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Synthesis and structures of *o*-phenylene-bridged Cp/phosphinoamide titanium complexes

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Abstract

Addition of R'_2PCl to anilines substituted with di- or trimethylcyclopentadienyl unit at *ortho*-position affords *ortho*-phenylene-bridged Me_2Cp or Me_3Cp/phosophinoamide ligands, $2-(RMe_2C_5H_2)C_6H_4NHPR'_2$ (R = Me or H; R' = Ph, iPr, or Cyclohexyl). Successive addition of $Ti(NMe_2)_4$ and Me_2SiCl_2 to the ligands affords the desired dichlorotitanium complexes, $[2-(\eta^5-RMe_2C_5H_2)C_6H_4NPR'_2-\kappa^2N,P]TiCl_2$ (R = H, R' = Ph, **9**; R = Me, R' = Ph, **10**; R = H, R' = iPr, **11**; R = Me, R' = iPr, **12**; R = H, R' = Cy, **13**; R = Me, R' = Cy, **14**). By using $Zr(NMe_2)_4$ instead of $Ti(NMe_2)_4$, a zirconium complex, $[2-(\eta^5-Me_3C_5H)C_6H_4NP(iPr)_2-\kappa^2N,P]ZrCl_2$ (**15**) is prepared. Molecular structures of **10**, **14** and $[2-(\eta^5-Me_2C_5H_2)C_6H_4NPPh_2-\kappa N]Ti(NMe_2)_2$ (**16**) were determined. The metric parameters determined on the X-ray crystallographic studies and the chemical shifts of the ^{31}P NMR signal indicate that the phosphorous atom coordinates to the titanium in the dichloro-complexes **9**–**15**. The titanium and zirconium complexes show negligible activity in ethylene and ethylene/1-hexene (co)polymerization when activated with MAO or $iBu_3Al/[Ph_3C][B(C_6F_5)_4]$.
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1. Introduction

The Constrained-Geometry Catalyst (CGC), $[Me_2Si(\eta^5-Me_4C_5)(N^tBu)]TiCl_2$ [1] typically represents the homogeneous Ziegler–Natta catalysts [2]. Various modifications have been successfully carried out either by replacement of the Me_4C_5-unit with other π-donor ligands [3] or by replacement of the N^tBu-unit with other amides or phosphides [4], but modification on the bridge has not been so abundant and successful [5]. Recently, we disclosed a novel preparation route for *o*-phenylene-bridged (dimethyl or trimethylcyclopentadienyl)/(amide or sulfonamide) ligand system [6]. Suzuki coupling reaction of 2-bromoaniline compounds with 2-dihydroxyboryl-3,4-dimethyl-2-cyclopenten-1-one or 2-dihydroxyboryl-3-methyl-2-cyclopenten-

1-one is a key step in the route (Eq. (1)). Replacement of the silylene-bridge with *o*-phenylene group leads to a structural change of narrower Cp(cent)–Ti–N angle, indicative of more "constrained feature" in the *o*-phenylene bridged complexes [6]. While the silicon atom in the CGC is severely deviated from the cyclopentadienyl plane [7], the elements constituting the chlelation in the *o*-phenylene bridged complexes are not situated in a severely strained position. Some complexes are superior to the CGC in ethylene/α-olefin copolymerization in terms of activity, α-olefin incorporation, and molecular weight of the obtained polymer. Herein, we report titanium complexes derived from *o*-phenylene-bridged di- or trimethylcyclopentadienyl/phosphinoamide ligands. Coordination chemistry utilizing phosphinoamide ligand ($[R_2P–NR']^-$) has drawn extensive attention recently [8]. Bis(phosphinoamido)titanium and zirconium dichloride [9] and unbridged Cp*/phosphinoamide titanium complexes, $Cp^*TiCl_2(\eta^2-Ph_2PNR)$ (R = tBu, nBu, and Ph) [10] were prepared to be tested as a polymerization catalyst

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but the bridged Cp/phosphinoamide analogues have not been reported yet.
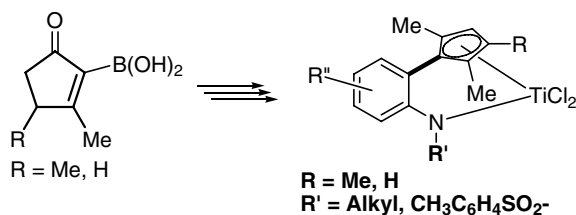
2. Results and discussion

