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Synthesis and Structures of Ti-Pd Heterobimetallic Complexes

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Dedicated to Professor Tamotsu Takahashi[‡] on the occasion of his 60th birthday

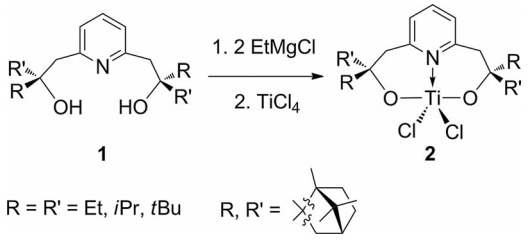
Keywords: Heterobimetallic complexes / Titanium / Palladium / Multidentate ligands / Ligand design

Heterobimetallic complexes containing titanium and palladium were prepared from *O*,*N*,*O*–*N*,*N* multidentate ligands. The ligands each contained an *O*,*N*,*O*-tridentate part based on a 2,6-lutidine scaffold and an *N*,*N*-bidentate di(pyridin-2-yl) part. The *O*,*N*,*O*-moiety selectively coordinated to a titanium atom on treatment with titanium(tetraisopropoxide), although one of the di(pyridin-2-yl) groups in the *N*,*N*-moiety coordinated to the titanium atom. The *N*,*N*-bidentate di(pyridin-2-yl) moiety coordinated to the palladium atom on treatment with bis(benzonitrile)palladium(II) chloride to afford a heterobimetallic complex. The dynamic behavior of the complexes in solution was studied by NMR spectroscopy.

Introduction

Early-late heterobimetallic (ELHB) complexes have received much attention owing to the potential synergetic effects of the early and late transition metals in catalytic reactions. Although there have been many examples of ELHB complexes,[1] less successful examples for effective cooperation of two metals in a heterobimetallic complex in catalytic reactions have been reported.[1n,1t,2] To achieve cooperative effects of two metals, one promising strategy must be ligand design that locates the two metal atoms at an appropriate distance from each other.[2d–2g,3] Multidentate ligands are useful tools for construction of ELHB complexes, although they have to coordinate to two different metal atoms selectively.

We have previously reported the synthesis and structures of titanium complexes **2** and their catalytic ability for ethylene polymerization.[4] We employed the *O*,*N*,*O*-tridentate ligands **1**, based on a lutidine scaffold (Scheme 1).[5] In this study we designed new multidentate ligands **4** to form ELHB complexes (Figure 1). We envisioned that the *O*,*N*,*O*-tridentate ligands must selectively coordinate to titanium because of the oxophilicity of the early transition metals. We introduced a di(pyridin-2-yl)methane group, known as a bidentate ancillary nitrogen ligand, on one of the side arms of the *O*,*N*,*O*-tridentate ligand to construct a moiety that coordinates to a late transition metal, because there have been many examples of late-transition-metal catalysts such as palladium with di(pyridin-2-yl)methane moieties.[6]



Scheme 1. Titanium complexes of *O*,*N*,*O*-tridentate ligands.

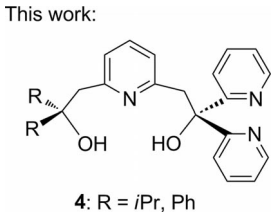


Figure 1. *O*,*N*,*O*–*N*,*N* Multidentate ligands.

Here we report the selective synthesis of titanium–palladium heterobimetallic complexes and their molecular structures.[2i–2k,7] The dynamic behavior of the complexes in solution is also presented.

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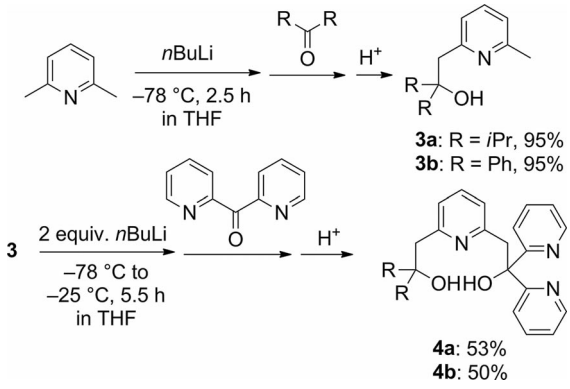
Results and Discussion

Preparation of *O*,*N*,*O*–*N*,*N* Ligands and Their Titanium Complexes

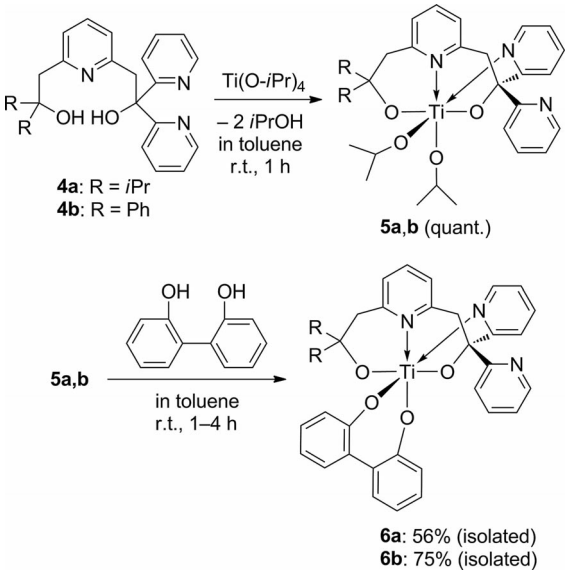
The *O*,*N*,*O*-tridentate ligands had been prepared from 2,6-lutidine in previous studies.[4,5b,5c,5g] We employed this methodology to synthesize *O*,*N*,*O*–*N*,*N* multidentate ligands **4**. These each have a neutral dipyridyl fragment on one of the alkoxide arms. Mono-ols **3a** and **3b** were prepared from monolithiated 2,6-lutidine and 2,4-dimethylpentan-3-one or benzophenone, respectively. The mono-ols **3** were each isolated and lithiated with two equiv. of *n*-butyllithium and then treated with di(pyridin-2-yl) ketone (Scheme 2). The multidentate ligands **4** were obtained in moderate yields. The synthesis of compounds **4** could be achieved in a one-pot process, without isolation of **3**, in good yield (**4a**: 67%, **4b**: 57%, based on 2,6-lutidine). The molecular structure of **4b** was determined by X-ray diffraction (see the Supporting Information).



