

# Titanium(IV) phosphinoamide as a unique bidentate ligand for late transition metals II: Ti–Ru heterobimetallics bearing a bridging chlorine atom

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Received 16 January 2006; received in revised form 25 March 2006; accepted 28 March 2006

Available online 25 April 2006

## Abstract

Treatment of a titanium phosphinoamide,  $(\text{Ph}_2\text{PN}^i\text{Bu})_2\text{TiCl}_2$  (**1**), with  $[\text{Cp}^*\text{RuCl}]_4$  in THF at room temperature afforded a Ti–Ru heterobimetallic complex, of which crystallographic study showed the molecular structure to be a six-membered dimetallacyclohexane,  $\text{Cp}^*\text{Ru}(\mu\text{-Cl})(\text{Ph}_2\text{PN}^i\text{Bu})_2\text{Ti}=\text{O}$  (**3**). A boat conformation of the dimetallacycle leads to effective linking of the two metal centers by two phosphinoamide ligands, and bridging of a chlorine atom over the Ti–Ru axis. The Ti–Ru heterobimetallics were synthesized by the reaction of **1** with  $\text{Cp}^*\text{Ru}(\text{COD})\text{Cl}$  or  $\text{Cp}^*\text{Ru}(\text{TMEDA})\text{Cl}$ , whereas no reaction occurred between **1** and  $\text{Cp}^*\text{Ru}(\text{PCy}_3)\text{Cl}$ . A primary product of this reaction would be a trichloride,  $\text{Cp}^*\text{Ru}(\mu\text{-Cl})(\text{Ph}_2\text{PN}^i\text{Bu})_2\text{TiCl}_2$  (**2**). In fact, careful treatment of **1** with  $[\text{Cp}^*\text{RuCl}]_4$  afforded **2** as the main product which was detected by NMR and ESI-MS spectra; **2** was converted to **3** in contact with 1 equivalent of water. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Phosphinoamide; Heterobimetallics; Lewis acid–base interaction

## 1. Introduction

Bidentate phosphines are one of the most visible and useful auxiliary ligands in organometallic and synthetic organic chemistry. It is well known that the electronic and steric properties of phosphine-containing complexes can be controlled by varying the substituents on the phosphorus atoms [1]. Recently, bidentate phosphines which have Lewis acidic moieties in the backbone have attracted great attention due to their unique properties. For instance, various early transition metal-containing phosphines were designed and used in the construction of early-late heterobimetallic (ELHB) complexes [2–4]. In these ELHB complexes, a combination of hard, Lewis acidic center (early transition metals) and a soft, Lewis basic center (late transition metals) in one molecule is

expected to provide special cooperative reactivity toward many organic substrates including polar molecules (Fig. 1). A typical example is synthesis of Zr–Rh heterobimetallic complexes,  $(\mu\text{-C}_5\text{H}_4\text{-PR}_2)_2\{\text{H}_3\text{C-Zr-Rh}(\text{CO})(\text{PPh}_3)\}$ , which was achieved by treatment of  $(\text{C}_5\text{H}_4\text{-PR}_2)_2\text{Zr}(\text{CH}_3)_2$  with  $\text{HRh}(\text{CO})\text{-}(\text{PPh}_3)_3$ , and the cooperative behavior of two metal centers is proposed to facilitate the insertion of a CO molecule into a metal–carbon bond [3a]. The Lewis acidic center of certain bidentate phosphines can react with anions to give the corresponding ate complexes; Peters and co-workers reported preparation of borate containing phosphines,  $[\text{Ph}_2\text{B}(\text{CH}_2\text{PPh}_2)_2]^-$ , and their ligation to transition metal precursors [5] such as Rh(I) species [5a]. The resulting rhodium complexes showed catalytic activity toward H–E (E = C, Si, B) addition reaction to olefins in both polar and non-polar solvent.

In our previous paper, we reported a unique bidentate phosphorus ligand having a Lewis acidic Ti(IV) center,

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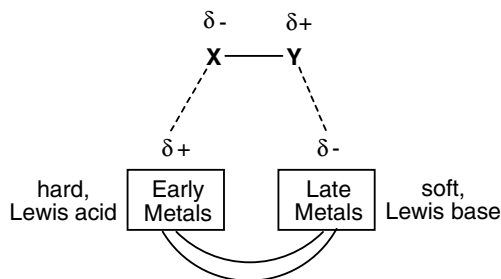


Fig. 1. Cooperative reactivity toward polar organic substrates.

(Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>TiCl<sub>2</sub> (**1**), which takes part in forming a series of Ti–Pt heterobimetallic complexes, YY′Pt(Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>TiCl<sub>2</sub> (Y, Y′ = Cl; Y = Me, Y′ = Cl; Y = *p*-Tol, Y′ = Cl; Y, Y′ = Me) by treatment with appropriate Pt(II) precursors (Scheme 1) [6]. Crystallographic studies revealed that these new Ti–Pt complexes have a six-membered ring consisting of two metallic, two phosphorus, and two nitrogen atoms with a boat conformation. For the compensation of the Lewis acidity of the titanium center, electron donation from a fully-occupied d<sub>z<sup>2</sup></sub> orbital of a square-planary arranged platinum center occurs through a Pt–Ti dative bond as shown in Fig. 2 (A). This is a unique example to investigate Lewis acid–Lewis base interaction of heterobimetallic complexes systematically, prompting us to carry out further elaboration to synthesize novel ELHB complexes using **1** as the metalloligand. As chemistry on this line, we were interested in replacement of the square-planary platinum species in YY′Pt(Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>TiCl<sub>2</sub> by tetrahedrally arranged metal moieties. As shown in Fig. 2, the replacement would result in possible bridging of a ligand connecting to the tetrahedrally arranged metal atom, giving heterobimetallic complexes with new structures.

In this paper, we wish to report the reaction of titanium phosphinoamide (**1**) with the “Cp\*RuCl” species such as [Cp\*RuCl]<sub>4</sub>, which forms Cp\*Ru(μ-Cl)(Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>Ti=O (**3**) through Cp\*Ru(μ-Cl)(Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>TiCl<sub>2</sub> (**2**) as an intermediate. The molecular structure of **3** revealed that a Ti and a Ru center were linked by two bridging phosphinoamide ligands; the resulting dimetallacycle skeleton has a boat-conformation. As we expected, the ligand arrangement around the ruthenium center is pseudo-tetrahedral. There is no dative bond between the two metal centers; instead, Lewis acidity of the Ti center is compensated by a lone pair of the bridging chlorine atom. The intermediate

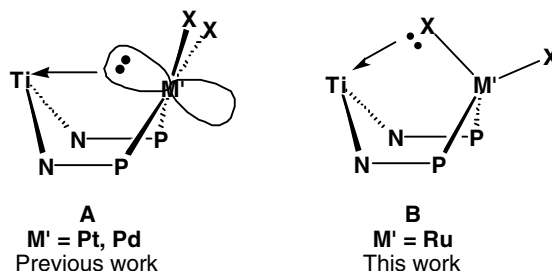


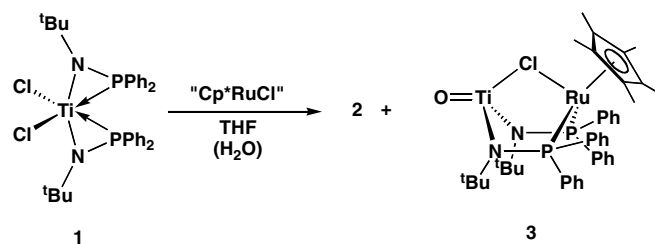
Fig. 2. The simplified structure of heterobimetallic phosphinoamide complexes of previous work (left) and this work (right).

**2** was detected by careful treatment of (Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>TiCl<sub>2</sub> (**1**) with [Cp\*RuCl]<sub>4</sub> in THF or CD<sub>2</sub>Cl<sub>2</sub>, which can be easily converted to complex **3** by the addition of 1 equivalent of water.

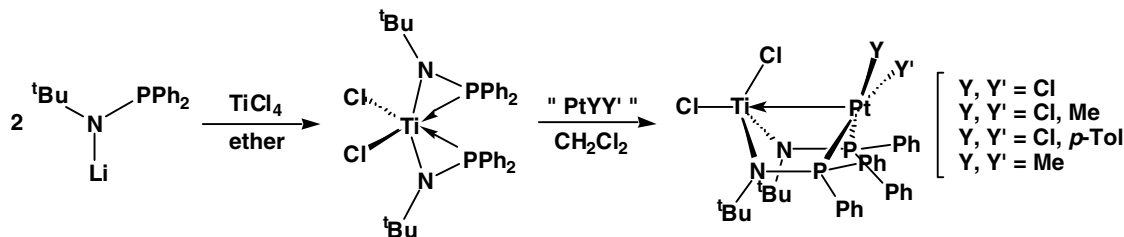
## 2. Results and discussion

### 2.1. Synthesis and characterization of Ti–Ru ELHB complexes, Cp\*Ru(μ-Cl)(Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>TiCl<sub>2</sub> (**2**) and Cp\*Ru(μ-Cl)(Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>Ti=O (**3**)

