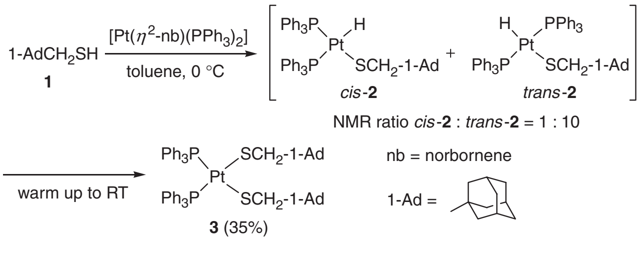
The oxidative addition of [Pt(η^2-nb)(PPh$_3$)$_2$] with a sterically hindered thiol, TripSH (**4**, Trip = 9-triptycyl) in toluene afforded *cis*-hydrido(thiolato) Pt^{II} complex [PtH(STrip)(PPh$_3$)$_2$] (**5**), as thermally and moisture-stable colorless crystals in 91% yield. Complex **5** was fully characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR and IR spectroscopies, and the molecular structure of **5** was determined by X-ray crystallography.

Transition metal catalyzed hydrothiolation and thiocarbonylation of alkynes are among the most attractive methods for the preparation of vinyl sulfides, which are valuable as synthetic intermediates in total syntheses and as precursors to a wide range of functionalized molecules.[1,2] In the Pt^0-catalyzed thiocarbonylations, hydrido(thiolato) Pt^{II} complexes are proposed as key intermediates.[3] Although the hydrido(thiolato) Pt^{II} complexes are readily obtained by the oxidative addition of thiol to Pt^0 complex, their full spectroscopic characterizations and crystal structure analyses have not been performed owing to their thermal instability. Only ^{1}H NMR and IR spectroscopic data of *trans*-[PtH(SPh)(PPh$_3$)$_2$] have been reported so far by Ugo et al.[4] and Ogawa et al.[3a]

Meanwhile, we have recently succeeded in the first isolation of stable hydrido(selenolato) platinum(II) complex *cis*-[PtH(SeTrip)(PPh$_3$)$_2$] (Trip = 9-triptycyl), which is postulated as the key intermediate in the Pt-catalyzed hydroselenation of alkynes.[5] In this paper, we report the synthesis of the stable *cis*-hydrido(thiolato) Pt^{II} complex by the reaction of an overcrowded alkanethiol with Pt^0 complex and its X-ray crystallographic analysis.

We first examined the reaction of 1-AdCH$_2$SH (**1**, 1-Ad = 1-adamantyl)[6] with 1 equiv of [Pt(η^2-nb)(PPh$_3$)$_2$] (nb = norbornene)[7] in toluene at 0 °C for 30 min (Scheme 1). The ^{1}H NMR spectrum of the reaction mixture showed characteristic high-field shifted signals at δ −8.69 (s, $J_{\text{Pt–H}} = 851$ Hz) and −5.11 (dd, $J_{\text{P–H}} = 195, 23$ Hz, $J_{\text{Pt–H}} = 1004$ Hz), indicating the generation of *trans*- and *cis*-hydrido(thiolato) Pt^{II} complexes (*trans*-**2**: *cis*-**2** = 10:1), together with a singlet assignable to the methylene protons (δ 3.25–3.33) of *cis*-(dithiolato) Pt^{II} complex [Pt(SCH$_2$-1-Ad)$_2$(PPh$_3$)$_2$] (**3**).[8] In the ^{31}P{^{1}H} NMR spectrum, the signals assigned to *cis*-**2** and *trans*-**2** were observed at δ 21.3 (d, $^1J_{\text{P–P}} = 15$ Hz, $^2J_{\text{Pt–P}} = 2945$ Hz) and 30.5 (d, $^1J_{\text{P–P}} = 15$ Hz, $^2J_{\text{Pt–P}} = 1960$ Hz) for *cis*-**2** and 31.6 (s, $^2J_{\text{Pt–P}} = 3053$ Hz) for *trans*-**2**. However, *cis*- and *trans*-**2** were thermally unstable and were converted gradually at room temperature to **3**. This conversion would occur by the reaction of *cis*- and/or *trans*-**2** with thiol **1** that remained in the reaction system. In fact, the reaction of **1** with a half amount of [Pt(η^2-nb)(PPh$_3$)$_2$] in toluene afforded only **3** in 35% isolated yield. The molecular structure of **3** was fully determined by NMR spectroscopic data[7] and X-ray crystallography.[9] The ^{31}P{^{1}H} NMR spectrum for **3** demonstrated a singlet signal with the ^{195}Pt satellites at δ 27.0 ($^1J_{\text{Pt–P}} = 2827$ Hz). In the X-ray analysis of **3** (Figure 1), two thiolato ligands were coordinated in cis position to the platinum center. The Pt–S bond lengths were 2.3500(15) and 2.3816(15) Å, which are slightly elongated compared with those of the aliphatic *cis*-dithiolato Pt^{II} complex [Pt(S$_2$C$_7$H$_8$)-(PPh$_3$)$_2$] (C$_7$H$_8$ = 1,3-cycloheptadiene-5,6-diyl) [2.339(4), 2.308(4) Å][10] because of the steric influence of the bulky 1-adamantyl groups.