Scheme 2. Preparation of *O*,*N*,O–*N*,*N*-multidentate ligand **4**.

We had previously reported the [ONO]$TiCl_2$ complexes **2**.[4] We tried reactions between lithium or magnesium salts of compounds **4** and $TiCl_4$. However, the reactions gave complex mixtures, presumably because of the coordinative ability of the di(pyridin-2-yl) groups on the side arm. We then added titanium tetraisopropoxide [Ti(O-*i*Pr)$_4$] to compounds **4** in solution. Dissociation of 2-propanol was observed by ^{1}H NMR after the mixture had been stirred at room temperature (r.t.) for 1 h, suggesting the quantitative formation of compounds **5** (Scheme 3). One of the methylene signals of **4** was shifted significantly downfield. The NMR signals varied depending on temperature, and dynamic behavior of compounds **5** was observed (vide infra).

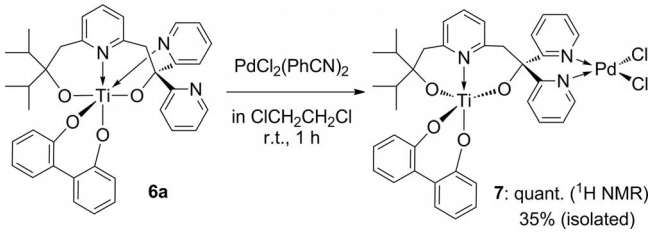
Although ^{1}H NMR observation suggested the formation of the complexes **5**, these were sticky solids and it was difficult to confirm the detailed molecular structure. Addition of an equimolar amount of 2,2′-biphenol to a solution of **5** gave 2,2′-biphenoxide complexes **6** in moderate to good yields as crystals. The molecular structure of **6a** and **6b** was determined by X-ray diffraction analysis. These results revealed that one of the pyridyl groups on the side arm coordinates to the titanium metal, and the complexes have six-coordinate structures (vide infra).



Scheme 3. Synthesis of titanium complexes **6** from *O*,*N*,*O*–*N*,*N* ligands **4**.

Preparation of Ti–Pd Heterobimetallic Complexes of the *O*,*N*,*O*–*N*,*N* Ligands 4

To accomplish the synthesis of heterobimetallic complexes containing both early and late transition metals, we employed **6a**, because **6b** had rather lower solubility in common organic solvents. We added $PdCl_2(PhCN)_2$ to a dichloroethane solution of **6a**. After the mixture had been stirred at room temp. for 1 h, changes in the chemical shifts of the pyridyl moieties were observed by ^{1}H NMR spectroscopy. One proton on each pyridyl group appeared significantly downfield (δ = 9.1 ppm). This suggested clean formation of the titanium–palladium heterobimetallic complex **7** (Scheme 4). Yellow crystals were obtained from the dichloroethane solution in 35% yield, and the molecular structure of **7** was determined by X-ray analysis. The pyridyl moiety on the side arm had dissociated from the titanium metal and coordinated to palladium, and the titanium showed a five-coordinate structure.



Scheme 4. Preparation of Ti–Pd complex **7**.

It should be noted that all reactions from the ligands **4** to the heterobimetallic complex **7** proceeded at room temp. within 1 h. These results indicate that the heterobimetallic structure should be readily accessible in situ in a solution. Although we have tried other late-transition-metal complexes such as Ni(cod)$_2$, $CoBr_2$, [Rh(cod)Cl]$_2$, and [Ir(cod)Cl]$_2$ in attempts to prepare heterodinuclear complexes, we

have not achieved synthesis of these complexes so far. In most of these cases the starting complexes **5** or **6** remained unreacted, as judged from NMR spectroscopy. To form the bimetallic complexes, the late transition metals must take the coordinated pyridyl moiety from the titanium atom. The di(2-pyridyl) complex moiety of a late transition metal atom has to be thermodynamically more stable than the intramolecular pyridyl coordination to titanium in **5/6**. This might make complexation with the second metal difficult. The problem in the reaction with $Ni(cod)_2$ is unclear at present, although it might be for steric reasons.

Molecular Structures of the Complexes

The molecular structures of **6a** and **6b** are shown in Figure 2. The *O*,*N*,*O*-moieties in the ligands **4** coordinate to the titanium atom as expected. Interestingly, one of the pyridyl groups on the side arm coordinates to the titanium metal, and the complexes have six-coordinate structures. One of the phenoxide oxygen atoms is located at the position *trans* to the nitrogen atom of the lutidine group, and the other is at the position *trans* to the nitrogen atom of the pyridyl group on the side arm. The angles O1–Ti–O2 in **6a** and **6b** are 155.8° and 158.9°, respectively, and these are smaller than 180° although much larger than 120°. The O1–Ti–N2 angles are 74° for both, because the geometry is constrained by the ligand molecules. These show the strained octahedral structures of the complexes **6** (Table 1).

