Dynamic Titanium Phosphinoamides as Unique Bidentate Phosphorus Ligands for Platinum

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Treatment of lithium phosphinoamides, $Ph_2PN(Li)R$ [R = ^tBu, ^iPr], with $TiCl_4$ results in formation of titanium phosphinoamides, $(Ph_2PNR)_2TiCl_2$ [R = ^tBu (**1a**), ^iPr (**1b**)]. Crystallographic studies show that there are covalent bonds between the titanium and two nitrogen atoms, whereas two phosphorus atoms are coordinated to the metal center intramolecularly. Variable-temperature NMR studies suggest reversible dissociation of the phosphorus moieties from the titanium in solution. The dissociated phosphorus moieties are effectively captured by Pt(II) species; reactions of **1a** with either (η^4-COD)$PtCl_2$, (η^4-COD)Pt(R)(Cl) (R = Me, *p*-Tol), or $[Me_2Pt(\mu\text{-}SMe_2)]_2$ afford the corresponding Ti−Pt heterobimetallic complexes. The molecular structures of these complexes reveal that they have a six-membered dimetallacycle, in which a titanium and a platinum are connected by two bridging phosphinoamide ligands; the Pt−Ti distances indicate the existence of a Pt→Ti dative bond. The conformation of the dimetallacycle is a boat form, with two metals at the bow and the stern in the crystal; however, dynamic conformational change involving cleavage and re-formation of the Pt→Ti dative bond is indicated from variable-temperature NMR studies.

Introduction

There have been numerous examples of the successful use of phosphorus ligands for late transition metals in metal-catalyzed organic or polymer syntheses.[1] Electronic and structural properties of phosphorus ligands actually affect the rate and selectivity of the catalytic reactions, and as control factors, Tolman's cone angle and χ values are generally considered for their structural and electronic design.[1a] For the metal complexes having bidentate phosphorus ligands, the importance of the bite angle is well recognized as an additional factor for a rational ligand design.[1b] Phosphorus compounds containing a metal center in the molecule have lately been attracting the attention of organometallic chemists as metal-containing ligands (metalloligands) for transition metals, of which potential interaction of the metal in the metalloligand with the transition metal bound to the phosphorus atoms may provide special reactivity of the transition metal center.[2−4] In particular, several trials have been made on the preparation of bidentate phosphorus compounds containing a titanium and zirconium moiety, and their ligation to late transition metals was studied.[2,3] Examples closely related to the present paper are $Cp_2M(PR_2)_2$,[2a−g] $Cp_2Zr(CH_2PR_2)_2$,[2h−n] and $Cp_2M(O{\sim}PPh_2)_2$,[2o−q] (M = Ti, Zr), which are coordinated to late transition metals such as Rh and Pt to give the corresponding heterobimetallic complexes of the type $Cp_2M(\mu\text{-}PR_2)_2M'L_n$ $Cp_2Zr(CH_2PR_2)_2M'L_n$, and $Cp_2M(O{\sim}PPh_2)_2M'L_n$ (M = Ti, Zr; $M'L_n$; late transition metal fragments), respectively.

In these earlier studies on the heterobimetallic complexes formed by the reaction of the above metalloligand with late transition metals, the titanium or zirconium center is considered to act as a Lewis acidic center (electron acceptor). In fact,

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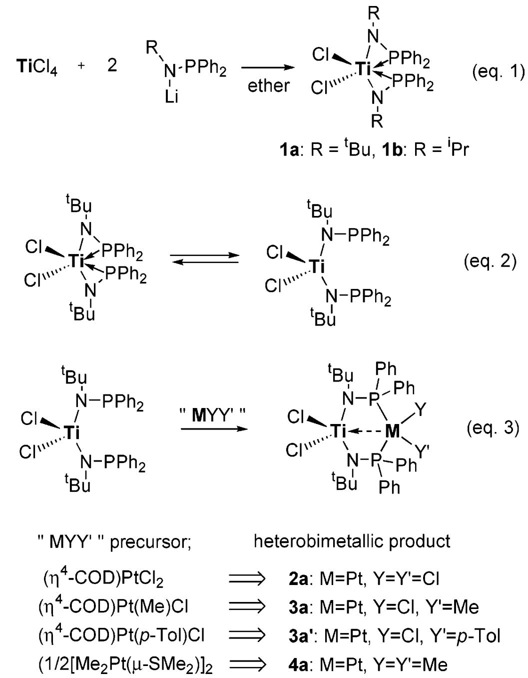
possible contribution of the Lewis acidic zirconium center to the cooperative reactivity with the late transition metal center in the activation step of CO was proposed in the rhodium-catalyzed hydroformylation of olefins with these Zr−Rh heterobimetallic complexes.[3b−d] However, it should be noted that the titanocene or zirconocene unit is not a strong electron acceptor, because the coordination of electron-donating Cp ligands reduces the Lewis acidity of the titanium or zirconium center. In this sense, replacement of the Cp_2Ti or Cp_2Zr unit by a Ti or Zr moiety with stronger Lewis acidity is of interest. If such metalloligands can be realized and successfully ligate to transition metals, donor−acceptor interaction between the late transition metal center and the Ti or Zr center would be more clearly visible. However, such complexes, e.g., $Cl_2Ti(\mu\text{-}PR_2)_2ML_n$ and $Cl_2Zr(\mu\text{-}CH_2PR_2)_2ML_n$, have not been synthesized to our knowledge. Part of the reason is enhanced Lewis acidity of the Ti or Zr moiety, which causes its strong intermolecular interaction with phosphorus atoms in the metalloligand, leading to their self-aggregation. The self-aggregation is likely to prevent the interaction of the phosphorus compounds containing the $TiCl_2$ or $ZrCl_2$ unit with late transition metals. In fact, compounds containing Lewis acidic R_2Al and Lewis basic R_2P units in one molecule are known as "amphoteric ligands".[5] In these compounds, self-aggregations are often seen, for example, $R_nCl_{2-n}AlCH_2PR_2$, in which two strong P→Al bonds provide a dimer with a six-membered ring structure.[5b] Although an aluminum phosphinoamide, $Ph_2P(^tBu)NAlEt_2$, was reportedly a monomer in a benzene solution,[5f] this was later contradicted by Labinger's NMR study.[5a] It is interesting, however, that $Ph_2P(^tBu)NAlEt_2$ reacted with certain metal carbonyls to give metallacyclic products, presumably due to the mechanisms involving its dissociation to a monomeric form.