Treatment of 0.25 equivalent of [Cp\*RuCl]<sub>4</sub> with titanium phosphinoamide, (Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>TiCl<sub>2</sub> (**1**), in CD<sub>2</sub>Cl<sub>2</sub> resulted in immediate formation of two Ti–Ru species with complete consumption of **1** and [Cp\*RuCl]<sub>4</sub> (Scheme 2). Similar results were obtained in either the reaction of **1** with Cp\*Ru(COD)Cl at 50 °C for 5 h, or that of **1** with Cp\*Ru(TMEDA)Cl at room temperature for 1 h. No reaction occurred between **1** and Cp\*Ru(PCy<sub>3</sub>)Cl. Recrystallization of the crude product obtained from the reaction of **1** with [Cp\*RuCl]<sub>4</sub> led to successful isolation of one of the Ti–Ru heterobimetallic species; crystallography of dark purple crystals grown from CH<sub>2</sub>Cl<sub>2</sub>/CPME showed the molecular structure to be Cp\*Ru(μ-Cl)(Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>Ti=O



Scheme 2.



Scheme 1.

(3). Fig. 3 shows the ORTEP view of **3**, and the selected bond distances and angles are listed in Table 1.

The crystal contains two independent but chemically equivalent molecules of **3**. Bond distances and angles of the second molecule are given in brackets in the table. Both the titanium and ruthenium centers adopt pseudo-tetrahedral coordination geometry, and the two metal centers are linked by two phosphinoamide ligands. The resulting six-membered dimetallacycle has a boat form which is similar to that of our previously reported Ti–Pt phosphinoamide complexes [6]. The long Ti–Ru distance of **3** (3.093(2) [3.073(2)] Å) precludes any metal–metal interaction, because the metal–metal bonds between Ti and Ru atoms are usually shorter than 3 Å [7]. As expected in the structure shown in Fig. 2, a chlorine atom bridges over the Ti–Ru axis, and interaction of its lone pair electrons compensate the Lewis acidity of the titanium center instead of the dative bond seen in the Ti–Pt heterobimetallic com-

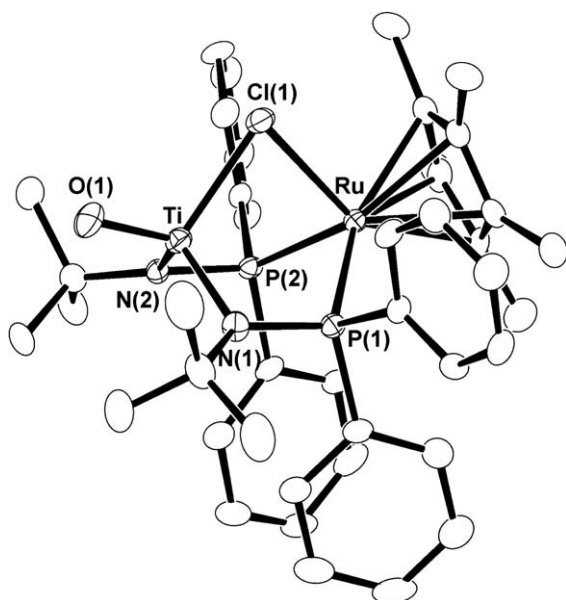
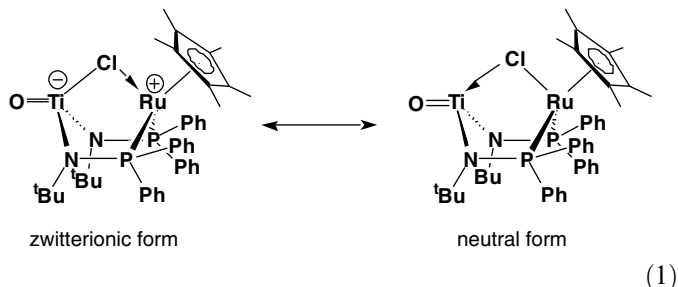


