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Synthesis and structure of thiolato bridged Pt–Ti heterobimetallic complexes with methyl group

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Abstract

Sulfur bridged Pt–Ti heterobimetallic complexes, $Cp_2Ti(\mu\text{-}SR)_2PtMe_2$, (R = Me (**1a**), Ph (**1b**)) have been prepared by the reaction of $Cp_2Ti(SR)_2$ with $PtMe_2(nbd)$. X-ray structure analysis of **1a** reveals the *syn* conformation of the compound, while a facile equilibration between *syn* and *anti* conformers is observed in toluene solution by variable temperature ^1H-NMR.

Keywords: Heterobimetallic complexes; Synthesis; Pt–Ti

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1. Introduction

Early-late heterobimetallic compounds (ELHB) attract considerable interests in relation to various heterometallic catalysis and a number of such complexes have been prepared [1–4]. Sulfur ligands are often used as good bridging ligands to form such bimetallic complexes [5] and the thiolato bridged ELHB complexes have been proposed as intermediates in the thiolato transfer reaction [6]. Among them, however, ELHB complexes containing a late transition metal–alkyl bond are still rare. We previously prepared a series of heterodinuclear organometallic complexes as a possible model for active intermediate in heterobimetallic catalysis [7]. As a part of our continuous investigation in this line, we prepared a new Pt–Ti complex having Pt–Me bonds, $Cp_2Ti(\mu\text{-}SR)_2PtMe_2$ whose molecular structure has been established by X-ray crystallography.

2. Experimental details

2.1. General procedures

All manipulations were performed under deoxygenated nitrogen or argon using Schlenk techniques. Solvents were purified by usual methods and were stored under nitrogen before use. $PtMe_2(nbd)$ (nbd, norbornadiene) [8] and Cp_2TiSR_2 [9] were prepared by the literature methods. Other chemicals were used as purchased. NMR spectra were measured by a JEOL LA-300 spectrometer and IR spectra were recorded on a JASCO FTIR-5M under nitrogen.

2.2. Synthesis of $Cp_2Ti(\mu\text{-}SMe)_2PtMe_2$

A mixture of $TiCp_2(SMe)_2$ (79.8 mg, 0.320 mmol) and $PtMe_2(nbd)$ (95.1 mg, 0.300 mmol) in benzene was stirred overnight at room temperature. During the time the color of the solution changed from deep purple to deep red. After evaporation of all the volatile matters in vacuo, the residual solid was washed with hexane. Resultant red solid was recrystallized from THF/hexane to give deep red plates. Yield 145 mg (76%). M.p.

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(dec) = 195–197°C. Anal. Found: C, 33.44; H, 4.66; S, 11.70%. Calc. for $C_{14}H_{22}PtS_2Ti$: C, 33.80; H, 4.46; N, 12.89%. ^{1}H-NMR (in $C_6D_5CD_3$ at room temperature): *Anti* isomer δ 1.81 (s, J(Pt–H) = 83 Hz, 6H, Me), 2.36 (s, J(Pt–H) = 34 Hz, 6H, MeS), 4.99 (s, 10H, Cp), *Syn* isomer δ 1.86 (s, J(Pt–H) = 83 Hz, 6H, Me), 2.23 (s, J(Pt–H) = 34 Hz, 6H, MeS), 5.02, 5.05 (s, 5H each, Cp), ^{13}C{^{1}H}-NMR (in $C_6D_5CD_3$ at room temperature): *Anti* isomer δ −4.2 (s, PtMe, Pt satellite was not detected because of the low S/N ratio), 23.0 (s, J(Pt–C) = 12.8 Hz, SMe), 106.8 (s, Cp). *Syn* isomer δ −4.6 (s, J(Pt–C) = 731 Hz, PtMe), 23.7 (s, J(Pt–C) = 6.8 Hz, SMe), 105.5, 108.8 (s, Cp). ^{1}H-NMR (in C_6D_6 at room temperature): *Anti* isomer δ 1.98 (s, J(Pt–H) = 83 Hz, 6H, Me), 2.36 (s, J(Pt–H) = 34 Hz, 6H, MeS), 4.97 (s, 10H, Cp). *Syn* isomer δ 2.04 (s, J(Pt–H) = 83 Hz, 6H, Me), 2.24 (s, J(Pt–H) = 34 Hz, 6H, MeS), 4.97, 5.06 (s, 5H each, Cp).