In our continuous efforts to synthesize new heterobimetallic complexes,[6,7] we were interested in the potential of $(PPh_2NR)_2TiCl_2$ (**1**) as a new type of bidentate phosphorus ligand containing a Lewis acidic $TiCl_2$ unit. The chemistry of phosphinoamides has lately received considerable attention because of two possible resonance structures, $[R'_2PNR]^-$ and $[R'_2P{=}NR]^-$, and detailed structural studies on the lithium phosphinoamides have been carried out since a pioneering study by Ashby and Li.[8] Several reports were published on the phosphinoamide and related phosphinoamide complexes of the early transition metals[9] and lanthanides.[10] In particular, successful preparation of $(Ph_2PNPPh_2)_2TiCl_2$ and $Zr(Ph_2PNPh)_4$ reported by Eisen and co-workers[9a] strongly suggested that **1** could be synthesized by careful treatment of $TiCl_4$ with 2 equiv of $Li[R'_2PNR]$. On the other hand, it was questionable when we started this research whether the formed **1** behaves as a bidentate phosphorus ligand; coordination of the phosphorus moieties in **1** to a late transition metal species should be competitive with the intramolecular coordination of the phosphorus moieties with the titanium center.

Scheme 1



In this paper, we wish to report that **1** can actually be synthesized and behaves as a metalloligand to Pt(II). Thus, $(Ph_2PNR)_2TiCl_2$ (**1a**, R = ^tBu; **1b**, R = ^iPr) were prepared according to Scheme 1, eq 1, and were characterized by spectroscopy and crystallography. Although the crystal structures of **1a** and **1b** showed coordination of the two phosphorus moieties to the titanium center, variable-temperature NMR suggested that this coordination was essentially reversible in solution (Scheme 1, eq 2). The dissociated phosphorus moieties were successfully captured by Pt(II) species to afford a series of early−late heterobimetallic (ELHB) complexes, $XX'M'(Ph_2PN^tBu)_2TiCl_2$ (**2a**, M′ = Pt, X, X′ = Cl; **2b**, M′ = Pd, X, X′ = Cl; **3a**, M′ = Pt, X = Me, X′ = Cl; **3a′**, M′ = Pt, X = *p*-Tol, X′ = Cl; **4a**, M′ = Pt, X, X′ = Me) (Scheme 1, eq 3). It is important that interaction of the Lewis acidic titanium center and the Lewis basic platinum center was proved by the existence of a dative bond seen in their crystal structures. The results clearly demonstrate the ability of **1** as a unique bidentate phosphorus ligand containing a Lewis acidic titanium, which is capable of interacting with platinum in the resulting Ti−Pt heterobimetallic complexes.

Results and Discussion

Preparation and Characterization of Titanium Phosphinoamides. Treatment of Ph_2PNHR (R = ^tBu, ^iPr) with *n*-BuLi in ether afforded the lithium phosphinoamide $Ph_2PN(Li)R$. The

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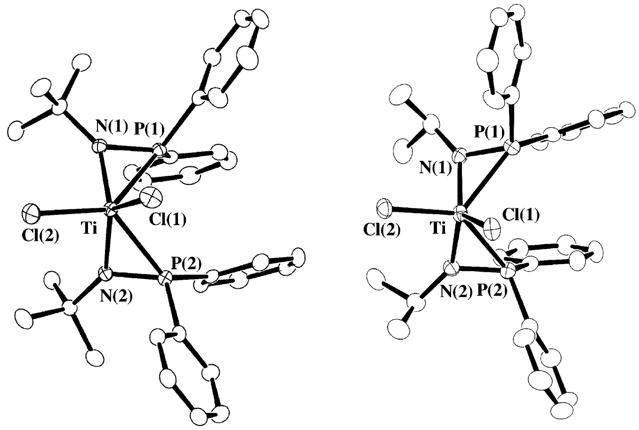
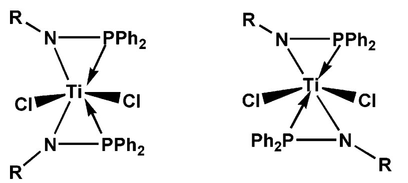


Figure 1. ORTEP drawings of **1a** (left) and **1b** (right).



C_s-symmetric (**A**) C_2-symmetric (**B**)

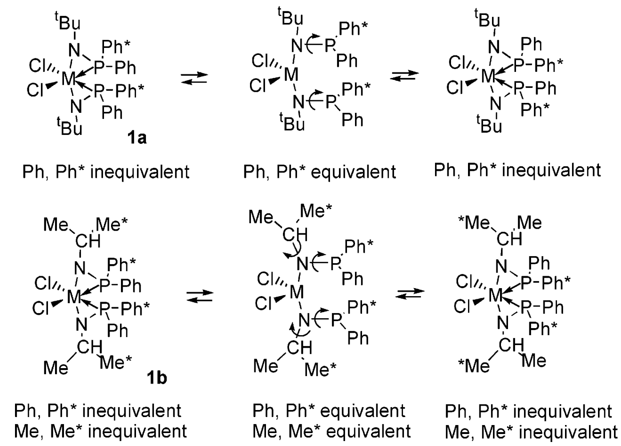
Figure 2. Possible isomers of titanium phosphinoamides.

Table 1. Representative Bond Lengths and Angles for 1a and 1b

	1a	**1b**
Bond Lengths (Å)		
Ti−Cl(1)	2.3247(9)	2.3044(16)
Ti−Cl(2)	2.3183(8)	2.3145(17)
Ti−P(1)	2.4223(9)	2.4754(14)
Ti−P(2)	2.4609(8)	2.4762(17)
Ti−N(1)	1.980(2)	1.939(3)
Ti−N(2)	1.970(2)	1.952(4)
P(1)−N(1)	1.643(2)	1.642(4)
P(2)−N(2)	1.641(2)	1.640(4)
Bond Angles (deg)		
Cl(1)−Ti−Cl(2)	94.07(3)	95.90(6)
N(1)−Ti−N(2)	110.05(10)	112.78(18)
P(1)−Ti−P(2)	89.79(2)	95.57(5)
N(1)−Ti−P(1)	42.34(7)	41.49(11)
N(1)−Ti−P(2)	99.21(7)	108.58(14)
N(2)−Ti−P(1)	126.09(7)	127.30(13)
N(2)−Ti−P(2)	41.67(7)	41.40(12)
Cl(1)−Ti−P(1)	95.03(3)	93.34(5)
Cl(1)−Ti−P(2)	100.93(3)	94.88(5)
Cl(2)−Ti−P(1)	124.79(3)	125.41(5)
Cl(2)−Ti−P(2)	140.93(3)	136.69(5)
N(1)−Ti−Cl(1)	132.32(8)	129.21(13)
N(1)−Ti−Cl(2)	96.71(7)	96.35(13)
N(2)−Ti−Cl(1)	112.74(8)	114.42(11)
N(2)−Ti−Cl(2)	99.27(7)	96.58(13)

