1988 *Organometallics* **2009,** *28,* 1988–1991

Nickel(II), Palladium(II), and Platinum(II) η^3-Allyl Complexes Bearing a Bidentate Titanium(IV) Phosphinoamide Ligand: A $\mathrm{Ti}\leftarrow\mathrm{M}_2$ Dative Bond Enhances the Electrophilicity of the π-Allyl Moiety

Hironori Tsutsumi,[†] Yusuke Sunada,[‡] Yoshihito Shiota,[‡] Kazunari Yoshizawa,[‡] and
Hideo Nagashima*,[†,‡]

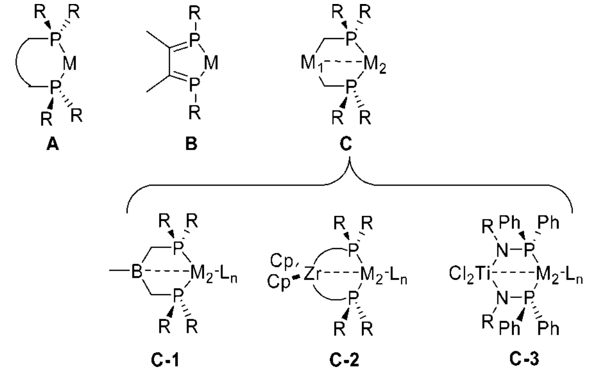
Institute for Materials Chemistry and Engineering and Graduate School of Engineering Sciences,
Kyushu University, Kasuga, Fukuoka 816-8580, Japan

Received November 21, 2008

Summary: Three Ti−M$_2$ (M$_2$ = Ni, Pd, Pt) heterobimetallic complexes, $[(\eta^3\text{-methallyl})\mathrm{M}_2(\mathrm{Ph}_2\mathrm{PN}^t\mathrm{Bu})_2\mathrm{TiCl}_2](\mathrm{OTf})$*, were synthesized in which a* $\mathrm{Ti}^{\mathrm{IV}}\leftarrow\mathrm{M}_2$ *interaction was suggested by crystallography and DFT calculations. The* $\mathrm{Ti}^{\mathrm{IV}}\leftarrow\mathrm{M}_2$ *interaction enhanced electrophilicity of the* η^3*-methallyl ligand of M$_2$, leading to high reactivity of the* η^3*-methallyl moiety with* $\mathrm{Et}_2\mathrm{NH}$ *compared with that of the dppp analogue.*

The importance of bidentate phosphine ligands in modern organometallic chemistry is well recognized, particularly for molecular catalysts useful for organic and polymer synthesis.[1] The structural design of metal−phosphine complexes is established by controlling the bulkiness of the substituents on the phosphorus atoms, the cone angle, and the bite angle.[1] In contrast, the electronic properties of the bidentate phosphine ligands are often tuned by the donor property of the substituents bonded to the phosphorus atoms, which is estimated by Tolman's χ value (Chart 1, **A**).[1] A unique bidentate phosphine ligand, which is not explained by the χ value, has been developed by Yoshifuji and Ozawa, in which effective use of a phosphorus analogue of a α-diimine ligand results in emphasizing back-donation from the metal center to the ligand (Chart 1, **B**).[2] The third approach for the electronic control is use of the metalloligand of type **C** in Chart 1, in which a metallic species is incorporated in a structure of the phosphines. For instance, a bidentate phosphorus ligand having a Lewis acidic boron center in the ligand backbone coordinates to a Rh or Au atom; existence of a $\mathrm{M}_2\rightarrow\mathrm{B}$ dative bond in **C-1** is suggested in the literature.[3,4] **C-2** type complexes are also synthesized, which are proposed to have $\mathrm{M}_2\rightarrow\mathrm{M}_1$ (M$_1$ = Ti, Zr, M$_2$ = Rh, Pt) interactions.[5]

Chart 1



In these preceding papers, the $\mathrm{M}_2\rightarrow\mathrm{M}_1$ interaction has been discussed on the basis of the metal−metal bond distance of the crystal structure, ^{11}B and/or ^{31}P NMR spectroscopy, and

---

* To whom correspondence should be addressed. E-mail: nagasima@cm.kyushu-u.ac.jp.

[†] Graduate School of Engineering Sciences.

[‡] Institute for Materials Chemistry and Engineering.