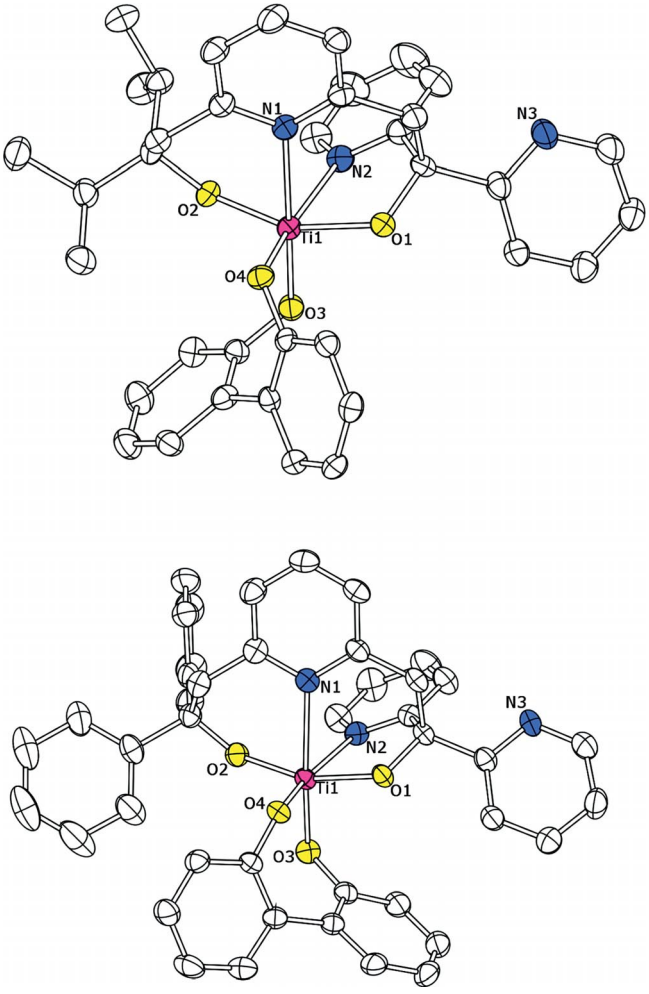


Figure 2. The molecular structures of **6a** (top) and **6b** (bottom). One of the two independent molecules of **6a** is shown.

Table 1. Selected interatomic distances (Å) and angles (°) in **6a**, **6b**, and **7**.

	6a (R = *i*Pr)[a]	**6b** (R = Ph)	**7** (R = *i*Pr)
Ti1–O1	1.885(2)	1.8649(16)	1.8637(13)
Ti1–O2	1.828(2)	1.8376(15)	1.7770(19)
Ti1–O3	1.874(2)	1.8774(16)	1.858(2)
Ti1–O4	1.876(2)	1.8641(17)	1.8423(18)
Ti1–N1	2.365(3)	2.3841(19)	2.259(2)
Ti1–N2	2.245(3)	2.262(2)	
Pd–N2			2.045(2)
Pd–N3			2.027(2)
O1–Ti1–O2	155.79(12)	158.89(7)	113.30(8)
O1–Ti1–O3	98.56(10)	98.82(7)	98.00(7)
O1–Ti1–O4	95.40(10)	92.67(7)	125.19(7)
O1–Ti1–N1	82.00(10)	80.59(7)	82.69(7)
O1–Ti1–N2	73.83(11)	74.19(7)	
O2–Ti1–O3	96.82(11)	94.93(7)	100.96(8)
O2–Ti1–O4	102.62(10)	102.57(7)	116.77(8)
O2–Ti1–N1	82.80(10)	83.48(7)	84.41(8)
O2–Ti1–N2	86.06(11)	89.28(7)	
O3–Ti1–N1	179.29(10)	171.65(7)	173.71(8)
N2–Ti1–N2	84.50(10)	79.04(7)	
Cl1–Pd–Cl2			90.43(3)
Cl1–Pd–N2			176.90(5)
Cl1–Pd–N3			91.07(6)
Cl2–Pd–N2			91.40(6)
Cl2–Pd–N3			175.99(5)
N2–Pd–N3			87.27(8)

[a] One of the two independent molecules is shown.

The molecular structure of **7** is depicted in Figure 3. The nitrogen atom N2, which was coordinated to Ti in complexes **6**, ligates to the palladium atom in **7**. The titanium

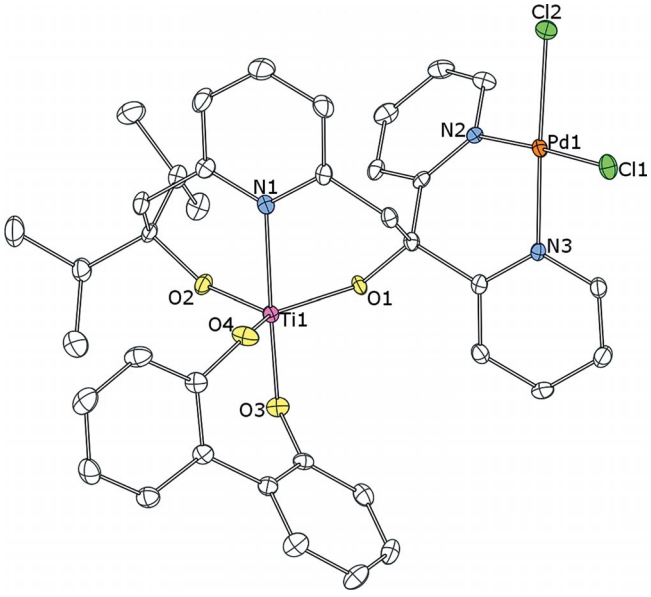


Figure 3. The molecular structure of **7**.

atom has a five-coordinate structure, and the N1–Ti–O3 angles in **6a**, **6b**, and **7** are 179.3°, 171.7°, and 173.1° respectively; these are almost linear. In contrast, the O1–Ti–O2 angle in **7** is 113.3°, significantly smaller than that in **6**. The sum of the three bond angles around Ti–O1, –O2, and –O4 is 355°. The angles around the palladium complexes are nearly right angles. Thus, complex **7** shows a trigonal-bipyramidal structure for titanium and a square-planar one for palladium. The dichloropalladium fragment is directed away from the titanium atom. This might be ineffective if one thinks of activation of a substrate that is captured by titanium. However, the dipyridyl palladium group shows a flexible conformation that enables the palladium atom to approach the titanium atom.