resulting solution was subjected to the reaction with $TiCl_4$ [a half equivalent to $Ph_2PN(Li)R$] to give the titanium phosphinoamides **1a** (R = ^{t}Bu) and **1b** (R = ^{i}Pr) in 84 to 81% yield. X-ray structure determination of **1a** and **1b** provided the molecular structures shown in Figure 1, and representative bond distances and angles are summarized in Table 1. Two chlorine, two nitrogen, and two phosphorus atoms make a distorted octahedral arrangement, and the chlorine atoms and centers of the N−P bonds are arranged tetrahedrally. Although there should be two isomeric structures, C_s-symmetric **A** and C_2-symmetric **B**, shown in Figure 2, only structure **A** was detected in the crystal. Two possible tautomeric structures of lithium phosphinoamides, $[R_2PN^-R']Li^+$ and $[R_2P^-{=}NR']Li^+$, were discussed in the literature from crystal structures and MO calculations, in which the N−P bond distance may suggest the double-bond nature of the N−P linkage.[8] The N−P distances of **1a** and **1b** are 1.640 to 1.643 Å, similar to the N−P distances of a series of lithium phosphinoamides, which are between typical P═N bonds and the sum of van der Waals radii of N and P. These suggest some contribution of $[R_2P^-{=}NR']$, similar to the lithium salts. The nitrogen atoms are sp^2-hybridized; this suggests that a lone pair electron of the nitrogen atom is delocalized by the P═N and N→Ti interaction.

Scheme 2



As described above, two phosphorus atoms in **1a** and **1b** are coordinated to the titanium center in the crystal structure. A single ^{31}P resonance at δ −15.8 (**1a**) and −19.2 (**1b**), which shows a 38.4 or 53.7 ppm higher field shift compared with that of Ph_2PNH^tBu (δ 22.6) or Ph_2PNH^iPr (δ 34.5), respectively, indicates the coordination of the P atom. In contrast, ^{1}H and ^{13}C NMR spectra of **1a** and **1b** did not provide clear evidence for the coordination at room temperature. Although the coordination makes two phenyl groups on the P atom inequivalent, only the signals due to the magnetically equivalent phenyl groups were seen in the ^{1}H and ^{13}C NMR spectra at room temperature. For example, the ^{1}H NMR spectrum of **1a** in CD_2Cl_2 showed a sharp singlet at δ 1.36 and three signals at δ 7.29, 7.41, and 7.53 in an integral ratio of 9:2:1:2, which are assignable to methyl of ^{t}Bu, *ortho*-phenyl, *para*-phenyl, and *meta*-phenyl protons, respectively. Similarly, ^{13}C NMR spectra showed only six peaks due to the ^{t}Bu and the magnetically equivalent two phenyl groups. The crystal structure of **1b** indicates an additional problem that two methyl groups due to the isopropyl moiety should be diastereotopic; however, only magnetically equivalent ^{1}H and ^{13}C resonances due to the methyl as well as the phenyl groups are visible at room temperature.

A clue to the understanding of the NMR spectra was obtained from the ^{1}H NMR spectra at low temperature. The ^{1}H resonances due to the phenyl groups in **1a** are significantly broadened at −105 °C; this may result from the reversible coordination shown in Scheme 2 (upper scheme). The ^{1}H signal due to the methyl groups of the isopropyl moiety in **1b** provides more clear evidence of the equilibrium shown in the lower scheme in Scheme 2; the methyl resonance is a sharp doublet at room temperature, starts to broaden at −60 °C, and turns to a broad singlet at −90 °C. At −105 °C, broadening of the signal results in significant decrease of the peak intensity. Similar broadening of the ^{13}C and ^{31}P resonances is visible in variable-temperature NMR measurements of **1a** and **1b**. The actual charts are shown in the Supporting Information. Although a technical problem prevents the experiment, two doublets due to the diastereotopic methyl groups would appear at a temperature below −105 °C.

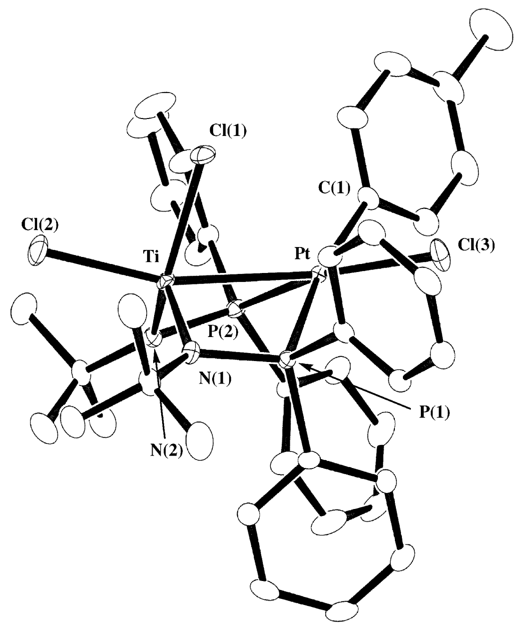


Figure 3. ORTEP view of **3a′**.

Eisen and co-workers observed the dynamic behavior of Zr-(Ph_2PNPh)$_4$ and proposed similar reversible dissociation of some of the phosphorus moieties in solution.[9a]