2.3. Synthesis of $Cp_2Ti(\mu\text{-}SPh)_2PtMe_2$

A mixture of $TiCp_2(SPh)_2$ (79.3 mg, 0.200 mmol) and $PtMe_2$(nbd) (61.9 mg, 0.195 mmol) in benzene was stirred overnight at room temperature. During the time the color of the solution changed from deep purple to deep red. After evaporation of all the volatile matters in vacuo, the residual solid was washed with hexane. Resultant red solid was recrystallized from THF/hexane to give deep red plates. Yield 54.2 mg (45%). M.p. (dec) = 100–105°C. Anal. Found: C, 45.76; H, 4.63; S, 9.40%. Calc. for $C_{24}H_{26}PtS_2Ti$: C, 46.38; H, 4.22; N, 10.32%. ^{1}H-NMR (in $C_6D_5CD_3$ at room temperature): *Anti* isomer δ 2.11 (s, J(Pt–H) = 83 Hz, 6H, Me), 5.04 (s, 10H, Cp), 6.8–8.0 (m, 10H, SPh). *Syn* isomer δ 2.13 (s, J(Pt–H) = 84 Hz, 6H, Me), 4.86, 5.26 (s, 5H each, Cp), 6.8–8.0 (m, 10H, SPh).

2.4. Reaction of $Cp_2Ti(\mu\text{-}SMe)_2PtMe_2$ with CO

A benzene-d_6 solution (600 µl) of $Cp_2Ti(\mu\text{-}SPh)_2PtMe_2$ (5 mg, 0.01 mmol) was exposed to CO (1 atm) at room temperature. Immediately after introduction of CO into the solution, $Cp_2Ti(\mu\text{-}SMe)_2PtMe_2$ completely disappeared and $Cp_2Ti(SMe)_2$ and $PtMe_2(CO)_2$ were produced in 66 and 67% yields, respectively. These yields were estimated by the ^{1}H-NMR spectrum by using 1,4-dioxane as an internal standard. $Cp_2Ti(SMe)_2$ and $PtMe_2(CO)_2$ were identified by comparing ^{1}H-NMR spectrum of their authentic samples [9,10]. $Cp_2Ti(SMe)_2$ given by this work (in C_6D_6): δ 2.71 (s, 6H, SMe), 5.70 (s, 10H, Cp); $Cp_2Ti(SMe)_2$ prepared by the literature method [9] (in C_6D_6): δ 2.71 (s, 6H, SMe), 5.71 (s, 10H, Cp); $PtMe_2(CO)_2$ given by this work (in C_6D_6): δ 1.07 (s, J(Pt–H) = 77.4 Hz, 6H, Me); $PtMe_2(CO)_2$ prepared by the literature method [10] (in C_6D_6): δ 1.07 (s, J(Pt–H) = 77.8 Hz, 6H, Me).

2.5. X-ray structure analysis

Red crystals suitable for X-ray analysis were obtained from THF/hexane solution of **1a**. One of the selected crystals was mounted on a glass capillary. Data were collected with Mo–K_α radiation at room temperature and the crystallographic data are outlined in Table 1. During the data collection, standard reflections were measured after every 200 reflections to check the stability of the crystal and the diffractometer. No crystal decay was noticed. The crystal system was monoclinic and the space group was $P2_1/a$. Selected bond distances and angles are listed in Table 2. The unique set contained 2886 reflections within $6 < 2\theta < 50°$. Using the criteria $|F_o| > 3.0\sigma(|F_o|)$, where $\sigma(|F_o|)$ is the estimated standard deviation derived from the counting statistics, 1553 out of 2886 reflections were used. The structure was solved by direct methods. All atoms were refined anisotropically except the hydrogens which were located on the ideal positions and were not refined. The final R (R_w) value was 0.039(0.029).

3. Results and discussion

Treatment of $TiCp_2(SMe)_2$ with $PtMe_2$(nbd) in benzene in a day at room temperature gave a red heterobimetallic complex $Cp_2Ti(\mu\text{-}SMe)_2PtMe$ (**1a**) in 76% yield. A μ-SPh analogue (**1b**) was also prepared similarly. These complexes are thermally stable in the solid state under air, but decomposed in solution. It is inter-

Table 1
Crystallographic data for **1a**

Empirical formula	$C_{14}H_{22}S_2PtTi$
Formula weight	497.44
Crystal dimensions (mm × mm × mm)	0.30 × 0.12 × 0.03
Crystal system	Monoclinic
Space group	$P2_1/a$ (#14)
a (Å)	11.597(2)
b (Å)	10.091(2)
c (Å)	13.533(2)
β (°)	104.52(1)
V (Å^3)	1533.2(4)
Z	4
μ (cm^{-1})	9.851
F_{000}	952.00
$D_{\text{calc.}}$ (g cm^{-3})	2.155
Radiation	Mo–K_α
Temp. (K)	296
Unique reflections	2886
Used reflections for refinement	1553
R^a	0.039
$R_w{}^b$	0.029
S	1.54
Method of phase determination	Direct methods

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{0.5}$.