Fig. 3. Molecular structure of  $\text{Cp}^*\text{Ru}(\mu\text{-Cl})(\text{Ph}_2\text{PN}'\text{Bu})_2\text{Ti}=\text{O}$  (**3**) showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

plexes. Both the Ti–Cl [8] and the Ru–Cl [9] distances are considerably longer than usually observed Ru–Cl distances; this may indicate contribution of the  $\text{Ti}^- \text{Ru}^+$  zwitterionic form shown in Eq. (1). The Ti–O distance is 1.651(5) [1.649(5)] Å which is comparable to those found in the known Ti(IV)=O complexes [10], e.g., 1.665(3) Å for  $\text{Cp}^*\text{Ti}(\text{O})(4\text{-phenylpyridine})$  [10a], 1.654(2) Å for  $\{\text{PhC}(\text{NSiMe}_3)_2\}_2\text{Ti}(\text{O})(\text{OPy})$  [10b], 1.637(3) Å for  $[(\text{Me}_3\text{tacn})\text{Ti}(\text{O})\text{Cl}_2]$  [10c]. The oxygen atom is slightly bent away from the Ti–Ru axis (Ru–Ti–O(1) 162.1(2)° [161.5(2)°]). The N–P bond distances of **3** are approximately 0.1 Å shorter than the normal N–P single bonds, which reflect the partial N–P double bond character. This was supported by the sum of the three angles at N (358.9–359.2°), which are very close to the theoretical value of 360° for the planar  $\text{sp}^2$ -hybridized nitrogen atom. The shorter bond distances of N–P were also observed in our Ti–Pt phosphinoamide complexes [6], previously reported phosphinoamide or its related complexes [11]. The Ti–N (1.969–1.983 Å) and Ru–P (2.349–2.3639 Å) bond distances are slightly longer than those of titanium amido [8] and ruthenium phosphine [9] complexes, respectively.



In the  $^1\text{H}$  NMR spectrum of **3**, one set of  $^t\text{Bu}$  and  $\text{Cp}^*$  signals was observed at 1.39 and 1.03 ppm, respectively, in an integral ratio of 18:15. The  $\text{Cp}^*$  signal is shifted to higher field than that of mononuclear ruthenium complexes [12], 1.28 ppm for  $\text{Cp}^*\text{Ru}(\text{dppp})\text{Cl}$  [12a] and 1.33 ppm for  $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$  [12b], due to the shielding by one of the phenyl rings of  $\text{PPh}_2$  moiety. In addition, the existence of coordinated phosphorus atoms is charac-

Table 1  
Representative bond lengths and angles for **3**

Bond length (Å)			
Ti–Ru	3.093(2) [3.073(2)]	Ru–P(1)	2.356(2) [2.364(2)]
Ti–N(1)	1.969(5) [1.974(5)]	Ru–P(2)	2.350(2) [2.353(2)]
Ti–N(2)	1.979(4) [1.983(4)]	Ru–Cl(1)	2.5182(14) [2.504(2)]
Ti–O(1)	1.651(5) [1.649(5)]	N(1)–P(1)	1.677(6) [1.672(6)]
Ti–Cl(1)	2.344(2) [2.336(2)]	N(2)–P(2)	1.661(6) [1.652(6)]
Bond angle (°)			
Ru–Ti–O(1)	162.1(2) [161.5(2)]	Ti–N(1)–P(1)	104.1(3) [103.6(3)]
Ru–Cl(1)–Ti	78.92(5) [78.75(6)]	Ti–N(2)–P(2)	104.0(3) [104.6(3)]
Cl(1)–Ti–O(1)	109.1(2) [108.4(2)]	Cl(1)–Ru–P(1)	93.07(5) [93.97(6)]
Cl(1)–Ti–N(1)	108.3(2) [108.0(2)]	Cl(1)–Ru–P(2)	93.07(5) [94.30(6)]
Cl(1)–Ti–N(2)	108.3(2) [109.3(2)]	P(1)–Ru–P(2)	94.23(6) [92.59(6)]
O(1)–Ti–N(1)	108.7(2) [108.9(2)]	Ru–P(1)–N(1)	113.0(2) [112.7(2)]
O(1)–Ti–N(2)	108.4(2) [108.8(2)]	Ru–P(2)–N(2)	113.6(2) [112.7(2)]
N(1)–Ti–N(2)	114.1(2) [113.3(2)]		