Titanium Phosphinoamides as a Metalloligand: Reactions with Organoplatinum Complexes. As described above, titanium phosphinoamides were successfully prepared and characterized, and the reversible dissociation of the phosphorus moieties in solution was indicated from the variable-temperature ^{1}H NMR. There should be a possible capture of the dissociated phosphorus moieties in the titanium phosphinoamides by appropriate transition metal species, leading to preparation of new heterobimetallic complexes. In fact, treatment of **1a** with (COD)$PtCl_2$, (COD)PtMeCl, and (COD)Pt(*p*-Tol)Cl actually gave the corresponding Ti−Pt bimetallic complexes **2a**, **3a**, and **3a′**, in 80, 84, and 65% yield, respectively. Although (COD)-$PtMe_2$ did not react with **1a**, treatment of [Me_2Pt(μ-SMe_2)]$_2$ with **1a** afforded **4a** in 81% yield. The molecular structures of all four of these complexes were determined by crystallography. Two of them, **3a** and **4a**, contain crystallographic problems, which are caused by disorder of the methyl and the chloro group in **3a**, and disorder of the solvates (Et_2O) in **4a**. However, careful examinations of the crystallography of **3a** and **4a** suggest that there should be no problem in discussing the six-membered dimetallacyclic structures. The ORTEP drawing of **3a′** is depicted in Figure 3 as representative of the whole structure, and the simplified molecular structures illustrating the six-membered dimetallacycles of **2a**, **3a**, and **4a** are shown in Figure 4. The representative bond distances and angles are summarized in Table 2. All of these four complexes have a similar dimetallacyclohexane framework, in which two nitrogen atoms are bonded to the titanium atom, whereas two phosphorus atoms are coordinated to the platinum center. The conformation of the six-membered ring is a boat form, with the two metal atoms at the bow and the stern. The Ti−Pt distances indicate that there is a possibility of a Pt→Ti dative bond, as discussed later in detail. Presumably due to this dative bond, two chlorine and two nitrogen atoms coordinated to the titanium atom are distorted significantly from tetrahedral to pseudo-trigonal bipyramidal, in which one chlorine atom and the platinum moiety are at the apical position, whereas the other chlorine atom and the two nitrogen ligands are at the basal position. The ligand arrangement around the platinum atom is square planar; however, the platinum center is somewhat out of plane due to the Pt−Ti interaction. The phosphinoamide ligands bridge over the Pt→Ti dative bond. The N−P distances around 1.66 Å are approximately 0.1 Å shorter than the sum of the van der Waals radii of N and P; a contribution of [R_2P^-═NR′] may exist similar to those seen in titanium phosphinoamides **1a** and **1b**. The nitrogen atoms are sp^2-hybridized; this suggests that a lone pair electron of the nitrogen atom is delocalized by the P═N and N→Ti interaction. The complexes bearing a bridging phosphinoamide ligand, $Cp_2ZrClN(SiMe_3)P(H)(^tBu)Fe(CO)_4$[11a] and $Cp_2ZrN(^tBu)PR_2Ir(H)Cp^*$,[11b] were synthesized by Majoral and Bergman, respectively. Although the former was characterized by spectroscopic methods in the solution state, the latter prepared from [Cp_2Zr(μ-N^tBu)$IrCp^*$] with HPRR′ (R = R′ = Et or R = cyclohexyl, R′ = H) was investigated in detail by

Table 2. Representative Bond Lengths and Angles for the Heterobimetallic Complexes

	2a	3a	4a	3a′
		Bond Lengths (Å)		
Pt−Ti	2.8358(8)	2.7547(10)	2.6860(11)	2.7234(4)
Pt−Cl(3)	2.3458(16)	2.347(1)		2.3476(7)
Pt−Cl(4)	2.3489(16)			
Pt−C(1)		2.154(13)	2.135(8)	2.058(2)
Pt−C(2)			2.116(11)	
Pt−P(1)	2.2772(15)	2.3507(18)	2.325(2)	2.4087(6)
Pt−P(2)	2.2868(16)	2.2632(17)	2.317(2)	2.2435(5)
Ti−Cl(1)	2.2749(17)	2.288(2)	2.322(2)	2.3075(8)
Ti−Cl(2)	2.2353(15)	2.2408(18)	2.283(2)	2.2722(9)
Ti−P(1)	2.7947(16)	2.728(2)	2.6846(19)	2.6555(8)
Ti−P(2)	2.7823(17)	2.7795(19)	2.700(3)	2.7849(7)
Ti−N(1)	1.950(4)	1.940(6)	1.926(8)	1.910(2)
Ti−N(2)	1.929(5)	1.965(6)	1.957(8)	1.998(2)
P(1)−N(1)	1.664(4)	1.665(5)	1.659(5)	1.683(2)
P(2)−N(2)	1.665(4)	1.663(5)	1.665(6)	1.657(2)
		Bond Angles (deg)		
P(1)−Pt−P(2)	102.48(5)	103.39(6)	103.39(7)	105.64(2)
Cl(3)−Pt−Cl(4)	83.36(5)			
P(1)−Pt−Cl(3)	86.45(5)	85.90(7)		85.94(2)
P(2)−Pt−Cl(4)	86.00(5)			
C(1)−Pt−Cl(3)		82.7(3)		81.34(7)
C(1)−Pt−P(1)		168.6(3)	87.4(3)	167.28(7)
C(1)−Pt−P(2)		87.7(3)	165.2(3)	86.44(7)
C(2)−Pt−P(2)			88.0(2)	
C(1)−Pt−C(2)			79.7(3)	

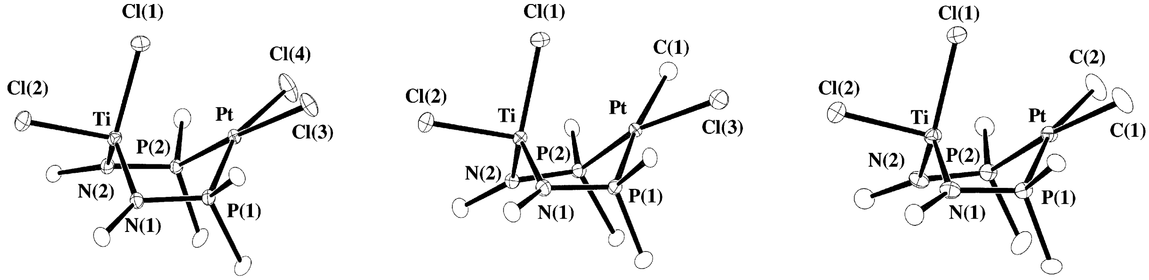
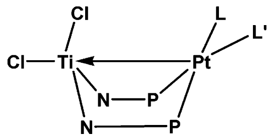


Figure 4. Simplified molecular structures of the heterobimetallic complexes **2a** (left), **3a** (center), and **4a** (right).



Pt-Ti bond length(Å)
2a: $PtCl_2$ 2.8358(8)
3a: PtMeCl 2.7547(10)
3a': Pt(*p*-Tol)Cl 2.7234(4)
4a: $PtMe_2$ 2.6860(11)

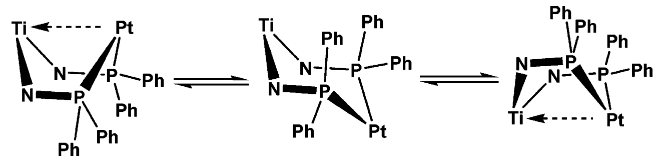
Figure 5.

crystallography [Zr−Ir distance: 2.642(1) Å]. The nitrogen atom is sp^2-hybridized (the sum of the three angles at N is 359.5°) with the N−P bond length of 1.666(3) Å. These structural features are similar to those seen in the Ti−Pt complexes described above. (The N−P bond distance = 1.657−1.683 Å, and the sum of the three angles at N is 357.9−359.3°.)