Table 2
Selected bond distances (A) and angles (°) for **1a**

Distances			
Pt(1)–Ti(1)	3.014(3)	Pt(1)–S(1)	2.358(5)
Pt(1)–S(2)	2.352(5)	Pt(1)–C(1)	2.09(2)
Pt(1)–C(2)	2.14(2)	Ti(1)–S(1)	2.436(5)
Ti(1)–S(2)	2.447(6)	S(1)–C(3)	1.82(2)
S(2)–C(4)	1.82(1)		
Angles			
Ti(1)–Pt(1)–S(1)	52.2(1)	Ti(1)–Pt(1)–S(2)	52.5(1)
Ti(1)–Pt(1)–C(1)	137.7(5)	Ti(1)–Pt(1)–C(2)	137.1(5)
S(1)–Pt(1)–S(2)	104.5(1)	S(1)–Pt(1)–C(1)	85.5(5)
S(1)–Pt(1)–C(2)	170.3(5)	S(2)–Pt(1)–C(1)	169.3(5)
S(2)–Pt(1)–C(2)	85.1(4)	C(1)–Pt(1)–C(2)	85.1(6)
Pt(1)–Ti(1)–S(1)	49.9(1)	Pt(1)–Ti(1)–S(2)	49.7(1)
S(1)–Ti(1)–S(2)	99.4(2)	Pt(1)–S(1)–Ti(1)	77.9(2)
Pt(1)–S(1)–C(3)	104.1(6)	Ti(1)–S(1)–C(3)	118.4(6)
Pt(1)–S(2)–Ti(1)	77.8(2)	Pt(1)–S(2)–C(4)	103.5(5)
Ti(1)–S(2)–C(4)	118.3(5)		

esting to note that the reaction of $TiCp_2(SMe)_2$ with $PtMe_2(cod)$ (cod, 1,5-cyclooctadiene) did not proceed. This result show the higher lability of the norbornadiene than the cod ligands [8].

$$Cp_2Ti(SR)_2 + PtMe_2(nbd) \xrightarrow[-\,nbd]{} Cp_2Ti(\mu - SR)_2PtMe_2 \quad (1)$$

R = Me (**1a**), Ph (**1b**)

Molecular structure of **1a** was unequivocally determined by X-ray structure analysis and the ORTEP drawing is depicted in Fig. 1. Crystallographic data and selected bond distances and angles are summarized in Tables 1 and 2.

The geometry at Pt is a typical square planar with *cis* configuration, whereas Ti has essentially tetrahedral structure. Two MeS ligands act as binder of the two metals constituting of bridging ligands. The bond distances of Ti(1)–S(1) [2.436(5) Å] and Ti(1)–S(2) [2.447(6) Å] in **1a** are almost comparable to those of $Cp_2Ti(SMe)_2$ [2.400(1) Å [9], 2.403(1) Å [11]. Only *syn* conformer was found in the solid state in spite of the known *anti* conformation of free $TiCp_2(SMe)_2$. This may be explained as the preferential crystallization of the *syn* conformer from the solution, which is the major species in benzene (vide infra). Although the bond distance between Ti(1)–Pt(1) [3.014(2) Å] is much longer than the sum of the covalent radii (2.61 Å), the bond angles of Ti(1)–S(1)–Pt(1) and Ti(1)–S(2)–Pt(1) are 77.9(2)° and 77.8(2)°, respectively, where the angles at bridging atoms less than 80° have been proposed as evidence for metal–metal interaction [9,12,13]. Taking into account these results, **1a** is considered to have a small contribution of the dative bond from Pt to Ti. The internal angles among the Pt(1), S(1), Ti(1), and S(2) atoms add up to 359.6°. Thus, the atoms Pt(1), S(1), Ti(1), and S(2) constitute a square plane without puckering.