2.1. Synthesis and characterization

Aniline compounds substituted with dimethylcyclopentadienyl or trimethylcyclopentadienyl-unit at *ortho*-position, 2- $(RMe_2C_5H_2)R'_2C_6H_2NH_2$ are prepared through the Suzuki-coupling reaction of 2-bromoanilines with 2-dihydroxyboryl-3,4-dimethyl-2-cyclopenten-1-one or 2-dihydroxyboryl-3-methyl-2-cyclopenten-1-one (Scheme 1). Addition of R'_2PCl (R' = phenyl, isopropyl, cyclohexyl) to the aniline derivatives in the presence of pyridine affords **3–8** in 60–90% yields. In case of the diphenylphosphino compounds, **3** and **4** addition of 1 equivalent of Ph_2PCl affords the desired compound and they are isolated as a solid by recrystallization in pentane. In case of the reactions of iPr_2PCl and Cy_2PCl, addition of slight excess of chlorophosphine (1.3 equivalents) is required for complete conversions. The remained iPr_2PCl can be easily removed by evacuation and spectroscopically pure **5** and **6** are afforded as oil. The remaining Cy_2PCl cannot be routinely removed by the evacuation and **7** and **8** are obtained, contaminated with some Cy_2PCl, which is used for the next reaction without further purification. The compounds are characterized by the ^1H, ^{13}C, and ^{31}P NMR spectroscopy
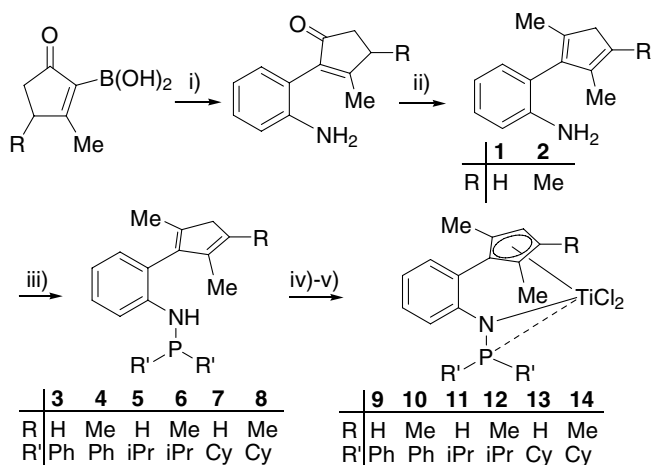
and the signals can be unambiguously assigned. Usually, a mixture of isomers is obtained for substituted cyclopentadiene compounds by the facile 1,5-sigmatropic rearrangement [11], but compounds **3–8** exist as a single isomer at room temperature, showing only a set of signals in the NMR spectra. The isomer where two hydrogens are attached on the sp³-carbon is substantially thermodynamically more stable and the isomer is predominant at room temperature. Signal of the two protons attached on the sp³-carbon of the cyclopentadiene unit are observed as an AB spin system in the ^1H NMR spectra, which implies that the rotation around carbon–carbon bond between the cyclopentadiene and phenylene is not free in the NMR time scale. The proton attached at the 6-position of the phenylene-unit is coupled with phosphorous with a coupling constant of $^4J_{PH} = 3$–4 Hz. In the ^1H NMR spectra of **5** and **6**, four isopropyl CH_3-signals are observed around 1 ppm as a doublet of doublet coupled with the phosphorous and the isopropyl-CH proton. Two signals show coupling constants of $^3J_{HH} = 6.8$ and $^3J_{PH} = 10$ Hz while the other two exhibiting the coupling constants of $^3J_{HH} = 6.8$ and $^3J_{PH} = 16$ Hz. In the ^{13}C NMR spectra, the 1, 2 and 6-carbons on the phenylene are coupled with phosphorus and observed as a doublet with coupling constants of $^2J_{PC} = 17, ^3J_{PC} = 4$, and $^3J_{PC} = 22$ ppm at ~146, ~124, and ~114 ppm, respectively.

Reaction of **3–8** with equimolar amount of $Ti(NMe_2)_4$ in benzene at 80 °C for 15 h affords a bis(dimethylamido)titanium complex. A single Me_2N-signal is observed as a singlet in the ^1H NMR spectra of the symmetrically substituted dimethylcyclopentadienyl complexes but two Me_2N-signals are observed for the trimethylcyclopentadienyl complexes. The phosphorus signals in the ^{31}P NMR spectra are not severely shifted by the metallation, which implies that the phosphorus atom does not coordinate with the titanium in the $(Me_2N)_2Ti$-complexes. The coupling constants between phosphorous and C–6 carbon on the phenylene ($^3J_{PC}$) are significantly changed by metallation (~21 Hz for **3–8** versus 6 Hz for the $(Me_2N)_2Ti$-complexes). The dependence of the coupling constants on the dihedral angle has been found empirically in many cases [12]. The phosphorous atom is not situated on the phenylene plane in the ligands **3–8** but it becomes coplanar with the phenylene plane by the metallation which triggers change of the P–N–C¹–C⁶ dihedral angle, consequently leading to the change of the coupling constant.