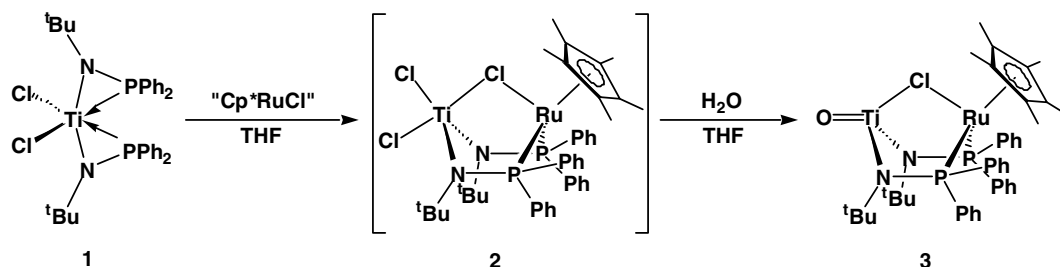
terized by a singlet  $^{31}\text{P}$  NMR signal at 37.3 ppm. This indicates the coordination of  $\text{PPh}_2$  moiety of **1** to the ruthenium center in a bidentate fashion.

Although a primary product expected from the reaction of **1** with “ $\text{Cp}^*\text{RuCl}$ ” is a trichloride,  $\text{Cp}^*\text{Ru}(\mu\text{-Cl})\text{-}(\text{Ph}_2\text{PN}^t\text{Bu})_2\text{TiCl}_2$  (**2**), the crystallographically determined complex is the oxide **3**,  $\text{Cp}^*\text{Ru}(\mu\text{-Cl})(\text{Ph}_2\text{PN}^t\text{Bu})_2\text{Ti=O}$ , bearing terminal oxo ligand instead of two chlorine atoms. As described above, we observed the formation of two products in the reaction of **1** with “ $\text{Cp}^*\text{RuCl}$ ”, and one of them is the oxide **3**. The other product is very unstable, detectable at the initial stage of the reaction, but decreased later. Careful experiments to exclude water from the reaction of **1** with  $[\text{Cp}^*\text{RuCl}]_4$  in a sealed NMR tube provided spectroscopic evidence that the other product was the trichloride **2**, which was extremely moisture sensitive and easily converted to the oxide **3** in contact with water (Scheme 3) [13]. In the  $^1\text{H}$  NMR spectrum of **2**, the resonance for the  $\text{Cp}^*$  hydrogens appeared as a singlet at 1.05 ppm, which is also high-field shifted due to the shielding by the phenyl rings. The signal derived from the methyl groups of  $^t\text{Bu}$  moiety appeared as a singlet at 1.33 ppm. The  $^{31}\text{P}$  NMR spectrum of **2** consists of one sharp peak at  $\delta$  30.9 ppm, which is higher than that of **3** (6 ppm) but exhibits a substantial low-field shift relative to those of the titanium phosphinoamide **1** (–15.8 ppm). The trichloride **2** was proved to be converted to **3** easily by the reaction with 1 equivalent of  $\text{H}_2\text{O}$  at  $-78^\circ\text{C}$ , which was isolated in 68% yield. The reaction of **2** with moisture can be monitored by the ESI-MS spectrum (see Supporting information); complex **2** was the major product when the reaction of **1** with “ $\text{Cp}^*\text{RuCl}$ ” was completed, however, the intensity of a peak due to **3** increased as soon as the solution was exposed to air. For instance, the ratio of **2** to **3** changed from 86:14 to 68:32 within 30 s. This unusually high reactivity of **2** with water resulting in  $\text{TiCl}_2$  species to  $\text{Ti=O}$  is not seen in the analogous  $\text{Ti-Pt}$  complexes,  $\text{YY}'\text{Pt}(\text{Ph}_2\text{PN}^t\text{Bu})_2\text{TiCl}_2$  ( $\text{Y}, \text{Y}' = \text{Cl}; \text{Y} = \text{Me}, \text{Y}' = \text{Cl}; \text{Y} = p\text{-Tol}, \text{Y}' = \text{Cl}; \text{Y}, \text{Y}' = \text{Me}$ ), and must be due to the special structure of **2**. Deduced from the structure of **3**, a possible molecular structure of **2** is as shown in Scheme 3, in which the titanium center is trigonal bipyramidal with one bridging and one terminal chlorine atom at the apical positions. We consider that this unusual instability of trichloride **2** toward water could be attributable to the intramolecular interaction of the lone pair electrons of the  $\mu\text{-Cl}$

atom at the apical position with the Lewis acidic titanium center, of which trans-influence destabilizes the bond between the titanium and the apical terminal chlorine atom. In consequence, the terminal chlorine atom at the apical position becomes susceptible to nucleophilic attack of  $\text{H}_2\text{O}$  at the titanium center to form  $\text{Ti=O}$  species.