(1) For reviews: (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Dierkes, P.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **1999**, 1519. (c) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741. (d) Appleby, T.; Woollins, J. D. *Coord. Chem. Rev.* **2002**, *235*, 21. (e) Freixa, Z.; van Leeuwen, P. W. N. M. *Dalton Trans.* **2003**, 1890. (f) Minahan, D. M. A.; Hill, W. E.; McAuliffe, C. A. *Coord. Chem. Rev.* **1984**, *55*, 31.

(2) (a) Minami, T.; Okamoto, H.; Ikeda, S.; Tanaka, R.; Ozawa, F.; Yoshifuji, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4501. (b) Ozawa, F.; Okamoto, H.; Kawagishi, S.; Yamamoto, S.; Minami, T.; Yoshifuji, M. *J. Am. Chem. Soc.* **2002**, *124*, 10968. (c) Hayashi, A.; Yoshitomi, T.; Umeda, K.; Okazaki, M.; Ozawa, F. *Organometallics* **2008**, *27*, 1970. (d) Hayashi, K.; Nakatani, M.; Hayashi, A.; Takano, M.; Okazaki, M.; Toyota, K.; Yoshifuji, M.; Ozawa, F. *Organometallics* **2008**, *27*, 2321. (e) Ozawa, F.; Yoshifuji, M. *Dalton Trans.* **2006**, 4987.

(3) (a) Bontemps, S.; Gornitzka, H.; Bouhadir, G.; Miqueu, K.; Bourissou, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1611. (b) Bontemps, S.; Sircoglou, M.; Bouhadir, G.; Puschmann, H.; Howard, J. A. K.; Dyer, P. W.; Miqueu, K.; Bourissou, D. *Chem. Eur. J.* **2008**, *14*, 731. (c) Sircoglou, M.; Bontemps, S.; Mercy, M.; Saffon, N.; Takahashi, M.; Bouhadir, G.; Maron, L.; Bourissou, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 8583.

(4) A notable related complex of **C-1**, $[\mathrm{R}_2\mathrm{B}^-(\mathrm{CH}_2\mathrm{PPh}_2)_2\mathrm{Pt}^+\mathrm{R}(\mathrm{THF})]$, with no direct M−B bond interaction was reported by Peters et al. In this complex, the electron-donating property of the borate moiety enhanced the electron density of phosphorus atoms, which resulted in higher electron density of the Pt center, leading to successful C−H bond activation of arenes. See: (a) Thomas, S. J.; Peters, J. C. *J. Am. Chem. Soc.* **2001**, *123*, 5100. (b) Thomas, S. J.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 8870.

(5) (a) Choukroun, R.; Iraq, A.; Gervais, D.; Daran, J. -C.; Jeannin, Y. *Organometallics* **1987**, *6*, 1197. For closely related examples, see: (b) Ferguson, G. S.; Wolczanski, P. T.; Párkányi, L.; Zonnevylle, M. C. *Organometallics* **1988**, *7*, 1967. (c) Baxter, S. M.; Ferguson, G. S.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4231.

(6) Hydroformylation of alkenes catalyzed by **C-2** has been well investigated as a typical reaction of heterobimetallic complexes. However, the rate enhancement observed is usually explained by bimetallic activation of CO through a $\mathrm{Cp}_2\mathrm{Zr}\leftarrow\mathrm{O}{=}\mathrm{C}{-}\mathrm{M}_2(\mathrm{CO})_n$ intermediate, and nothing has been discussed about the effect of the $\mathrm{Zr}\leftarrow\mathrm{M}_2$ interaction, which reduces the electron density of M$_2$ and enhances the electrophilicity of the CO ligand on M$_2$. See: (a) Cornelissen, C.; Erker, G.; Kehr, G.; Fröhlich, R. *Organometallics* **2005**, *24*, 214. (b) Bosch, B. E.; Brümmer, I.; Kunz, K.; Erker, G.; Fröhlich, R.; Kotila, S. *Organometallics* **2000**, *19*, 1255. (c) Cornelissen, C.; Erker, G.; Kehr, G.; Fröhlich, R. *Dalton Trans.* **2005**, *24*, 4059. (d) See ref 5.

(7) For other examples of early−late heterobimetallic complexes which can act as catalysts for hydroformylation, see: (a) Choukroun, R.; Gervais, D.; Kalck, P.; Senocq, F. *J. Organomet. Chem.* **1987**, *335*, C9. (b) Choukroun, R.; Gervais, D.; Rifai, C. *Polyhedron* **1989**, *8*, 1760. (c) Trzeciak, A. M.; Ziólkowski, J. J.; Choukroun, R. *J. Organomet. Chem.* **1991**, *420*, 353. (e) Choukroun, R.; Dahan, F.; Gervais, D.; Rifai, C. *Organometallics* **1990**, *9*, 1982. (f) Mattheis, C.; Braunstein, P.; Fischer, A. *Dalton Trans.* **2001**, 800. (g) Priya, S.; Balakrishna, M. S.; Mague, J. T. *J. Organomet. Chem.* **2004**, *689*, 3335.