NMR Spectroscopy of the Complexes

The dynamic behavior of the complex **5a** in solution was observed by NMR spectroscopy at various temperatures (Figure 4). At room temp. (22 °C), broad signals of methylene groups were observed. These signals became sharp singlets at 60 °C at 3.4 (○) and 4.0 (●) ppm. Methine protons of the isopropoxy groups appeared as one septet at 60 °C at 5.13 (Δ) ppm. In contrast, as the temperature decreased, these signals split. At –40 °C, for example, two sets of doublets assignable to inequivalent geminal protons of the methylene groups were observed in the 2.4–4.3 ppm region. Two septets for the methine protons of the isopropoxy groups appeared at δ = 5.2 and 5.5 ppm.

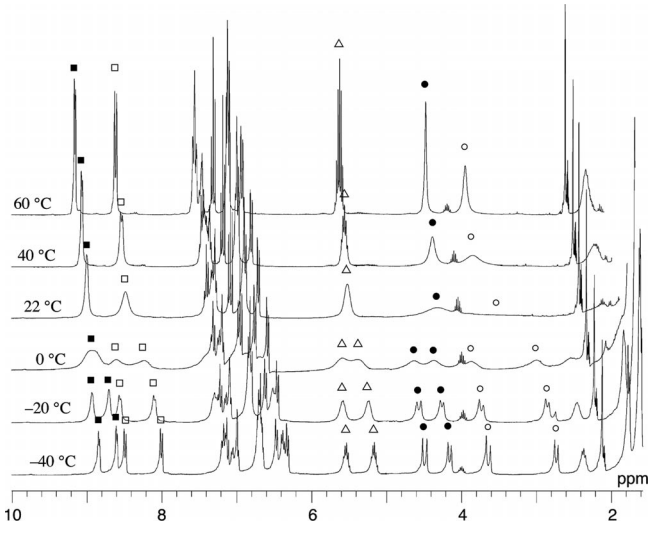
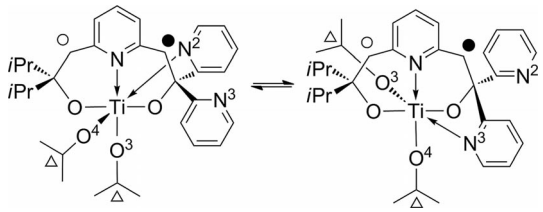


Figure 4. ^{1}H NMR spectra of **5a** at various temperatures. Open and closed squares probably represent pyridin-2-yl protons on the side arm.

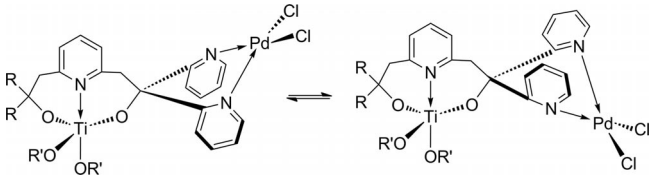
These results suggested that coordination by one of the two pyridyl groups on the side arm flips more rapidly than the NMR timescale at 60 °C (Scheme 5). The flipping is slow enough at –40 °C that two nonequivalent protons can be distinguished by ^{1}H NMR spectroscopy.



Scheme 5. Flipping of coordinated pyridyl moieties in **5a**.

The 2,2′-biphenoxy complex **6a** showed broader signals than those of **5a** even at –40 °C. This is probably because of diastereomeric conformers of the 2,2′-biphenoxide structure.

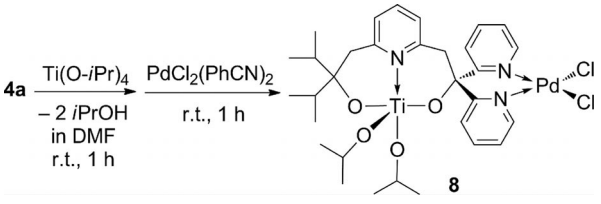
Interestingly, NMR spectroscopy revealed that the titanium–palladium heterobimetallic complex **7** also showed dynamic behavior in solution. One of the methylene protons appeared very broad at room temp. This signal was still broad at –40 °C. The reason for these broad signals is unclear at present; it is presumably because the dipyridylpalladium moiety can have two conformations. One of those was observed in the crystal structure, in which the $PdCl_2$ fragment is directed away from Ti, and the other conformer has the $PdCl_2$ fragment closer to the Ti atom. This "flipping" of the dipyridyl palladium is depicted in Scheme 6. This might make cooperative reactivity of Ti and Pd atoms possible.



Scheme 6. Possible conformers of the bimetallic complex **7**.

Preliminary Study on Catalytic Reactions

A few catalytic reactions involving the heterobimetallic complex have been preliminarily investigated. The complex **8** was prepared in situ by adding $Ti(O\text{-}iPr)_4$ and $PdCl_2(PhCN)_2$ in that order to a solution of **4a** (Scheme 7). The formation of **8** was confirmed by ^{1}H NMR spectroscopy.



Scheme 7. In situ preparation of the bimetallic complex **8**.

For example, the Mizoroki–Heck reaction between acrylic acid and iodobenzene was carried out in the presence of catalytic amounts of **8** (1 mol-%). Cinnamic acid was obtained in good yield (81%) after the mixture had been stirred at 140 °C for 2 h. Reactions in the presence of

8 resulted in better yields than those without Ti(O-*i*Pr)$_4$ in some cases. However, we encountered poor reproducibility of the catalytic reactions. Thus further investigation will be necessary to elucidate the role of the heterobimetallic structure in the catalytic reactions.