### 3. Conclusion

As described above, we were successful in synthesizing the  $\text{Ti-Ru}$  heterobimetallic complexes using a titanium phosphinoamide as the bridging bidentate phosphorus ligand. Since titanium phosphinoamide **1** is not a strongly coordinated ligand because of the reversible intramolecular coordination/dissociation process of  $\text{PPh}_2$  moiety of **1** as mentioned in our previous paper [6], use of ruthenium precursors bearing the easily replaceable auxiliary ligands are favored to force the reaction toward the construction of ELHB complexes similar to the analogous  $\text{Ti-Pt}$  chemistry. The molecular structure of oxide **3** was determined by X-ray diffraction analysis, in which two metal centers were effectively linked by two phosphinoamide ligands to form the six-membered dimetallacycle. As we expected, the complex has a pseudo-tetrahedrally arranged ruthenium moiety, and the bridging  $\text{Cl}$  atom donates the electrons to the titanium center intramolecularly; this provides a different type of intramolecular Lewis acid–Lewis base interaction from the  $\text{Ti-Pt}$  dative interaction. The primary product **2** was only detectable spectroscopically in the experiments in which moisture was carefully excluded from the reaction media. The unusually high reactivity of trichloride **2** toward water is explained by the intramolecular donor–acceptor interaction between the lone pair electrons of the  $\mu\text{-Cl}$  atom and the Lewis acidic titanium center, which forces the titanium atom of **2** to adopt the trigonal bipyramidal coordination geometry with one bridging and one terminal chlorine atom at the apical positions. The trans-influence of the apical  $\mu\text{-Cl}$  atom leads to facile replacement of the terminal chlorine atom at the apical position with water to afford **3**. These new findings demonstrate the utility of the titanium phosphinoamide **1** as the metalloligand, which may provide an unique entry to the catalyst design. Current efforts are being directed toward synthesizing new types of ELHB complexes from **1** by the reaction with several late transition metal species with different coordination geometries from square-planar



Scheme 3.



and tetrahedral, which have never been investigated in our previous or present work. Their dynamic properties will bring about systematic understanding of the intramolecular Lewis acid–Lewis base interaction in the ELHB complexes.

## 4. Experimental

### 4.1. General procedures

Manipulation of air and moisture sensitive organometallic compounds was carried out under a dry argon atmosphere using standard Schlenk tube techniques associated with a high-vacuum line, or in a glovebox equipped with a constant nitrogen flash. All solvents were distilled over appropriate drying reagents prior to use (THF, toluene, hexane, pentane, Et<sub>2</sub>O and cyclopentylmethylether (CPME); Ph<sub>2</sub>CO/Na, CH<sub>2</sub>Cl<sub>2</sub>; CaH<sub>2</sub>). <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR spectra were recorded on a JEOL Lambda 600 spectrometer at ambient temperature. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR chemical shifts (δ values) were given in ppm relative to the solvent signal (<sup>1</sup>H, <sup>13</sup>C) or standard resonances (<sup>31</sup>P; external 85% H<sub>3</sub>PO<sub>4</sub>). ESI mass spectra were recorded on a JEOL JMS-T100CS apparatus. Starting materials, titanium phosphinoamide [6], [Cp\*RuCl]<sub>4</sub> [14], Cp\*Ru(COD)Cl [15], Cp\*Ru(TMEDA)Cl [16] and Cp\*Ru(PCy<sub>3</sub>)Cl [17] were synthesized by the method reported in the literature.