When Me_2SiCl_2 is employed as a chlorinating agent, the ^1H NMR spectra indicate that both Me_2N-ligands are replaced with the chloride ligands [13]. By the chlorination, chemical shifts of the phosphorous signals are dramatically upfield-shifted from ~45 ppm to ~7 ppm for the diphenylphosphino complexes. Similarly, large chemical-shift change ((Δ(chemical shifts) = ~36 ppm) is observed in the diisopropylphosphino and the dicyclohexylphosphino complexes. The dramatic chemical-shift change suggests the coordination of the phosphorous atom to the titanium. The coupling constants between phosphorous

Scheme 1. (i) 2-BrC₆H₂(R′)₂ NH₂, Na₂ CO₃, Pd(PPh₃)₄ (1 mol%); (ii) MeLi/CeCl₃, then HCl (2 N); (iii) R′₂PCl, pyridine; (iv) Ti(NMe₂)₄ and (v) Me₂SiCl₂.

	1	2
R	H	Me

	3	4	5	6	7	8
R	H	Me	H	Me	H	Me
R'	Ph	Ph	iPr	iPr	Cy	Cy

	9	10	11	12	13	14
R	H	Me	H	Me	H	Me
R'	Ph	Ph	iPr	iPr	Cy	Cy

and C-6 carbon on the phenylene ($^3J_{PC}$) are not changed significantly by the chlorination (3 Hz for **9–14**).

A zirconium complex is prepared from **6** by using $Zr(NMe_2)_4$ instead of $Ti(NMe_2)_4$ (equation 2). The phosphorus signal is observed at 44 and 34 ppm in the ^{13}P NMR spectra of the $(Me_2N)_2Zr$-complex and Cl_2Zr-complex, respectively. For the titanium complexes, slight change of the ^{31}P chemical shift is observed by metallation to $(NMe_2)_2$-Ti complexes (Δ(chemical shifts) <5 ppm) but significant chemical-shift change ((Δ(chemical shifts) = 30–40 ppm) is observed by replacing the Me_2N-ligand with the chloride ligand. We attribute the large change of the chemical shift to the coordination of the phosphorus with the titanium. In the case of zirconium, chemical-shift change (Δ(chemical shifts)) of 17 ppm is observed in the first metallation to the $(Me_2N)_2Zr$-complex and an additional 10 ppm change occurs in the second chlorination step. We assume that phosphorus atom coordinates with the zirconium in both $(Me_2N)_2Zr$- and Cl_2Zr-complexes with stronger interaction in the latter complex. The signal pattern of the ^1H and ^{13}C NMR spectra is not far from that observed for the corresponding titanium complex.
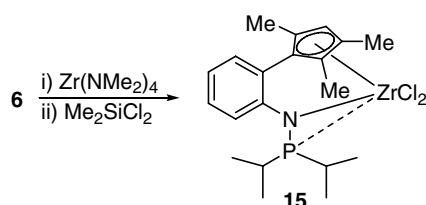
2.2. X-ray crystallographic studies

Single crystals of **10** suitable for X-ray crystallography are obtained by vapor-phase addition of pentane to a benzene solution. Fig. 1 shows the structure, and the selected bond distances and angles are tabulated in Table 1. The Ti–P distance (2.6881(19) Å) is close to those observed for titanium complexes coordinated with phosphine ligand
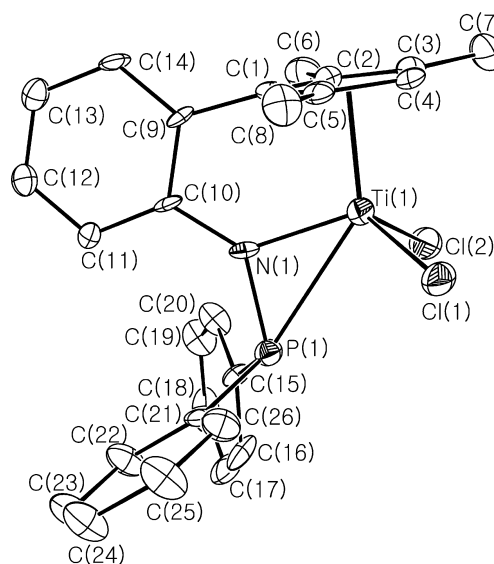

Fig. 1. Thermal ellipsoid plot (30% probability level) of **10**. Hydrogen atoms are omitted for clarity.