Comparisons in the six-membered dimetallacyclic skeleton among the four complexes are summarized in Figure 5. Of particular interest is the Ti−Pt distance, which is decreased in the order **2a** [2.8358(8) Å] > **3a** [2.7547(10) Å], **3a′** [2.7234(4) Å] > **4a** [2.6860(11) Å]. Differences in electron negativity between the chlorine and methyl or tolyl ligands suggest that electron density of the platinum atom should be increased in the order $PtCl_2$ < PtMeCl, Pt(*p*-Tol)Cl < $PtMe_2$. The order of the electron density of the platinum moiety is indeed suggested from the ^{195}Pt−^{31}P coupling constant: **2a** ($PtCl_2$, 2769 Hz) < **3a** (PtMeCl, average = 2384 Hz), **3a′** [Pt(*p*-Tol)Cl, average = 2486 Hz] < **4a** ($PtMe_2$, 1569 Hz).[12,13a] The above order of Ti−Pt distance can be explained by the fact that there is a Pt→Ti dative bond, and the electron-rich platinum center makes a stronger Pt→Ti interaction and shorter Pt−Ti distance. As other examples of the complexes that would have a Pt→Ti bond, [$Cp_2TiCH_2PtX(Me)L$] (X = Cl, Me, L = PMe_3, PMe_2Ph, $PMePh_2$) were reported by Grubbs, Lalinde, and Welter, in which the Pt→Ti bond distances are similar to those of **2a**−**4a** (2.71−2.96 Å).[14]

Two instances of support for the existence of the Pt→Ti dative bond were obtained from the NMR studies of Ti−Pt heterobimetallic complexes. First, variable-temperature NMR studies of **4a** showed the following fluxional process. Although the molecular structure of **4a** revealed that the phenyl groups bound to the phosphorus atom are structurally not identical, these could be independently observed in the ^{1}H NMR. Only one set of ^{1}H resonances due to the phenyl groups was seen above room temperature, but two sets were observed below −20 °C, and broadening of the signals (coalescence) was visible between these temperatures. Similar fluxional processes were seen in variable-temperature ^{1}H NMR of **2a** and **3a**, and it is noteworthy that the coalescence temperature is **2a** < **3a** < **4a**. One explanation for this fluxional process is a conformational change from a boat form to another boat form via the chair form transition state, as shown in Scheme 3, which takes place by way of breaking and re-forming of the dative bond. The order of the coalescence temperature may reflect the order of the dative bond strength described above. The second confirmation by NMR spectroscopy of **4a** is the coupling constant of the ^{195}Pt satellites observed for ^{31}P NMR. The ^{31}P resonance due

Scheme 3



to the Pt−P group of **4a** appears at δ 15.0 ppm with the satellite signal of J_{Pt-P} = 1569 Hz. The J_{Pt-P} values were significantly smaller than those of Me_2Pt(dppe) (J_{Pt-P} = 1783 Hz), Me_2Pt(dppp) (J_{Pt-P} = 1767 Hz),[13] and Me_2Pt(dppf) (J_{Pt-P} = 1905 Hz). The data clearly demonstrate the $PtMe_2$ species in **4a** is poorer in electron density than the others, and a plausible explanation is the movement of electrons from the Pt species to the Lewis acidic titanium species through the dative bond.

Concluding Remarks

As described above, we were successful in synthesizing the titanium phosphinoamide **1** and its use as a bidentate metalloligand for several organoplatinum(II) species. As often seen in the chemistry of amphoteric ligands, the Lewis basic phosphorus atoms of **1** interact with the Lewis acidic titanium center to result in P→Ti coordination; however, the coordination is in an intramolecular fashion and reversible. Therefore, the dissociated phosphorus atoms in **1** have the ability to react with the Pt(II) species to afford the corresponding Ti−Pt heterobimetallic complexes. A striking feature of **1** as a bidentate phosphorus ligand is its boat conformation bearing a Pt→Ti dative bond. Due to this special conformation, the bite angle (P−Pt−P) is in the range 102−106°, which is larger than the reported data of dppp giving a six-membered chelate and rather similar to that of EtXantphos (9,9-dimethyl-4,5-bis(diethylphosphino)xanthene)[15a] and *o*-$C_6H_4\{CH_2P(C_8H_{14})\}_2$[15b] complexes. The intramolecular donor (Pt)−acceptor (Ti) interaction through the Pt→Ti dative bond results in substantial decrease in electron density of the platinum species; this means that **1** is a relatively less electron-donating bidentate phosphorus ligand. The boat conformation, existence of the dative bond, and the fewer electron-donating properties showed this titanium phosphinoamide **1** to be a more unique bidentate phosphorus ligand than others extensively studied in organometallic chemistry. Of interest is how versatile the use of this ligand is for transition metals. Preliminary results showed that **1a** behaves as a ligand for Pd(II) and Rh(I) species similar to Pt(II) as described above: for example, treatment of (COD)$PdCl_2$ and [(COD)RhCl]$_2$ resulted in formation of insoluble organometallic products in quantitative releasing of the COD to the solution. The Ti−Pd product is a microcrystal, of which crystallography gave a molecular structure closely similar to **2a**, though the quality of the crystal is inadequate to complete the structure determination (*R* = 18%). On the other hand, the reaction of **1a** with [(COD)RhCl]$_2$ afforded a product, of which elemental analysis was consistent with "ClRh(Ph_2PN^tBu)$_2TiCl_2$"; however, further attempts to carry out characterization of this Ti−Rh compound were unsuccessful due to its poor solubility. In contrast, attempted reactions of **1a** with $Pd_2(dba)_3$·$CHCl_3$ or Pt(dba)$_2$ resulted in complete recovery of the starting materials. This is interesting in comparison with a metalloligand, ClTi-

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$[N(SiMe_3)(C_6H_4)PPh_2]_3$, reported by Love,[16] which has no Ti−P intramolecular interaction and is capable of reacting with Pt(0) precursors. This implicates that the intramolecular coordination of phosphorus ligands to the titanium center sometimes predominates over the ligation to late transition metal species. At present, we consider that the ligation of **1** to the transition metal species is competitive with dissociation of **1** from the heterobimetallic product, and the regeneration of **1** is more favorable than the heterobimetallic formation in the reactions with Pd(0) and Pt(0) precursors. In other words, a clue for the application of **1** as the bidentate phosphorus ligand would be effective control of the equilibrium constant, e.g., destabilization of **1** by the substituent effect and the stabilization of the heterobimetallic product by appropriate choice of the structure, valency, and element of the metal species.