### 4.2. Synthesis of Cp\*Ru(μ-Cl)(Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>TiCl<sub>2</sub> (2)

Treatment of (Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>TiCl<sub>2</sub> (**1**) with [Cp\*Ru(μ-Cl)]<sub>4</sub> (0.25 equiv. to **1**) in THF at room temperature gave a mixture of **2** and **3**; the ratio of **2** to **3** was dependent on the reaction time and the amount of moisture in the reaction medium, usually ranging from 77:23 to 88:12. The trichloride **2** was extremely air and moisture sensitive, and detectable at either the initial stage of the reaction or under the conditions where water was carefully removed. The following is the best example of the selective preparation of **2** in our experiments: (Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>TiCl<sub>2</sub> (**1**) (200 mg, 0.317 mmol) and [Cp\*Ru(μ-Cl)]<sub>4</sub> (0.25 equiv. to **1**, 86 mg, 0.079 mmol) were dissolved in freshly prepared THF (8 mL), then stirred at room temperature for 1 h in a glove box. This solution stood overnight at room temperature to give dark purple microcrystals. After washing with THF (10 mL), compound **2** was obtained as the dark purple microcrystals (164 mg). This sample contains ca. 8% of **3**, but it is enough to assign the spectroscopic data shown below. Mass (M+H<sup>+</sup>) (ESI) = 905.16. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 600 MHz, r.t.) δ 1.05 (s, 15H, Cp\*), 1.33 (s, 18H, <sup>t</sup>Bu), 7.40–7.46 (m, 4H, Ph), 7.47–7.55 (m, 4H, Ph), 7.62–7.71 (m, 8H, Ph), 7.87–7.93 (m, 4H, Ph). <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 9.51 (C<sub>5</sub>Me<sub>5</sub>), 33.5 (CMe<sub>3</sub>), 68.0 (CMe<sub>3</sub>), 98.7 (C<sub>5</sub>Me<sub>5</sub>), 129.0 (m, Ph), 129.2 (m, Ph), 132.5 (Ph), 132.6 (Ph), 133.7 (m, Ph), 133.8 (m, Ph). <sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 30.9 (s).

### 4.3. Synthesis of Cp\*Ru(μ-Cl)(Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>Ti=O (3) from in situ generated 2

Treatment of (Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>TiCl<sub>2</sub> (**1**) (200 mg, 0.317 mmol) with [Cp\*Ru(μ-Cl)]<sub>4</sub> (0.25 equiv. to **1**, 86 mg, 0.079 mmol) in THF (8 mL) at room temperature for 1 h gave a mixture of **2** and **3**. Recrystallization of this mixture (e.g., 77:23) from CH<sub>2</sub>Cl<sub>2</sub>/CPME resulted in selective isolation of **3** as dark purple crystals. Alternatively, a THF solution (15 mL) of **1** (200 mg, 0.317 mmol) and [Cp\*Ru(μ-Cl)]<sub>4</sub> (0.25 equiv. to **1**, 86 mg, 0.079 mmol) were stirred at room temperature for 1 h. After the reaction was completed (confirmed by NMR), one equivalent of H<sub>2</sub>O (6 μL, 0.317 mmol) was added to the reaction mixture at –78 °C, and the mixture was stirred for an additional 5 min. After removal of the solvent in vacuo, the resulting solid was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The extracts were combined, and an insoluble material was removed by centrifugation. The supernatant was evaporated to dryness. The dark purple solid was washed with pentane (5 mL), from which compound **3** was afforded as dark purple powder in 68% yield (184 mg, 0.217 mmol). Single crystals of **3** for X-ray diffraction analysis were obtained as dark purple crystals from saturated CH<sub>2</sub>Cl<sub>2</sub> solution and CPME at –35 °C. This complex was somewhat more stable than **2**, but decomposed rapidly on exposure to air. Mass (M+H<sup>+</sup>) (ESI) = 849.10. Exact mass (ESI-TOF): Calcd. for <sup>12</sup>C<sub>42</sub><sup>1</sup>H<sub>54</sub><sup>14</sup>N<sub>2</sub><sup>31</sup>P<sub>2</sub><sup>35</sup>Cl<sub>1</sub><sup>32</sup>O<sub>1</sub><sup>48</sup>Ti<sub>1</sub><sup>102</sup>Ru<sub>1</sub>: 849.19228. Found: 849.19158. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 600 MHz, r.t.) δ 1.03 (s, 15H, Cp\*), 1.39 (s, 18H, <sup>t</sup>Bu), 7.35–7.41 (m, 4H, Ph), 7.47–7.54 (m, 4H, Ph), 7.58–7.67 (m, 8H, Ph), 7.95–8.04 (m, 4H, Ph). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 9.13 (C<sub>5</sub>Me<sub>5</sub>), 33.9 (CMe<sub>3</sub>), 67.9 (CMe<sub>3</sub>), 101.1 (C<sub>5</sub>Me<sub>5</sub>), 128.7 (m, Ph), 129.3 (m, Ph), 131.6 (Ph), 131.8 (Ph), 134.0 (m, Ph). <sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 37.3 (s).

### 4.4. Synthesis of Cp\*Ru(μ-Cl)(Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>Ti=O (3) from isolated 2

To a THF solution (15 mL) of **2** (containing ca. 8% of **3**, 100 mg) was added approximately 1 equivalent of H<sub>2</sub>O (2 μL, 0.111 mmol) at –78 °C, and the mixture was stirred for 5 min. After removal of the solvent in vacuo, the resulting solid was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined extracts were centrifuged to remove the insoluble materials. Removal of the solvent and subsequent washing with pentane afforded 57 mg of **3** as dark purple powder.