Conclusions

Multidentate *O*,*N*,*O*–*N*,*N* ligands were prepared from 2,6-lutidine. Titanium–palladium heterobimetallic complexes were selectively synthesized from these ligands by a simple synthetic method. The molecular structure of the heterobimetallic complex was confirmed by X-ray diffraction analysis, and it revealed a five-coordinate structure around titanium.

Experimental Section

General: All manipulations involving organometallic compounds were conducted under inert atmosphere with use of standard Schlenk techniques or in a glove box. Anhydrous tetrahydrofuran and dichloromethane were purchased from Kanto Chemical Co., Inc. and purified with a Glass Contour Solvent System™ (SG Water, USA) prior to use. Hexane and dichloroethane (dehydrated grade) were purchased from Kanto Chemical Co., Inc. and degassed prior to use. Titanium(IV) isopropoxide, 2,6-lutidine, 2,4-dimethylpentan-3-one, benzophenone, and *n*-butyllithium (hexane solution) were purchased from Kanto Chemical Co., Inc. and used as received. Di(pyridin-2-yl) ketone was purchased from Sigma–Aldrich Co. LLC. 2,2′-Biphenol was purchased from Tokyo Chemical Industry Co., Ltd. Bis(benzonitrile)palladium(II) chloride was prepared according to the literature.[8] NMR spectra were recorded with JEOL ECX 300 and ECA 500 spectrometers, and infrared spectra with a Shimadzu FT-IR 8300 instrument. Elemental analyses were measured with a Perkin–Elmer PE2400 Series II CHNS/O instrument.

Synthesis of the *O*,*N*,*O*–*N*,*N* Ligand 4a:[4,5b] *n*-Butyllithium (1.6 M hexane solution, 20 mmol) was added dropwise at –78 °C to a solution of 2,6-lutidine (2.14 g, 20 mmol) in THF (15 mL), and the orange mixture was stirred for 2.5 h. 2,4-Dimethylpentan-3-one (2.28 g, 20 mmol) was added, and the yellow mixture was allowed to warm to room temp. and stirred overnight. Hydrochloric acid was then added, and the mixture was neutralized with $NaOH_{aq}$ and extracted with dichloromethane. The organic layer was washed with water and dried with $MgSO_4$. The solvent was removed in vacuo to leave the mono-ol intermediate **3a** (95%) as a crude product. A portion of the obtained **3a** (1.93 g, 8.71 mmol) was dissolved in THF (12 mL), and *n*-butyllithium (in hexane 1.64 M, 17.4 mmol) was added dropwise to this solution at –78 °C. The mixture was allowed to warm to –20 °C over 5.5 h with stirring. The mixture was then cooled again to –78 °C, and di(2-pyridyl) ketone (1.6 g, 8.7 mmol) was added. The solution was stirred overnight at room temp. Dilute hydrochloric acid was added, and the mixture was neutralized with $NaOH_{aq}$ and extracted three times with dichloromethane. The organic layers were combined, washed with water, dried with $MgSO_4$, and purified by column chromatography (silica gel, hexane/EtOAc 4:1) to give the title compound **4a** as a yellow oil (2.16 g, 53%). ^{1}H NMR ($CDCl_3$, Me_4Si, 300 MHz): δ = 0.81 (d, J = 6.9 Hz, 12 H, CH_3), 1.75 (sept, J = 6.9 Hz, 2 H, C*H*), 2.65 (s, 2 H, CH_2), 3.91 (s, 2 H, CH_2), 5.95 (br., 1 H, O*H*), 6.68 (br., 1 H, O*H*), 6.86 (d, J = 7.6 Hz, 1 H), 7.09 (m, 3 H), 7.37 (t, J = 7.6 Hz, 1 H, Py-*H*), 7.62 (m, 2 H, Py-*H*), 7.85 (d, J = 7.9 Hz, 2 H, Py-*H*), 8.45 (m, 2 H, Py-*H*) ppm. ^{13}C NMR ($CDCl_3$, 75.6 MHz): δ = 17.58 (*C*H$_3$), 16.58 (*C*H$_3$), 34.60 (*C*H), 37.49 (*C*H$_2$), 48.50 (CH$_2$), 77.37 [q, *C*(OH)], 78.02 [q, *C*(OH)], 120.86 (*C*H, Py), 121.47 (*C*H, Py), 122.27 (*C*H, Py), 135.82 (*C*H, Py), 136.15 (*C*H, Py), 146.93 (*C*H, Py), 156.04 (q, Py), 159.54 (q, Py), 162.21 (q, Py) ppm. IR (NaCl): $\tilde{\nu}$ = 752, 1076, 1262, 1396, 1435, 1589, 2878, 2932, 3058, 3325 cm^{-1}. HRMS: calcd. for $C_{25}H_{31}N_3O_2$ 405.2416; found 405.2422.