Scheme 1.

To obtain a stable hydrido(thiolato) Pt^{II} complex, we next examined the oxidative addition of the thiol having an extremely bulky Trip group with a Pt^0 complex. Thus, treatment of TripSH (**4**) with [Pt(η^2-nb)(PPh$_3$)$_2$] in toluene resulted in the immediate formation of *cis*-hydrido(thiolato) Pt^{II} complex [PtH(STrip)-(PPh$_3$)$_2$] (**5**), which was isolated as colorless crystals in 91% yield (Scheme 2).[11] In the ^{1}H NMR of **5**, the platinum hydride resonated as a doublet of doublets at δ −5.96 ($^2J_{\text{P–H}} = 189$, 18 Hz, $^1J_{\text{Pt–H}} = 947$ Hz), which is shifted downfield relative to that of *trans*-[Pt(H)(SPh)(PPh$_3$)$_2$] [δ −10.01 ($^2J_{\text{P–H}} = 14$ Hz, $^1J_{\text{Pt–H}} = 961$ Hz)]. The ^{31}P{^{1}H} NMR spectrum of **5** displayed two doublets with the ^{195}Pt satellites at δ 23.1 ($^1J_{\text{Pt–P}} = 3189$ Hz) and 32.4 ($^1J_{\text{Pt–P}} = 1963$ Hz), which were assigned to the signals due to the phosphorus atoms lying trans to the thio-

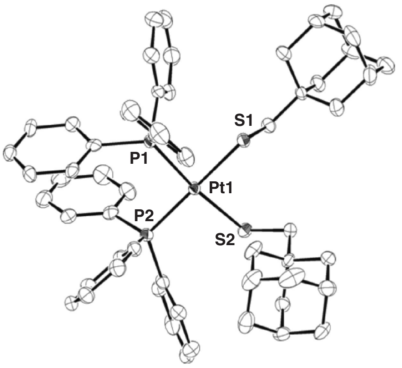
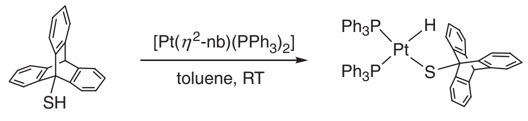


Figure 1. ORTEP drawing of **3** (30% thermal ellipsoids). Two solvated toluene molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1–S1 = 2.3500(15), Pt1–S2 = 2.3816(15), Pt1–P1 = 2.2738(16), Pt1–P2 = 2.2924(15), S1–Pt1–S2 = 92.50(5), P1–Pt1–P2 = 98.18(6), P1–Pt1–S1 = 88.69(6), P2–Pt1–S2 = 81.77(5), P1–Pt1–S2 = 177.47(6), P2–Pt1–S1 = 173.14(6).



4 **5** (91%)

Scheme 2.

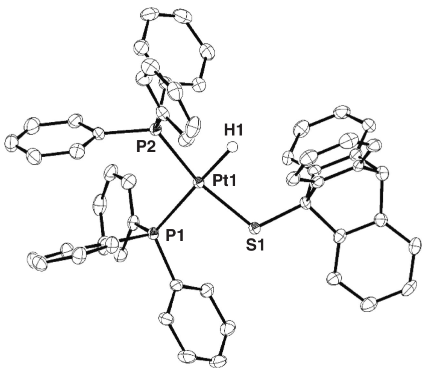
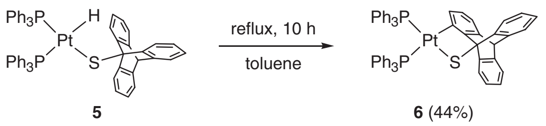


Figure 2. ORTEP drawing of **5** (30% thermal ellipsoids). Two solvated CH_2Cl_2 molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1–S1 = 2.3172(12), Pt1–H1 = 1.684(10), Pt1–P1 = 2.3411(12), Pt1–P2 = 2.2511(12), S1–Pt1–H1 = 88(2), P1–Pt1–P2 = 103.25(4), P1–Pt1–S1 = 90.51(4), P2–Pt1–H1 = 78(2), P2–Pt1–S1 = 165.75(4), P1–Pt1–H1 = 178(2).