Experimental Section

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. All solvents were distilled over appropriate drying reagents prior to use (toluene, hexane, pentane, Et_2O; Ph_2CO/Na, CH_2Cl_2; CaH_2, acetone; MS 4A). ^1H,^{13}C, and ^{31}P NMR spectra were recorded on a JEOL Lambda 600 or a Lambda 400 spectrometer at ambient temperature unless otherwise noted. ^1H, ^{13}C, and ^{31}P NMR chemical shifts (δ values) were given in ppm relative to the solvent signal (^1H, ^{13}C) or standard resonances (^{31}P; external 85% H_3PO_4). Melting points were measured on a Yanaco SMP3 micro melting point apparatus. Elemental analyses were performed by the Elemental Analysis Center, Faculty of Science, Kyushu University. Starting materials, phosphinoamide,[17] (COD)PtRR′ (R, R′ = Me, Cl, *p*-Tol), $[Me_2Pt(\mu\text{-}SMe_2)]_2$, and $[(COD)RhCl]_2$[18] were synthesized by the method reported in the literature.

Preparation of Titanium Phosphinoamides $(Ph_2PNR)_2TiCl_2$ [R = ^{t}Bu (1a), ^{i}Pr (1b)]. In a 100 mL Schlenk tube, Ph_2PNH^tBu (350 mg, 1.36 mmol) was dissolved in Et_2O (30 mL). A hexane solution of ^{n}BuLi (0.74 mL, 1.59 M, 1.36 mmol) was added to the solution at −78 °C, and the solution was slowly warmed to room temperature. After the mixture was stirred at room temperature for 3 h, it was cooled to −78 °C, and $TiCl_4$ (0.075 mL, 0.68 mmol) was added dropwise. The slightly yellow solution turned to dark red, and an orange solid precipitated. After 12 h, all of the volatiles were removed in a vacuum, and the formed crude product was dissolved in toluene (40 mL). The insoluble materials were filtered off through a G3 filter, and the resulting dark red filtrate was concentrated until the volume reached 5 mL. Hexane (20 mL) was added to this supersaturated toluene solution. The desired product was obtained as yellow microcrystals in 84% yield (360 mg, 0.57 mmol). In a similar fashion, **1b** was obtained in 81% yield. **1a**: mp 136−137 °C (dec). ^1H NMR (CD_2Cl_2): δ 1.36 (s, 18H, ^{t}Bu), 7.29 (m, 8H, *ortho*-Ph), 7.41 (m, 4H, *para*-Ph), 7.53 (m, 8H, *meta*-Ph). ^{13}C NMR (CD_2Cl_2): δ 33.1 (C*Me*$_3$), 64.6 (m, *C*Me$_3$), 128.6 (m, *meta*-Ph), 130.7 (*para*-Ph), 132.6 (*ipso*-Ph), 133.9 (m, *ortho*-Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −15.8 (s). Anal. Calcd for $C_{32}H_{38}N_2P_2Cl_2Ti$: C, 60.87; H, 6.07; N, 4.44. Found: C, 60.47; H, 6.11; N, 4.29. **1b**: mp 140−141 °C (dec). ^1H NMR (CD_2Cl_2): δ 1.27 (d, 12H, J_{H-H} = 6.6 Hz, $(CH_3)_2CH$), 4.22 (m, 2H, $(CH_3)_2CH$), 7.27 (m, 8H, *meta*-Ph), 7.36−7.46 (m, 12H, *ortho* and *para*-Ph). ^{13}C NMR (CD_2Cl_2): δ 25.8 ($(CH_3)_2CH$), 58.5 ($(CH_3)_2CH$), 128.8 (m, *meta*-Ph), 130.8 (*para*-Ph), 132.6 (m, *ipso*-Ph), 133.4 (m, *ortho*-Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ -19.2 (s). Anal. Calcd for $C_{30}H_{34}N_2P_2Cl_2Ti$: C, 59.72; H, 5.68; N, 4.64. Found: C, 60.03; H, 6.01; N, 4.21.

Table 3. Crystallographic Data for Titanium Phosphinoamides

	1a	1b
empirical formula	$C_{32}H_{38}Cl_2N_2P_2Ti$	$C_{30}H_{34}Cl_2N_2P_2Ti$
fw	631.42	603.37
cryst syst	monoclinic	triclinic
lattice type	primitive	primitive
space group	$P2_1/c$ (#14)	$P\bar{1}$ (#2)
a, Å	10.617(2)	14.498(5)
b, Å	16.443(4)	20.028(6)
c, Å	36.429(8)	22.641(6)
α, deg	90	68.639(7)
β, deg	94.995(2)	88.126(9)
γ, deg	90	84.128(8)
volume, Å^3	6336(2)	6090(3)
Z value	8	8
D_{calc}, g/cm^3	1.324	1.316
F(000)	2640.00	2512.00
μ(Mo Kα), cm^{-1}	5.638	5.832
cryst color, habit	yellow, platelet	yellow, platelet
cryst dimens, mm	0.18 × 0.08 × 0.07	0.23 × 0.21 × 0.16
no. observations (all reflns)	14 501	27 659
no. variables	779	1469
refln/param ratio	18.63	18.83
R (all reflns)	0.089	0.137
R_1 ($I > 2.00\sigma(I)$) [a]	0.050	0.061
wR_2 (all reflns) [b]	0.129	0.123
GOF	0.996	1.005
max. shift/error in final cycle	0.000	0.000
max. peak in final diff map, e$^-$/Å^3	0.85	1.08
min. peak in final diff map, e$^-$/Å^3	−0.72	−1.27

[a] $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

Preparation of the Ti−Pt Heterobimetallic Complex $Cl_2Pt(Ph_2PN^tBu)_2TiCl_2$ (2a). In a 20 mL Schlenk tube were placed **1a** (34 mg, 0.054 mmol) and (COD)$PtCl_2$ (20 mg, 0.054 mmol), and the atmosphere was replaced by argon. The mixture was dissolved in CH_2Cl_2 (2 mL), and the tube was sealed by a stopcock and heated in an oil bath, of which the temperature was controlled at 50 °C for 5 h. The color of the solution changed from orange to red, from which red precipitates were formed. After removal of the solvent in vacuo, the solid was washed with hexane (2 mL × 3). The crude product was dissolved in warm CH_2Cl_2, and the insoluble materials were filtered off. The filtrate was cooled at −30 °C to form dark red microcrystals of **2a** in 80% yield (39 mg, 0.043 mmol). The Pd homologue **2b** was synthesized (87%) from **1a** (30 mg, 0.042 mmol) and (COD)$PdCl_2$ (13 mg, 0.048 mmol) in CH_2Cl_2 as dark red insoluble microcrystals (34 mg, 0.042 mmol). **2a**: mp 131−133 °C (dec). ^1H NMR (CD_2Cl_2): δ 1.43 (s, 18H, ^{t}Bu), 7.13−7.18 (m, 4H, Ph), 7.32−7.53 (m, 14H, Ph), 7.67−7.72 (m, 2H, Ph). ^{13}C NMR (CD_2Cl_2): δ 34.2 (C*Me*$_3$), 71.5 (m, *C*Me$_3$), 128.0, 128.7, 128.8, 131.6, 131.7, 132.4 (Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 6.75 (s with a satellite signal due to the coupling with ^{195}Pt, J_{Pt-P} = 2769 Hz). Anal. Calcd for $C_{32}H_{38}N_2P_2Cl_4TiPt$: C, 42.83; H, 4.27; N, 3.12. Found: C, 42.81; H, 4.30; N, 3.08.