10.1021/om8011085 CCC: $40.75

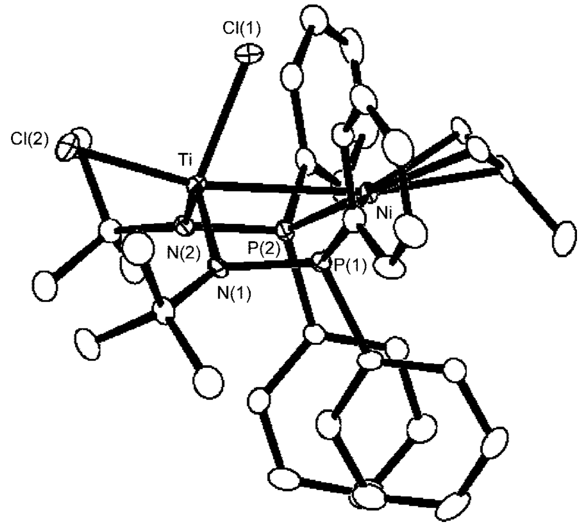


Figure 1. Molecular structure of **2a** with 50% probability ellipsoids. The counteranion (OTf) and hydrogen atoms are omitted for clarity. ORTEP drawings of **2b**,**c** are given in the Supporting Information.

theoretical calculations;[3] however, there are a few reports on the effect of the interaction from the viewpoint of reactivity of the complex.[6,7] The $M_2 \rightarrow M_1$ interaction is expected to reduce the electron density of M_2. This would increase the electrophilicity of the ligand bonded to M_2, leading to its facile reaction with nucleophiles. However, to the best of our knowledge, there has been no report which demonstrates that complex **C** is susceptible to facile transformation of the ligand on M_2 by reaction with nucleophiles.[8,9] We have recently reported the synthesis of titanium phosphinoamides, $(Ph_2PN^tBu)_2TiCl_2$, the reaction of which with Pd(II), Pt(II), and other metallic species affords complexes of the **C-3** type.[10] This prompted us to synthesize (η^3-allyl)palladium derivatives of **C-3**, because (η^3-allyl)palladium(II) complexes are known to undergo facile nucleophilic attack at the η^3-allyl ligand. As we expected, the palladium complex **2b**, the Ti(IV)←Pd interaction of which is proved by the Ti−Pd bond distance determined by crystallography, NMR spectroscopy, and DFT calculations, is much more reactive with Et_2NH or aniline than (dppp)Pd(η^3-methallyl) (**3b**). Similar studies on the nickel and platinum homologues of **2b** showed similar enhancement of the electrophilicity of the η^3-methallyl ligand. The results clearly demonstrate that the $M_1 \leftarrow M_2$ interaction produced by the metalloligand $(Ph_2PN^tBu)_2TiCl_2$ is a good entry for facile nucleophilic transformation of the ligand on M_2.

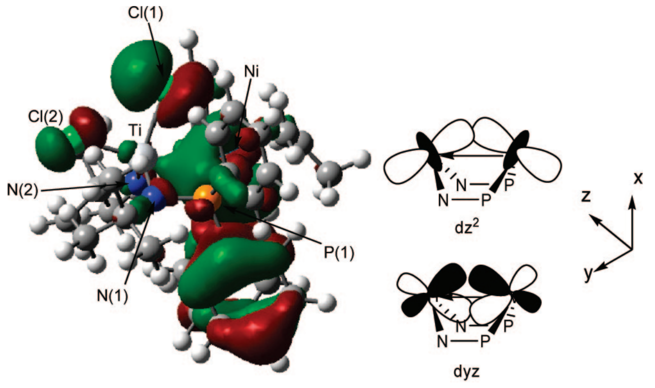


Figure 2. Gaussview depiction of the HOMO for the full molecule of **2a**. See the Supporting Information for the molecular orbitals of **2b**,**c**.