Synthesis of the *O*,*N*,*O*–*N*,*N* Ligand 4b: The title compound was prepared in a similar manner to that used for **4a**, but with benzophenone instead of 2,4-dimethylpentan-3-one, as a white solid (50% isol.). The molecular structure of **4b** was determined by X-ray diffraction analysis. ^{1}H NMR ($CDCl_3$, Me_4Si, 300 MHz): δ = 3.45 (s, 2 H, CH_2), 3.85 (s, 2 H, CH_2), 6.66 (d, J = 7.9 Hz, 1 H, Py), 6.90 (d, J = 7.6 Hz, 1 H, Py), 7.01–7.21 (m, 9 H, Ph), 7.38 (d, J = 7.6 Hz, 4 H, Ph), 7.54 (td, J = 7.7, 1.7 Hz, 2 H, Py), 7.80 (d, J = 6.9 Hz, 2 H, Py), 8.42 (d, J = 4.8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, Me_4Si, 75.6 MHz): δ = 47.02 (*C*H$_2$), 48.82 (*C*H$_2$), 78.14 [q, *C*(OH)], 78.41 [q, *C*(OH)], 121.22 (Ph), 121.98 (Ph), 122.03 (Py), 123.03 (*C*H, Py), 126.24 (Ph), 126.24 (*C*H, 6 C) 127.72 (Ph), 136.27 (Py), 136.67 (Ph), 147.39 (q), 147.41 (CH), 156.54 (q, Py), 157.58 (q, Py), 162.51 (q, Py) ppm. IR (KBr): $\tilde{\nu}$ = 698, 756, 783, 802, 999, 1022, 1056, 1076, 1257, 1404, 1434, 1493, 1589, 2345, 2376, 2920, 3058, 3283, 3568, 3591, 3634, 3653, 3680, 3692, 3753, 3807, 3842, 3857, 3904, 3935 cm^{-1}. HRMS: calcd. for $C_{31}H_{27}N_3O_2$ 473.2103; found 473.2094.

One Pot Synthesis of 4a: An alternative one-pot synthesis of the ligand **4a** is as follows. Typically, *n*-butyllithium (1.60 M hexane solution, 5.0 mmol) was added dropwise at –78 °C to a solution of 2,6-lutidine (536 mg, 5.0 mmol) in THF (8 mL) and the mixture was stirred for 1 h. 2,4-Dimethylpentan-3-one (575 mg, 5.0 mmol) was added to this orange solution, and the reaction mixture was allowed to warm to room temp. After stirring overnight, the mixture was again cooled to –78 °C, *n*-butyllithium (5.0 mmol) was added, and the mixture was allowed to warm slowly to –40 °C over 5 h. The dark brown solution was cooled to –78 °C, and di(pyridin-2-yl) ketone (921 mg, 5.0 mmol) was added. The reaction mixture was allowed to warm to room temp. and stirred overnight, and dil. HCl was added. It was neutralized with $NaOH_{aq}$ and extracted with dichloromethane, and the organic layer was washed with water and dried with $MgSO_4$. The volatiles were removed in vacuo and the residue was purified with column chromatography. The ligand **4a** was obtained as a yellow oil (1.36 g, 67%).

Preparation of the Titanium Complex 5a: The ligand **4a** (102 mg, 0.25 mmol) and titanium tetraisopropoxide (74 mL, 0.25 mmol) were dissolved in toluene (1.5 mL) and stirred at room temp. for 1.5 h. Quantitative formation of titanium complex **5a** was observed by ^{1}H NMR spectroscopy. ^{1}H NMR ([D$_8$]toluene, 300 MHz, 80 °C): δ = 1.06 (d, J = 6.9 Hz, 6 H, CH_3), 1.11 (d, J = 6.9 Hz, 6 H, CH_3), 1.23 (d, J = 6.2 Hz, 6 H, CH_3), 1.41 (d, J = 6.2 Hz, 6 H, CH_3), 1.84 (sept, J = 6.9 Hz, 2 H, C*H*), 3.44 (s, 2 H, CH_2), 3.96 (s, 2 H, CH_2), 5.09 (sept, J = 6.5 Hz, 2 H, C*H*), 6.45 (d, J = 7.6 Hz, 1 H, Py), 6.61–6.65 (m, 3 H, Py), 6.83 (t, J = 7.6 Hz, 1 H), 7.06 (m, 2 H, Py), 8.09 (d, J = 8.3 Hz, 2 H), 8.65 (m, 2 H) ppm.

Preparation of the Titanium Complex 5b: The ligand **4b** (19 mg, 0.04 mmol) and titanium tetraisopropoxide (12 μL, 0.04 mmol) were dissolved in toluene (1.5 mL) and stirred at room temp. for 1 h. Quantitative formation of titanium complex **5b** was observed by ^{1}H NMR spectroscopy. ^{1}H NMR ([D$_8$]toluene, 300 MHz, 80 °C): δ = 1.23 (d, J = 6.0 Hz, 6 H, CH$_3$), 1.34 (d, J = 6.0 Hz, 6

H, CH_3), 3.93 (s, 2 H, CH_2), 4.07 (s, 2 H, CH_2), 5.03 (sept, J = 6.0 Hz, 2 H, CH), 6.37 (m, J = 7.6 Hz, 1 H, Py), 6.43 (d, J = 7.6 Hz, 1 H, Py), 6.60 (m, 2 H, Py), 6.72 (t, J = 7.7 Hz, 1 H), 6.96–7.18 (m, 8 H, Py), 7.60 (d, J = 7.6 Hz, 4 H, Py), 8.09 (d, J = 7.9 Hz, 2 H), 8.65 (d, J = 5.0 Hz, 2 H) ppm.