Preparation of Ti−Pt Heterobimetallic Complexes $RClPt(Ph_2PN^tBu)_2TiCl_2$ [R = Me (3a); R = *p*-Tol (3a′)]. In a 20 mL Schlenk tube were placed **1a** (370 mg, 0.586 mmol) and (COD)PtMeCl (208 mg, 0.589 mmol), and the atmosphere was replaced by argon. The mixture was dissolved in CH_2Cl_2 (8 mL), and the

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Table 4. Crystallographic Data for the Heterobimetallic Complexes

	2a	3a	3a′	4a
empirical formula	$C_{32}H_{38}Cl_4N_2P_2PtTi$	$C_{33}H_{41}Cl_3N_2P_2PtTi$	$C_{39}H_{45}Cl_3N_2P_2PtTi\cdot CH_2Cl_2$	$C_{34}H_{44}Cl_2N_2P_2PtTi$
fw	897.42	877.00	1038.03	856.58
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
lattice type	primitive	primitive	primitive	C-centered
space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/n$ (#14)	$C2/c$ (#15)
a, Å	18.131(3)	18.153(3)	17.861(2)	28.131(5)
b, Å	9.1326(14)	9.2052(13)	10.7169(11)	16.217(2)
c, Å	20.976(4)	20.901(3)	22.273(3)	22.080(4)
β, deg	105.446(3)	105.6693(5)	96.2475(15)	126.2680(5)
volume, Å^3	3347.9(10)	3362.7(9)	4238.1(8)	8122(2)
Z value	4	4	4	8
D_{calc}, g/cm^3	1.780	1.732	1.627	1.401
F(000)	1768.00	1736.00	2064.00	3408.00
μ(Mo Kα), cm^{-1}	48.365	47.362	38.936	38.567
cryst color, habit	red, platelet	red, platelet	red, chip	red, platelet
cryst dimens, mm	0.05 × 0.05 × 0.04	0.17 × 0.16 × 0.13	0.23 × 0.15 × 0.08	0.13 × 0.09 × 0.07
no. observations (all reflns)	7662	7643	9673	9061
no. variables	417	411	507	423
refln/param ratio	18.37	18.60	19.08	21.42
R (all reflns)^a	0.061	0.034	0.028	0.065
R_1 ($I > 2.00\sigma(I)$)^b	0.037	0.031	0.025	0.049
wR_2 (all reflns)	0.088	0.089	0.071	0.168
GOF	0.868	1.011	1.006	1.005
max. shift/error in final cycle	0.000	0.000	0.000	0.000
max. peak in final diff map, e$^-$/Å^3	2.33	3.56	1.70	4.72
min. peak in final diff map, e$^-$/Å^3	−1.37	−1.13	−1.16	−1.00

^{a} $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$. ^{b} $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

solution was stirred at room temperature for 3 h. The color of the reaction mixture changed from orange to deep red, from which red precipitates were formed. After removal of the solvent in vacuo, the solid was washed with pentane (5 mL). The crude product was dissolved in a 1:1 solution of pentane and CH_2Cl_2, and the insoluble materials were filtered off. The filtrate was cooled at −30 °C to form dark red microcrystals of **3a** in 84% yield (431 mg, 0.494 mmol). By a similar procedure, the *p*-tolyl homologue **3a′** was synthesized (65%). **3a**: mp 137−138 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 1.19 (dd with a satellite signal due to the coupling with ^{195}Pt, 3H, Pt-Me, J_{P-H} = 5.4, 5.6 Hz, J_{Pt-H} = 54 Hz), 1.32 (s, 9H, ^{t}Bu), 1.47 (s, 9H, ^{t}Bu), 6.96−7.05 (m, 2H, Ph), 7.10−7.82 (m, 18H, Ph). ^{13}C NMR (CD_2Cl_2): δ 31.6 (Pt-Me), 33.7 (C*Me*$_3$), 33.8 (C*Me*$_3$), 68.6 (d, J_{C-P} = 9.2 Hz, *C*Me$_3$) 70.8 (d, J_{C-P} = 10.4 Hz, *C*Me$_3$), 127.8, 128.3, and 128.7 (*meta*-Ph), 130.3, 131.0, 131.4, and 131.6 (*para*-Ph), 131.1, 132.4, 133.7, and 134.3 (*ortho*-Ph). Few *ipso*-carbon resonances were assigned due to the poor solubility of **3a** to CD_2Cl_2. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 1.56 (s with a satellite signal due to the coupling with ^{195}Pt, J_{Pt-P} = 3368 Hz, P trans to Cl), 14.7 (s with a satellite signal due to the coupling with ^{195}Pt, J_{Pt-P} = 1400 Hz, P trans to Me). Anal. Calcd for $C_{33}H_{41}N_2P_2Cl_3TiPt$: C, 45.20; H, 4.71; N, 3.19. Found: C, 45.02; H, 4.68; N, 3.13. **3a′**: mp 181−182 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 1.22 (s, 9H, ^{t}Bu), 1.50 (s, 9H, ^{t}Bu), 2.06 (s, 3H, *CH*$_3$-Tol), 6.20−6.29 (m, 1H, Ph), 6.39−6.46 (m, 2H, Ph), 6.88−7.26 (m, 8H, Ph), 7.31−7.67 (m, 10H, Ph), 7.95−8.05 (m, 3H, Ph). ^{13}C NMR (CD_2Cl_2): δ 20.6 (*C*H$_3$-Tol), 33.7 (d, J_{C-P} = 4.6 Hz, C*Me*$_3$), 34.0 (d, J_{C-P} = 4.6 Hz, C*Me*$_3$), 68.4 (d, *C*Me$_3$, J_{C-P} = 9.2 Hz), 70.9 (d, *C*Me$_3$, J_{C-P} = 10.4 Hz), 127.3, 127.9, 128.0, 128.4, 129.1 (*meta*-Ar), 130.3, 130.3, 131.5, 131.7, 131.9 (*para*-Ar), 132.8, 132.9, 133.5, 135.2, 135.3 (*ortho*-Ar). Few *ipso*-carbon resonances were assigned due to the poor solubility of **3a′** to CD_2Cl_2. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −2.5 (s with a satellite signal due to the coupling with ^{195}Pt, J_{Pt-P} = 3584 Hz, P trans to Cl), 16.7 (s with a satellite signal due to the coupling with ^{195}Pt, J_{Pt-P} = 1388 Hz, P trans to Tol). Anal. Calcd for $C_{39}H_{45}N_2P_2Cl_3TiPt\cdot CH_2Cl_2$: C, 46.29; H, 4.56; N, 2.70. Found: C, 46.33; H, 4.56; N, 2.69.