Scheme 1

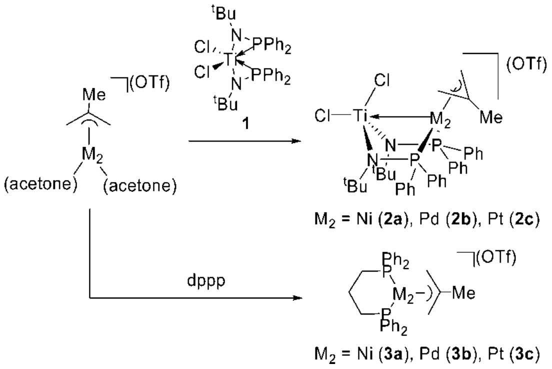


Table 1. Ti−M_2 Bond Distances of 2a−c, Determined by X-ray Diffraction Analysis, Sum of the Covalent Radii of Ti and M_2, and Bond Order Estimated by DFT Calculation

	Ti−Ni (**2a**)	Ti−Pd (**2b**)	Ti−Pt (**2c**)
Ti−M_2 dist determined by X-ray: R_1 (Å)	2.604(2)	2.8155(5)	2.765(2)
sum of the covalent radii of Ti and M_2: R_2 (Å)	2.84	2.99	2.96
deviation: $(R_1/R_2) \times 100$ (%)	91.7	94.2	93.4
ΣTi_α[a]	351.1	352.5	353.5
bond order	0.33	0.29	0.35

[a] Sum of the three angles around the titanium atom (N(1)−Ti−N(2), N(1)−Ti−Cl(1), and N(2)−Ti−Cl(1)).

Treatment of the titanium phosphinoamide $(Ph_2PN^tBu)_2TiCl_2$ with $[M_2(\eta^3\text{-methallyl})(acetone)_2](OTf)$ (M_2 = Ni, Pd, Pt) afforded the Ti−M_2 heterobimetallic complexes $[(\eta^3\text{-methallyl})M_2(Ph_2PN^tBu)_2TiCl_2](OTf)$ (M_2 = Ni (**2a**), Pd (**2b**), Pt (**2c**)) in 57, 73, and 81% yield, respectively (Scheme 1). In the same manner, $[(\eta^3\text{-methallyl})M_2(dppp)]OTf$ complexes (M_2 = Ni, Pd, Pt) were synthesized.

The molecular structures of **2a**−**c** were unequivocally determined by X-ray diffraction analysis; the molecular structure of **2a** is described in Figure 1, and detailed bond distances and angles are given in the Supporting Information. The complexes **2a**−**c** have a six-membered dimetallacyclohexane skeleton with a boat conformation. The titanium center is bound to two nitrogen and two chloride atoms assuming a tetrahedral coordination geometry, and the M_2 center adopts the square-planar coordination geometry. These structural features are nearly identical with those of our previously reported Ti−Pt heterobimetallic complexes.[10] The Ti−Ni, Ti−Pd, and Ti−Pt bond lengths (2.604(2) Å for **2a**, 2.8155(5) Å for **2b**, and 2.765(2) Å for **2c**) are shorter than the sum of the covalent radii of Ti and M_2 (91.7% (M_2 = Ni), 94.2% (M_2 = Pd), and 93.4% (M_2 =

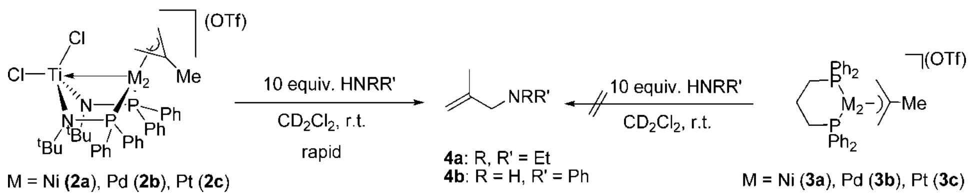
---

(8) Complexes of type **C** including early and late transition elements have been investigated in the chemistry of early−late heterobimetallic (ELHB) complexes. There are several ELHB complexes with a dative bond, in which the M_1−M_2 interaction is discussed from the point of view of crystallography and theoretical calculations.[9] However, only a few papers have been reported on the reactivities.

(9) (a) Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41. (b) Adams, R. D.; Cotton, F. A. *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Wiley-VCH: New York, 1998. (c) Braunstein, L. A.; Oro, L. A.; Raithby, P. R. *Metal Clusters in Chemistry*; Wiley-VCH: New York, 1999; Vol. 2. (d) Wheatley, N.; Kalck, W. *Chem. Rev.* **1999**, *99*, 3379. (e) Gade, L. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2658.