Synthesis of the Titanium Complex 6a: The volatiles, including free propan-2-ol, were removed in vacuo from the toluene solution of complex **5a** (1.18 mmol) obtained above. The residue was again dissolved in toluene (2 mL), and 2,2′-biphenol (219 mg, 1.18 mmol) was added. The yellow solution turned dark orange, and after it had been stirred at room temp. for 1 h. ^{1}H NMR observation revealed that isopropoxy groups had been quantitatively replaced with biphenoxy moieties. The mixture was filtered and hexane (0.25 mL) was slowly added to the filtrate. The title compound **6a** was obtained as orange block crystals (433 mg, 56%). ^{1}H NMR ($CDCl_3$, Me_4Si, 300 MHz, 60 °C): δ = 0.74 (d, J = 6.9 Hz, 6 H, CH_3), 0.91 (d, J = 6.9 Hz, 6 H, CH_3), 1.63 (sept, J = 6.9 Hz, 2 H, CH), 3.53 (s, 2 H, CH_2), 4.06 (s, 2 H, CH_2), 6.57 (dd, J = 7.9, 1.0 Hz, 2 H, Py), 6.85 (td, J = 7.5, 1.2 Hz, 2 H, Py), 7.02–7.18 (m, 6 H), 7.30 (dd, J = 7.6, 1.7 Hz, 2 H, Py), 7.50–7.60 (m, 5 H), 8.74 (d, J = 4.8 Hz, 2 H, Py) ppm. ^{13}C NMR ($CDCl_3$, 75.6 MHz): δ = 18.87 (2 C, *i*Pr, CH_3), 19.30 (2 C, *i*Pr, CH_3), 35.77 (2 C, *i*Pr, CH), 42.71 (CH_2), 47.51 (CH_2), 86.06 (C-OH, q), 89.33 (C-OH, q), 118.12 (2 C, CH), 120.10 (2 C, CH), 122.08 (2 C, CH) 122.11 (2 C, CH), 124.04 (CH), 125.24 (CH), 127.58 (2 C, CH), 127.58 (q, overlapped, 2 C), 128.93 (q, 2 C), 131.34 (2 C, CH), 137.83 (2 C, CH), 138.09 (CH), 147.57 (2 C, CH), 158.01 (q), 160.72 (q), 163.24 (q, 2 C) ppm. IR (KBr): $\tilde{\nu}$ = 621, 644, 667, 690, 717, 756, 876, 941, 1037, 1099, 1153, 1230, 1277, 1431, 1470, 1489, 1574, 1593, 2878, 2959, 3059 cm^{-1}. $C_{37}H_{37}N_3O_4Ti$ (635.6): calcd. C 69.92, H 5.87, N 6.61; found C 69.92, H 5.82, N 6.61.

Synthesis of the Titanium Complex 6b: Ti(O-*i*Pr)$_4$ (59 μL, 0.20 mmol) was added at room temp. to a solution of the *O*,*N*,*O*–*N*,*N* ligand **4b** (94 mg, 0.20 mmol) in toluene (1.5 mL). The mixture was stirred for 1 h at room temp. 2,2′-Biphenol (37 mg, 0.20 mmol) was added to the mixture at room temp. The mixture was stirred for an additional 1 h at room temperature. The product was recrystallized by adding *n*-hexane (0.2 mL). The title compound was obtained as orange crystals (105 mg, 75%). ^{1}H NMR ([D_8]toluene, Me_4Si, 300 MHz, 80 °C): δ = 3.88 (s, 2 H, CH_2), 4.10 (s, 2 H, CH_2), 6.37 (d, J = 7.9 Hz, 1 H, Py), 6.53 (m, 3 H, CH), 6.44 (dd, J = 7.9, 1.4 Hz, 2 H, CH), 6.77 (t, J = 7.9 Hz, 1 H, Py), 6.91–7.09 (m, 6 H), 7.33 (d, J = 1.4 Hz, 2 H, CH), 7.36 (d, J = 2.1 Hz, 2 H, CH), 7.46 (dd, J = 7.6, 1.7 Hz, 2 H, CH), 7.49 (dt, J = 7.90, 0.90 Hz, 2 H, Py), 8.56 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, Me_4Si, 75.6 MHz, 60 °C): δ = 47.77 (CH_2), 50.94 (CH_2), 87.14 (q, C-OH), 87.17 (q, C-OH), 117.80 (2 C, CH), 120.55 (2 C, CH), 122.00 (2 C, CH), 122.20 (2 C, CH), 124.51 (C, CH), 125.38 (CH), 125.74 (CH), 126.15 (2 C, Ph, CH), 126.64 (4 C, Ph, CH), 127.55 (2 C, Ph, CH), 127.55 (q, overlapped, 2 C), 127.79 (2 C, CH), 128.29 (2 C, CH), 128.53 (q, 2 C), 129.10 (1 C, CH), 131.21 (2 C, CH), 137.86 (q, 2 C), 138.54, (CH), 147.76 (2 C, CH), 158.07 (q, Py), 158.96 (q, Py), 163.07 (q, 2 C, Py) ppm. IR (KBr): $\tilde{\nu}$ = 625, 648, 675, 694, 718, 756, 876, 949, 1038, 1096, 1146, 1231, 1277, 1431, 1470, 1489, 1570, 1597, 2280, 2345, 2372, 2515, 2870, 3020, 3059, 3402, 3634, 3653, 3738, 3753, 3807, 3842, 3857, 3903 cm^{-1}. $C_{43}H_{33}N_3O_4Ti$ (703.7): calcd. C 73.40, H 4.73, N 5.97; found C 73.14, H 4.82, N 5.84.