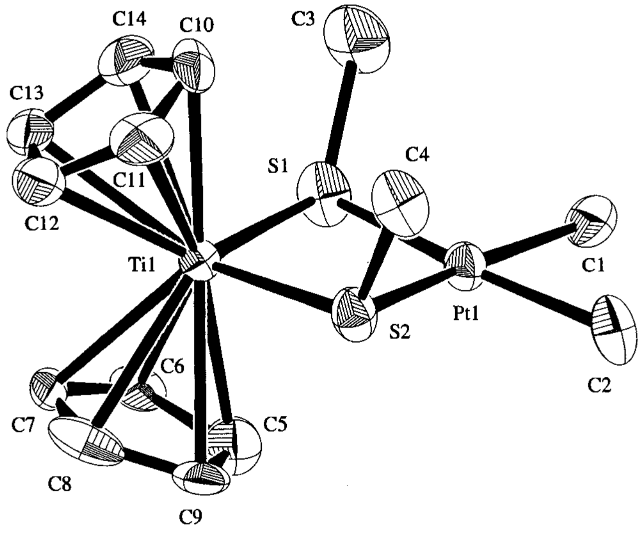


Fig. 1. Molecular strucure of **1**. All hydrogen atoms are omitted for clarity.

In contrast to the observation of only *syn* isomer in the solid state as mentioned above, ^1H-NMR of **1a** revealed the presence of both *syn* and *anti* conformers in C_6D_6. Thus, two signals due to the PtMe moiety appears at 2.04 and 1.98 ppm as singlets with Pt satellites in ca. 3:1 ratio. Two SMe groups assignable to both *syn* and *anti* conformers are also observed as singlets with Pt satellites at 2.24 and 2.36 ppm in the same ratio, being consistent with the coordination of two SMe groups to Pt. The *anti* isomer shows a signal due to Cp at 4.97 ppm, while the *syn* isomer displays two singlets at 4.97 and 5.06 ppm due to magnetically inequivalent Cp ligands. $^{13}C\{^1H\}$-NMR spectrum of **1a** also shows two sets of signals due to *anti* and *syn* conformers. Thus, two signals at -4.2 and -4.6 ppm and two signals at 23.0 and 23.7 ppm are assigned to PtMe and SMe carbons of *anti* and *syn* conformers, respectively. Three signals at 105.5, 106.8 and 108.8 are assigned to Cp carbons. The equilibrium constants K ($=[anti]/[syn]$) for **1a** and **1b** are estimated as ca. 0.3 and 0.1 at 23°C indicating that both **1a** and **1b** favor the *syn* conformation under these conditions.

Variable temperature NMR (VT ^1H-NMR) spectra of **1a** in toluene-d_8 showed fluxionality of the molecule. As shown in Fig. 2, two signals due to Cp protons of *syn* conformer gradually broadened with temperature increase and coalesced at ca. 50°C. Cp protons , also, but slowly, broadened at the same time, due to the *anti* conformer. Raising the temperature to 77°C all signals coalesced to give one broad signal. This stepwise coalescence of **1a** in the VT ^1H-NMR spectra may be interpreted by assuming the following two facile exchange processes (Scheme 1). The first process is taking place within the *syn* molecule, where either facile and