(10) (a) Nagashima, H.; Sue, T.; Oda, T.; Kanemitsu, A.; Matsumoto, T.; Motoyama, Y.; Sunada, Y. *Organometallics* **2006**, *25*, 1987. (b) Sunada, Y.; Sue, T.; Matsumoto, T.; Nagashima, H. *J. Organomet. Chem.* **2006**, *691*, 3176. (c) Sue, T.; Sunada, Y.; Nagashima, H. *Eur. J. Inorg. Chem.* **2007**, *18*, 2897.

Scheme 2

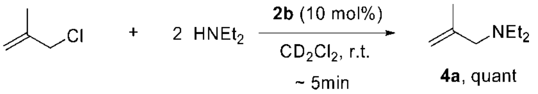


Pt) of the sum of the radii, respectively) (Table 1).[11] The M_2 atom deviates by 0.2123, 0.1622, and 0.1466 Å from the least-squares plane around the M_2 atom defined by two phosphorus atoms and the methallyl moiety due to the Ti−M_2 interaction. The sum of the four angles around the basal plane of M_2 is 357.7° for **2a**, 357.8° for **2b**, and 359.0° for **2c**, which is slightly distorted from the theoretical value of 360° for a square-planar coordination geometry. In contrast, the sum of the three angles around the titanium atom (N(1)−Ti−N(2), N(1)−Ti−Cl(1), and N(2)−Ti−Cl(1): 351.1° for **2a**, 352.5° for **2b**, and 353.5° for **2c**) showed that the geometry of the titanium centers of **2a**−**c** deviates significantly from tetrahedral and is rather close to trigonal bipyramidal. These structural features can be ascribed to the presence of the Ti−M_2 bond interaction.

NMR spectroscopy of these heterobimetallic complexes suggests that the Ti(IV)←M_2 interaction in **2a**−**c** leads to lower electron density of M_2 in comparison with that of the dppp analogues **3a**−**c**, which affects the ^{13}C resonances of the η^3-methallyl moiety as well as the ^{31}P signal of the phosphorus ligand. Two ^{13}C signals appeared for the η^3-methallyl moiety of **2b**, which are due to the terminal and central carbons; both of them are shifted to a lower field than those of the dppp analogues, **3b**. The ^{13}C NMR spectrum of **2b** showed two signals at 83.0 (t, $J_{C-P} = 11.6$ Hz, CH_2=C(Me)) and 141.1 (t, $J_{C-P} =$ 4.3 Hz, CH_2=C(Me)) which are ca. 9 and 3 ppm shifted to lower field compared with that of **3b**. A single ^{31}P resonance is visible for **2a** (δ 14.1), **2b** (δ 9.75), and **2c** (δ 0.60), which is shifted lower by 20, 1.1, and 0.3 ppm, respectively, compared with those of **3a**−**c**.[12]

Computational studies on the full models of **2a**−**c** were carried out using density functional theory (DFT) with the B3LYP functional and the LanL2DZ basis set based on the geometry determined by X-ray diffraction analysis. This suggests that the HOMO (for **2a**,**c**) or HOMO-1 (for **2b**) may involve some Ti−M_2 bonding interaction by donating the electrons from the d_{z^2} and d_{yz} orbitals of M_2 to the titanium center (Figure 2).[13] Mayer atomic bond order analysis revealed that each M_2−Ti bond was found to have a bond order of 0.33 for **2a**, 0.29 for **2b**, and 0.35 for **2c**, respectively, suggesting weak bonding between the two metal centers. Similar to the bond distances, the bond orders decrease in the trend Ti−Ni ≈ Ti−Pt > Ti−Pd, suggesting that the Ti−Pd bond is somewhat weaker than the Ti−Ni and Ti−Pt interactions.