Synthesis of the Heterobimetallic Complex 7: The titanium complex **6a** (54 mg, 0.077 mmol) was dissolved in dichloroethane (4 mL), and to this solution $PdCl_2(PhCN)_2$ (31 mg, 0.081 mmol) was added. The mixture was stirred at room temp. for 1 h, and quantitative formation of the title compound was observed by ^{1}H NMR spectroscopy. The mixture was filtered with a glass filter (G4) and Celite. The filtrate was concentrated in vacuo and allowed to stand to give **7** as yellow crystals (22 mg, 35%). ^{1}H NMR ($CDCl_3$, Me_4Si, 300 MHz): δ = 0.83 (d, J = 7.2 Hz, 6 H, CH_3), 0.94 (d, J = 6.9 Hz, 6 H, CH_3), 1.78 (m, 2 H, CH), 3.38 (s, 2 H, CH_2), 6.0 (br., 1 H, CH_2), 6.89 (d, J = 7.9 Hz, 2 H), 7.06 (td, J = 7.2, 1.0 Hz, 2 H, Py), 7.20–7.30 (m, 5 H), 7.40 (dd, J = 7.3, 1.5 Hz, 2 H, Py), 7.62–7.72 (m, 3 H), 7.84 (d, J = 7.6 Hz, 1 H, Py), 7.92 (d, J = 7.6 Hz, 2 H), 9.12 (dd, J = 5.8, 1.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, Me_4Si, 75.6 MHz): δ = 18.18 (2 C, *i*Pr, CH_3), 18.71 (2 C, *i*Pr, CH_3), 34.95 (2 C, *i*Pr, CH), 42.30 (CH_2), 89.10 (C-OH, q), 95.11 (C-OH, q), 117.55 (2 C, CH), 122.22 (2 C, CH), 123.42 (2 C, CH), 124.37 (2 C, CH), 125.06 (CH), 125.52 (CH), 127.22 (q, 3 C), 128.18 (q, 1 C), 128.49 (2 C, CH), 131.58 (2 C, CH), 139.45 (2 C, CH), 140.54 (CH), 153.48 (q), 153.62 (2 C, CH), 158.23 (q), 158.29 (q), 160.66 (q, 1 C) ppm. IR (KBr): $\tilde{\nu}$ = 644, 675, 721, 760, 880, 949, 1026, 1096, 1130, 1180, 1234, 1273, 1435, 1466, 1489, 1543, 1570, 1601, 1655, 1686, 1701, 1720, 2345, 2380, 3653, 3676, 3807, 3823, 3842, 3857, 3873, 3904 cm^{-1}. Elemental analysis did not give satisfactory results despite our attempts, probably because of the instability of the compound. The product was structurally characterized by X-ray diffraction analysis.

Heck Reactions Catalyzed by Ti–Pd Heterobimetallic Complex: A typical procedure is as follows. Titanium(IV) isopropoxide (6 μL, 0.02 mmol) was added to a solution of ligand **4a** (8 mg, 0.02 mmol) in DMF (2 mL) in a 20 mL Schlenk tube and the mixture was stirred for 0.5 h at room temp. Bis(benzonitrile)palladium(II) chloride (8 mg, 0.02 mmol) was added, and the mixture was stirred for 0.5 h. Acrylic acid (144 mg, 2.0 mmol), iodobenzene (408 mg, 2.0 mmol), and triethylamine (414 mg, 4.2 mmol) were added to this reddish brown solution, and the mixture was stirred at 140 °C for 2 h. The reaction mixture was diluted with diethyl ether and dilute HCl was added. The mixture was extracted with diethyl ether/dichloromethane (10:1). The organic layers were combined, washed with water, and dried with magnesium sulfate. Volatiles were removed in vacuo to leave the crude product as a brownish solid (291 mg crude). The solid was dissolved in $CDCl_3$ and measured by ^{1}H NMR with use of toluene (1.0 mmol) as internal standard to determine the yield of cinnamic acid (81%).

X-ray Diffraction Analyses of the Titanium Complex 6a: Crystals were obtained by evaporation of solvent from a dichloromethane solution. A yellow block crystal (0.15 × 0.10 × 0.10 mm) was mounted on a polyamide film (MicroMounts™, MiTegen) and coated with paraffin. All data were collected with a Rigaku Mercury CCD area detector and use of graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 153 K. The structure was solved by direct methods[9] and expanded by use of Fourier techniques.[10] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by use of the riding model. The cell units consist of two crystallographically independent molecules of **6a**, which have fundamentally identical structures. The final cycle of full-matrix, least-squares refinement on F^2 was based on 14560 observed reflections and 819 variable parameters. All calculations were performed by use of the CrystalStructure[11] crystallographic software. Crystallographic data are summarized in the Supporting Information. CIF data were deposited in the Cambridge Structural Database (CCDC-1019249).

X-ray Diffraction Analyses of the Titanium Complex 6b: Crystals were obtained by recrystallization from a toluene solution. A yellow block crystal (0.30 × 0.30 × 0.15 mm) was mounted on a polyamide film (MicroMounts™, MiTegen) and coated with paraffin. All data were collected with a Rigaku Mercury 70 CCD area detec-

tor and use of graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 193 K. The structure was solved by direct methods[12] and expanded by use of Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by use of the riding model. The unit cell contained one toluene molecule per molecule of **6b**. The final cycle of full-matrix, least-squares refinement on F^2 was based on 9442 observed reflections and 523 variable parameters. All calculations were performed by use of the CrystalStructure[11] crystallographic software package except for refinement, which was performed by use of SHELXL-97.[10] Crystallographic data are summarized in the Supporting Information. CIF data were deposited in the Cambridge Structural Database (CCDC-1019248).

X-ray Diffraction Study of the Ti–Pd Heterobimetallic Complex 7: Single crystals were obtained by recrystallization from a dichloroethane solution. A yellow crystal ($0.20 \times 0.10 \times 0.07$ mm) was mounted on a polyamide film (MicroMounts™, MiTegen) and coated with paraffin. All data were collected with a Rigaku Mercury 70 CCD area detector and use of graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 93 K. The structure was solved by direct methods[9] and expanded by use of Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined by use of the riding model. The final cycle of full-matrix, least-squares refinement on F^2 was based on 7940 observed reflections and 437 variable parameters. All calculations were performed by use of the CrystalStructure[11] crystallographic software package. Crystallographic data are summarized in the Supporting Information. CIF data were deposited in Cambridge Structural Database (CCDC-1019250).

CCDC-1019249 (**6a**), -1019248 (**6b**), and -1019250 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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