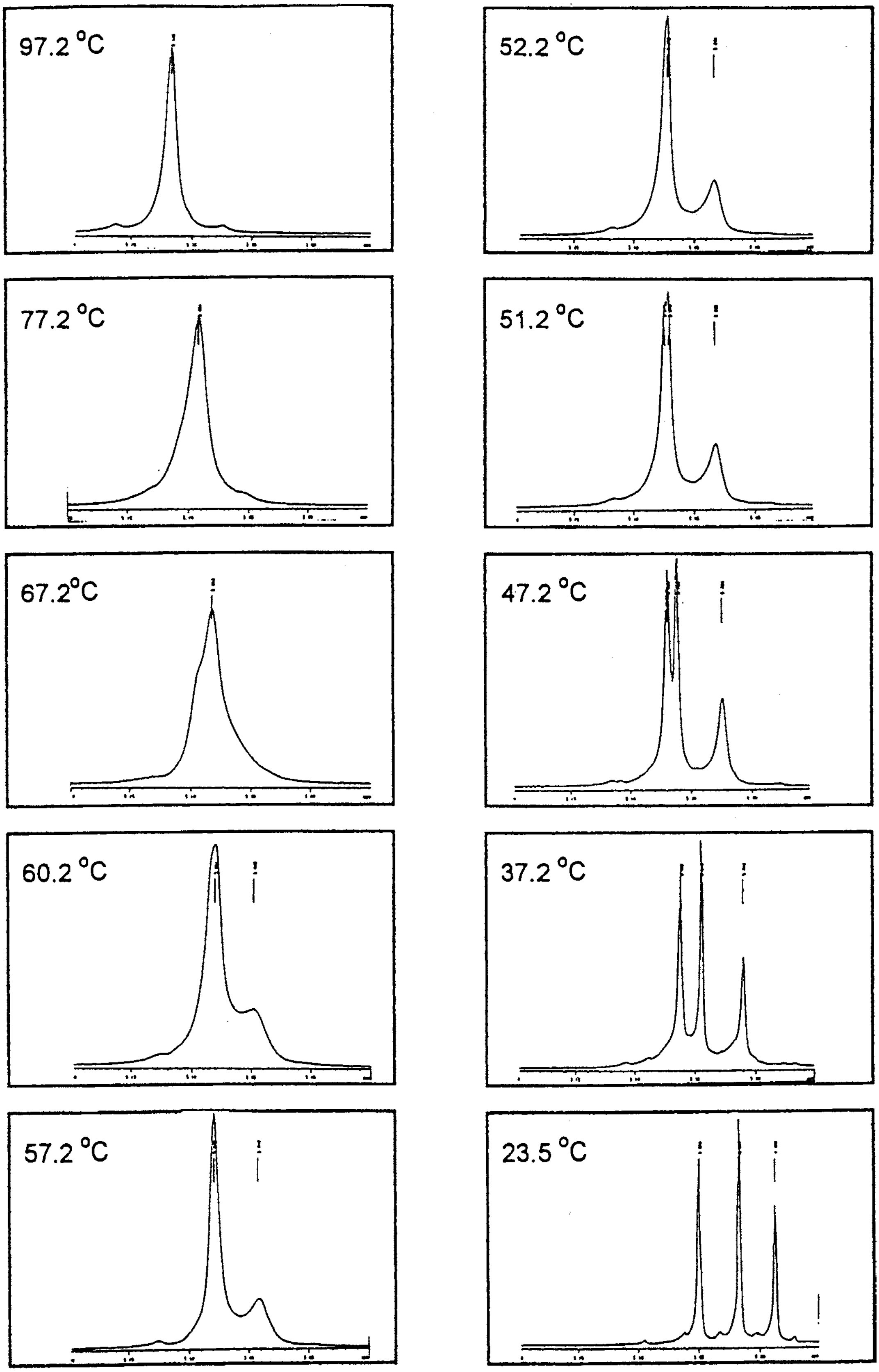
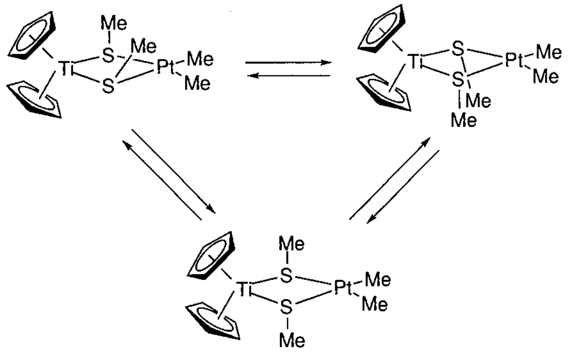


Fig. 2. Variable temperature ^{1}H-NMR spectra of the cyclopentadienyl region (4.95–5.20 ppm) of **1a** in toluene-d_8.



Scheme 1.

simultaneous inversion of the S–Me groups making the two Cp ring magnetically equivalent, or exchange of two Cp rings at the Ti metal. This concerted simultaneous inversion was proposed for $Cp_2Mo(\mu\text{-}SMe)_2PtCl_2$ [14]. The second process is the interconversion between *syn* and *anti* conformers. Such a process is proposed for $Cp_2Ti(\mu\text{-}SAr)_2Mo(CO)_4$ [15]. This would be understood by occurrence of the fast inversion at S atom, making all the signals equivalent.

In order to seek the chemical reactivity of **1a**, reaction with CO and olefins were carried out. Complex **1a** reacted with CO (1 atm) completely and immediately in C_6D_6 at room temperature to give $Cp_2Ti(SMe)_2$ [9] and $PtMe_2(CO)_2$ [10] in 66 and 67% yields, respectively (Eq. (2)).

$$Cp_2Ti(\mu - SMe)_2PtMe_2 \xrightarrow[\text{r.t.}]{\text{xs CO (1 atm)}} Cp_2Ti(SMe)_2 + PtMe_2(CO)_2 \qquad (2)$$

The reaction is regarded as a ligand displacement of the thiolate by CO at Pt to cleave the thiolate bridge. Similar bond cleavage reaction by CO is reported for $Cp_2Ti(\mu\text{-}SAr)_2Mo(CO)_4$ by Darensbourg [15]. On the other hand, treatment of **1a** with ethylene or acrylonitrile remained intact even at 50°C.

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