Scheme 3



All of the above results indicate that the M_2 center donates the electron density of the d orbital to the titanium center via a Ti(IV)←M_2(II) dative bond, leading to reduction of the electron density of M_2, which should enhance the electrophilicity of the η^3-methallyl ligand in **2a**−**c** compared with that of their dppp analogues. The following experiments clearly demonstrate that this is true. Treatment of **2a** with 10 equiv of $HNEt_2$ in CD_2Cl_2 at room temperature resulted in quantitative formation of a corresponding diethylmethallylamine (**4a**) within 5 min (Scheme 2).[14] This is in sharp contrast to the fact that no formation of **4a** was observed in the reaction of $HNEt_2$ with **3a** for a prolonged reaction time (2 h). Similarly, reaction of **2b**,**c** with $HNEt_2$ was completed within 5 min in CD_2Cl_2 to give **4a** in quantitative yield, whereas only a trace amount (ca. ∼4%) of **4a** was obtained by treatment of **3b**,**c** with $HNEt_2$ under the same conditions. The reaction of **2b** with 10 equiv of aniline also proceeded effectively to afford the corresponding *N*-methallylaniline (**4b**) in 23% yield after 5 min and 85% yield after 12 h at room temperature. In contrast, **3b** was totally unreactive toward aniline under the same reaction conditions. Ozawa and Yoshifuji have described similar enhancement of the electrophilicity of the allyl moiety in their (DPCB)Pd(η^3-allyl) complexes; treatment of the Pd complex with $HNEt_2$ led to the instant formation of diethylallylamine in 82% yield. Similarly, the reaction of aniline afforded a 45% yield of *N*-allylaniline and a 72% yield after 24 h.[2a]

The high reactivity of our Ti−M_2 heterobimetallic complexes was also demonstrated in the catalytic allylation of $HNEt_2$. Reaction of 2 equiv of $HNEt_2$ with methallyl chloride catalyzed by **2b** (10 mol %) was performed in CD_2Cl_2 at room temperature, from which quantitative formation of **4a** was confirmed within 5 min by the NMR spectrum (Scheme 3).[15] The same reaction was examined either in the absence of catalyst or in the presence of **3b** (10 mol %), revealing that the yields of **4a** were 7% and 11%, respectively, after 1.5 h.

---

(11) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832.

(12) ^{31}P NMR spectra suggest the presence of a Ti−M_2 bond interaction. Single ^{31}P resonances are visible for **2a** (δ 14.1), **2b** (δ 9.75), and **2c** (δ 0.60), which are shifted lower by 20, 1.1, and 0.3 ppm, respectively, compared with those of **3a**−**c**. The J_{Pt-P} value (3216 Hz) in **2c** is smaller than that of **3c** ($J_{Pt-P} = 3512$ Hz). Although the possibility of showing a significant difference in ^{31}P NMR spectra owing to the presence of nitrogen atoms in the bidentate phosphine backbone could not be ruled out, these spectral features could indicate that the electron densities around the M_2 center of **2a**−**c** were reduced compared with those of **3a**−**c**.

(13) One of the reviewers suggested that NBO analysis may be a better tool for understanding the bonding situation. According to this suggestion, we carried out the NBO calculations of complexes **2a**−**c** at various levels of theory. However, the Ti−M interaction is too weak to describe the bonding situation in **2a**−**c** for NBO calculations.

(14) The reactions of **2a**−**c** with Et_2NH or aniline gave the corresponding methallylamine and the product derived from the metallic component. The ^{1}H and ^{31}P NMR spectra of the latter are complicated, suggesting decomposition of **2a**−**c** under these conditions.

(15) Catalytic allylation with nucleophiles is generally performed by using allyl carboxylates or allyl carbonates.[16] Since the complexes **2a**−**c** are generally sensitive toward compounds containing oxygen atoms, exposure of **2a**−**c** to allyl carboxylates or allyl carbonates instantly results in decomposition of the complexes. Interestingly, **2a**−**c** are stable toward the compounds containing halogen atoms, and the reactions with allyl chloride proceed smoothly as described in the text.

(16) (a) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: Chichester, U.K., 1995. (b) Harrington, P. J. Transition Metal Allyl Complexes: Pd, W, Mo-assisted Nucleophilic Attack. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York, 1995; Vol. 12,Chapter 8.2. (c) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley: New York, 2002. (d) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089.

In conclusion, we have demonstrated that the electrophilicity of the η^3-methallyl moiety can be significantly enhanced due to the Ti←M_2 dative bond by introducing the Lewis acidic titanium center in the bidentate phosphine backbone. In other words, this work opens a new and alternative way to enhance the reactivity of the η^3-allyl moiety. This may lead to new ideas in exploring the new transition-metal catalysts which have unique reactivities and chemical properties.

Acknowledgment. This work was supported by a Grant-in-Aid for Science Research on Priority Areas (No. 18064014, Synergy of Elements) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information Available: Text, figures, tables, and CIF files giving a detailed experimental section, the molecular structures of **2a**−**c**, details of crystallographic studies (**2a**−**c**), Gaussview depiction of HOMO or HOMO-1 for the full molecules of **2a**−**c**, and the actual ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR data and ESI-tof-MS spectra of **2a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8011085