lato ligand and the hydride, respectively. In the IR spectrum, the absorption due to the Pt–H stretching vibration for **5** was observed at a somewhat lower wavenumber (2100 cm^{-1}) compared to that of stable hydrido(selenolato) Pt^{II} complex *cis*-[PtH(SeTrip)(PPh$_3$)$_2$] (2093 cm^{-1}).[5] The molecular structure of **5** was determined by X-ray crystallography as depicted in Figure 2.[9] In the crystalline state, the platinum core lies at the centre of a distorted square-planar coordination sphere consisting of two PPh$_3$ ligands, sulfur, and hydrogen atoms. The P1–Pt1–P2 angle of 103.25(4)° considerably deviated from the ideal 90° of square-planar geometry. The Pt1–S1 bond length was 2.3172(12) Å, which is in the range of typical values of reported dithiolato Pt^{II} complexes *cis*-[Pt(1,8-S$_2$-Np)(PPh$_3$)$_2$] (Np = naphthalene) [2.320(1), 2.326(1) Å],[12] and [Pt(S$_2$C$_7$H$_8$)(Ph$_3$P)$_2$] [2.339(4), 2.308(4) Å].[10] The Pt1–P1 bond length [2.3411(12) Å] was slightly longer than that of the Pt1–P2 [2.2511(12) Å], suggesting the lower trans influence of the hydride compared to the thiolato ligand.

While complex **5** is thermally stable in the solid state (Mp: 136–138 °C), heating a toluene solution of **5** at 100 °C for 10 h gave a five-membered thiaplatinacycle **6**,[13] which is formed by an intramolecular C–H activation leading to the cyclometalation (Scheme 3). The ^1H NMR spectrum of **6** exhibited a characteristic signal due to the aromatic proton neighboring the Pt atom at δ 5.92, which is similar to that of the corresponding selenaplatinacycle (δ 5.85).[5] The $^{31}P\{^1H\}$ NMR spectrum of **6** showed two doublets with the ^{195}Pt satellites at δ 24.5 ($^2J_{P-P} = 21$ Hz, $^1J_{Pt-P} = 1852$ Hz) and 26.2 ($^2J_{P-P} = 21$ Hz, $^1J_{Pt-P} = 3183$ Hz). While there are some reports on six-membered thiaplatinacycles prepared by the insertion reactions of Pt^0 complexes into the C–S bond of thiophene derivatives,[14] this result is the first example of five-membered thiaplatinacycles.



5 **6** (44%)

Scheme 3.

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8 **3**: mp 148 °C, ^1H NMR (C_6D_6, 400 MHz, δ): 1.70 (br s, 24H), 2.00 (br s, 6H), 3.25–3.33 (m, 4H), 6.88–7.00 (m, 18H), 7.58–7.60 (m, 12H); $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, δ): 27.0 (s, $^1J_{Pt-P} = 2827$ Hz). Anal. Calcd for $C_{58}H_{64}P_2PtS_2$: C, 64.37; H, 5.96%. Found: C, 63.68; H, 6.06%.

9 Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-721303 for **3** and CCDC-721304 for **5**.

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11 **5**: mp 136–138 °C, ^1H NMR ($CDCl_3$, 400 MHz, δ): −5.96 (dd, $^2J_{P-H} = 189$, 18 Hz, $^1J_{Pt-H} = 947$ Hz, 1H), 5.28 (s, 1H), 6.91–7.04 (m, 12H), 7.13–7.35 (m, 24H), 7.60–7.64 (m, 6H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, δ): 23.1 (d, $^2J_{P-P} = 15$ Hz, $^1J_{Pt-P} = 3189$ Hz), 32.4 (d, $^2J_{P-P} = 15$ Hz, $^1J_{Pt-P} = 1963$ Hz). IR (KBr) (ν, cm^{-1}): 2100. Anal. Calcd for $C_{56}H_{44}P_2PtS \cdot 2(CH_2Cl_2)$: C, 59.24; H, 4.11%. Found: C, 59.29; H, 3.99%.

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13 **6**: mp 253–254 °C, ^1H NMR ($CDCl_3$, 400 MHz, δ): 5.24 (s, 1H), 5.92 (dt, $J = 8.1$ Hz, 1H), 6.52 (t, $J = 8$ Hz, 1H), 6.73 (d, $J = 7$ Hz, 1H), 6.88–6.98 (m, 12H), 7.12–7.40 (m, 18H), 7.62–7.69 (m, 6H), 7.89 (d, $J = 8$ Hz, 2H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, δ): 24.5 (d, $^2J_{P-P} = 21$ Hz, $^1J_{Pt-P} = 1852$ Hz), 26.2 (d, $^2J_{P-P} = 21$ Hz, $^1J_{Pt-P} = 3183$ Hz). Anal. Calcd for $C_{56}H_{42}P_2PtS$: C, 66.99; H, 4.22. Found: C, 66.68; H, 4.11.

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