### 4.5. Typical reactions of (Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>TiCl<sub>2</sub> with several Ru precursors

In a NMR tube were placed (Ph<sub>2</sub>PN<sup>t</sup>Bu)<sub>2</sub>TiCl<sub>2</sub> (20 mg, 0.032 mmol) and Cp\*Ru(COD)Cl or Cp\*Ru(TMEDA)Cl (0.032 mmol). Then, CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was added, and the resulting solution was heated at 50 °C for 5 h in the reaction with Cp\*Ru(COD)Cl, or was shaken at room temperature for 1 h in that with Cp\*Ru(TMEDA)Cl. The reaction

was monitored periodically, and formation of **2** and **3** was detected by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra.

#### 4.6. X-ray data collection and reduction

Single crystals of **3** were grown from  $\text{CH}_2\text{Cl}_2/\text{CPME}$ . X-ray crystallography was performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71070 \text{ \AA}$ ). The data were collected at 123(2) K using  $\omega$  scan in the  $\theta$  range of  $3.0^\circ \leq \theta \leq 27.5^\circ$ . Data were collected and processed using Crystal-Clear (Rigaku) on a Pentium computer. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods [18], and expanded using Fourier techniques [19]. The non-hydrogen atoms were refined anisotropically except for atoms of the solvent molecule (CPME). Hydrogen atoms were refined using the riding model. The occupancy of the solvent molecule (CPME) was refined and then fixed at 0.5. The final cycle of full-matrix least-squares refinement on  $F^2$  was based on 12137 observed reflections and 1047 variable parameters. Neutral atom scattering factors were taken from Cromer and Waber [20]. All calculations were performed using the CrystalStructure [21,22] crystallographic software package. Details of final refinement are summarized in Table 2, and the numbering scheme employed is shown in Fig. 1, which was drawn with ORTEP at 50% probability ellipsoid. Detailed data as well as the bond distances and angles are shown in Supporting information.

Table 2  
Crystal data for  $\text{Cp}^*\text{Ru}(\mu\text{-Cl})(\text{PPh}_2\text{N}^t\text{Bu})_2\text{Ti}=\text{O}$  (**3**)

Empirical formula	$\text{C}_{84}\text{H}_{106}\text{Cl}_2\text{N}_4\text{P}_4\text{O}_2\text{Ru}_2\text{Ti}_2 \cdot 0.5 \text{ C}_6\text{H}_{12}\text{O}$
Formula weight	1796.69
Crystal system	Monoclinic
Lattice type	Primitive
Space group	$P2_1/c$ (#14)
$a$ (Å)	21.68(3)
$b$ (Å)	21.18(2)
$c$ (Å)	20.64(2)
$\beta$ (°)	117.4(2)
Volume (Å <sup>3</sup> )	8420(2)
Z value	4
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	1.418
$F(000)$	3744.00
$\mu$ (Mo $\text{K}\alpha$ ) (cm <sup>-1</sup> )	7.263
Crystal color, habit	Dark-purple
Crystal dimensions (mm)	0.20 × 0.15 × 0.05
Radiation	Mo $\text{K}\alpha$ ( $\lambda = 0.71070 \text{ \AA}$ )
Number of observations [ $I > 2.00\sigma(I)$ ]	12137
Number of variables	1047
Reflection/parameter ratio	11.595
$R_1$ [ $I > 2.00\sigma(I)$ ]	0.0631
$wR_2$ [ $I > 2.00\sigma(I)$ ]	0.1566
Goodness-of-fit	1.004
Maximum shift/error in final cycle	0.000
Maximum peak in final diffraction map (e <sup>-</sup> /Å <sup>3</sup> )	1.86
Minimum peak in final diffraction map (e <sup>-</sup> /Å <sup>3</sup> )	-0.82

#### Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 14078101, “Reaction Control of Dynamic Complexes”) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

#### Appendix A. Supporting information

The CIF files for the compound **3**,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra of **2** and **3**, and ESI mass spectra of **2** and **3**. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 294799 for compound  $\text{Cp}^*\text{Ru}(\mu\text{-Cl})(\text{Ph}_2\text{PN}^t\text{Bu})_2\text{Ti}=\text{O}$  (**3**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or [www://http.ccdc.cam.ac.uk](http://www://http.ccdc.cam.ac.uk)). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.03.038.

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