Preparation of the Ti−Pt Heterobimetallic Complex $Me_2Pt(Ph_2PN^tBu)_2TiCl_2$ (4a). In a 50 mL Schlenk tube were placed **1a** (50 mg, 0.079 mmol) and $[Me_2Pt(\mu\text{-}SMe_2)]_2$ (23 mg, 0.04 mmol), and the atmosphere was replaced by argon. The mixture was dissolved in CH_2Cl_2 (15 mL), and the solution was stirred at room temperature for 1 h. The color of the reaction mixture changed from orange to deep red. After removal of the solvent in vacuo, the solid was washed with Et_2O (7 mL). The crude product was dissolved in a 1:1 solution of Et_2O and CH_2Cl_2, and the insoluble materials were filtered off. The filtrate was cooled at −30 °C to form dark red microcrystals of **4a** in 81% yield (55 mg, 0.064 mmol). **4a**: mp 142−143 °C (dec). ^{1}H NMR (CD_2Cl_2, rt): δ 0.78 (dd with a satellite signal due to the coupling with ^{195}Pt, 6H, J_{P-H} = 4.9, 8.2 Hz, J_{Pt-H} = 66 Hz, Pt-Me), 1.39 (s, 18H, ^{t}Bu), 7.03−7.17 (m, 4H, Ph), 7.20−7.33 (m, 6H, Ph), 7.37−7.49 (m, 6H, Ph), 7.65−7.82 (m, 4H, Ph). ^{1}H NMR (CD_2Cl_2, −90 °C): δ 1.39 (br s, 18H, ^{t}Bu), 7.07 (m, 2H, *meta*-Ph), 7.17 (m, 2H, *ortho*-Ph), 7.24 (m, 1H, *para*-Ph), 7.27 (m, 1H, *meta*-Ph), 7.32 (m, 1H, *ortho*-Ph), 7.41 (m, 1H, *para*-Ph), 7.53 (m, 1H, *meta*-Ph), 8.02 (m, 1H, *ortho*-Ph). ^{13}C NMR (CD_2Cl_2, rt): δ 16.3 (dd with a satellite signal due to the coupling with ^{195}Pt, J_{P-C} = 5.8, 65.0 Hz, J_{Pt-C} = 598 Hz, Pt-Me), 33.6 (C*Me*$_3$), 68.7 (d, J_{P-C} = 11.6 Hz, *C*Me$_3$), 128.2, 128.3 (*meta*-Ph), 130.0, 130.9 (*para*-Ph), 131.0, 133.7 (*ipso*-Ph), 131.4, 134.0 (*ortho*-Ph). ^{31}P{^{1}H} NMR (CD_2Cl_2, rt): δ 15.0 (s with a satellite signal due to the coupling with ^{195}Pt, J_{Pt-P} = 1569 Hz). Anal. Calcd for $C_{34}H_{44}N_2P_2Cl_2TiPt$: C, 47.68; H, 5.18; N, 3.27. Found: C, 47.71; H, 5.21; N, 3.24.

Reaction of $(Ph_2PN^tBu)_2TiCl_2$ (1a) with $[(COD)RhCl]_2$. In a 20 mL Schlenk tube were placed **1a** (20 mg, 0.032 mmol) and $[(COD)RhCl]_2$ (8 mg, 0.016 mmol), and the atmosphere was replaced by argon. The mixture was dissolved in CH_2Cl_2 (5 mL), and the solution was stirred at 60 °C for 5 h. After filtration of the resulting solution, the solvent was removed in vacuo, from which a dark green powder was obtained (30 mg), mp 142−143 °C (dec). Anal. Calcd for $C_{32}H_{38}N_2P_2Cl_3TiRh$: C, 49.93; H, 4.98; N, 3.64. Found: C, 50.21; H, 4.68; N, 3.54.

X-ray Data Collection and Reduction. Single crystals of all complexes were grown from CH_2Cl_2/pentane. X-ray crystallography was performed on a Rigaku Saturn CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å). The data were collected at 123(2) K using ω scans in the θ range of 3.1° ≤ θ ≤

27.5° (**1a**), 3.0° ≤ θ ≤ 27.5° (**1b**), 3.0° ≤ θ ≤ 27.5° (**2a**), 1.2° ≤ θ ≤ 31.0° (**3a**), 3.0° ≤ θ ≤ 27.5° (**3a′**), and 3.1° ≤ θ ≤ 27.5° (**4a**). 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 heavy-atom Patterson methods[19] for **4a** and by direct methods[20] for **1a**, **1b**, **2a**, **3a**, and **3a′**, and expanded using Fourier techniques.[21] The non-hydrogen atoms were refined anisotropically except for the Cl and C atoms on the platinum atom in **3a**. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 14 501 observed reflections and 779 variable parameters for **1a**, 27 659 observed reflections and 1469 variable parameters for **1b**, 7662 observed reflections and 417 variable parameters for **2a**, 7643 observed reflections and 411 variable parameters for **3a**, 9673 observed reflections and 507 variable parameters for **3a′**, and 9061 observed reflections and 423 variable parameters for **4a**. Neutral atom scattering factors were taken from Cromer and Waber.[22] All calculations were performed using the CrystalStructure[23,24] crystallographic software package. Details of final refinement are summarized in Tables 3 and 4, and the numbering scheme employed is shown in Figures 1, 3, and 4, which were drawn with ORTEP with 50% probability ellipsoids. Detailed data as well as the bond distances and angles are shown in the Supporting Information.

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Supporting Information Available: Variable-temperature NMR data (**1a**, **1b**, **2a**, **3a**, **4a**), ^{1}H, ^{13}C, and ^{31}P NMR data (**1a**, **1b**, **2a**, **3a**, **3a′**, **4a**), and details of crystallographic studies (**1a**, **1b**, **2a**, **3a**, **3a′**, **4a**). This material is available free of charge via the Internet at http://pubs.acs.org.

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