($\approx$2.63 Å) [14] indicating a chemical bonding between these two atoms, but it is somewhat longer than those observed for the unbridged analogues, $Cp^*TiCl_2(\eta^2$-$Ph_2PNtBu)$ (2.4928(9) Å) and $Cp^*TiCl_2(\eta^2$-$Ph_2PNPh)$ (2.477(2) Å).[10] By the coordination, C(10)–N–P (129.9(2)°) angle is increased from the ideal 120° while Ti–N–P angle (95.93(15)°) is contracted. The Ti–N distance (1.935(3) Å) is longer than those observed for $[2$-$(\eta^5$-2,3,5-$Me_3C_5H)$-$C_6H_3NC_6H_{11}]TiCl_2$ (1.9003(13) Å)[6a] and the standard CGC (1.907(4) Å)[7] but substantially shorter than those observed for the sulfonamide complex, $[C_6H_4(\eta^5$-Me_2-$H_2C_5)(NTs$-$\kappa N,O)]TiCl_2$ (2.005(5) Å)[6b] and the unbridged complexes $Cp^*TiCl_2(\eta^2$-$Ph_2PNtBu)$ (2.004(2) Å) and $Cp^*TiCl_2(\eta^2$-$Ph_2PNPh)$ (1.983(5) Å). The P–N distance (1.677(3) Å) is slightly longer than those observed for the unbridged analogues $Cp^*TiCl_2(\eta^2$-$Ph_2PNtBu)$ (1.638(2) Å) and $Cp^*TiCl_2(\eta^2$-$Ph_2PNPh)$ (1.652(5) Å). The Cp(cent)–Ti–N angle has been used as a qualitative measure for the "constrained geometry". The smaller the Cp(cent)–

Table 1
Selected bond distances (Å) and angles (°)

	10	14	16
Ti–P	2.6881(19)	2.621(3)	3.0343(12)
Ti–NP	1.935(3)	1.919(6)	2.034(2)
Ti–Cp^{Centroid}	2.032	2.031	2.042
Ti–Cl or Ti–NMe$_2$	2.2934(19) 2.300(2)	2.299(2) 2.293(2)	1.907(3) 1.905(3)
P–N	1.677(3)	1.667(6)	1.697(3)
Cp^{Centroid}–Ti–NP	103.19	102.19	104.08
C^{Bridge}–N–P	134.1(2)	135.6(6)	126.45(19)
Ti–N–P	95.93(15)	93.6(3)	108.49(13)
Ti–N–C^{Bridge}	129.9(2)	130.8(5)	124.54(19)
Cl–Ti–Cl (or Me$_2$N-Ti-NMe$_2$)	108.01(9)	104.97(9)	101.72(14)
C^{Bridgehead}–Cp^{Centroid}–Ti	88.55	89.00	89.81
Cp^{Centroid}–C^{Bridgehead}–C^{Bridge}	171.66	172.98	170.65
C^{Bridgehead}–C^{Bridge}–C^{Bridge}	113.5(3)	112.6(7)	115.0(3)
C^{Bridge}–C^{Bridge}–N	112.7(3)	112.3(8)	115.5(2)

Ti–N angle is, the more pronounced the "constrained geometry" features should be. The Cp(cent)–Ti–N angle (103.19° is larger than those observed for the *o*-phenylene-bridged Cp/sulfonamido complex, [C$_6$H$_4$(η^5-Me$_2$-H$_2$C$_5$)(NTs-$\kappa N,O$)]TiCl$_2$ (100.91° but it is smaller than those observed for the standard CGC (107.6° and the *o*-phenylene-bridged Cp/amido complex, [C$_6$H$_4$(η^5-Me$_2$H$_2$C$_5$)(NC$_6$H$_{11}$-κN)]TiCl$_2$ (104.8°. The *iso*-carbon on the phenylene bridge (C(9)) is not severely deviated from the cyclopentadienyl plane (Cp(cent)–C(1)–C(9) angle, 171.66° and the Cp(cent)–Ti vector is situated almost perpendicularly to the cyclopentadienyl plane (Ti-Cp(cent)–C(1) angle, 88.55°. The nitrogen atom is trigonal and the sum of bond angle around nitrogen is 360°. The cyclopentadienyl plane is almost perpendicularly situated to the phenylene plane (angle between the plane, 84.41(16)° and all the Ti, N, and P atoms are situated on the phenylene plane.

Fig. 2 shows the structure of **14**. The phosphorus atom in **14** is a better donor than that in **10**, hence either stronger Ti–P or stronger Ti–N bonding interaction is expected. As expected, the distances of Ti–P and Ti–N are shorter than the corresponding distances observed for **10**, respectively (Table 1). The Cp(cent)–Ti–N angle (102.19° is slightly smaller than that observed for **10** (103.19°. Other metrical parameters and molecular shape are close to those observed for **10**.

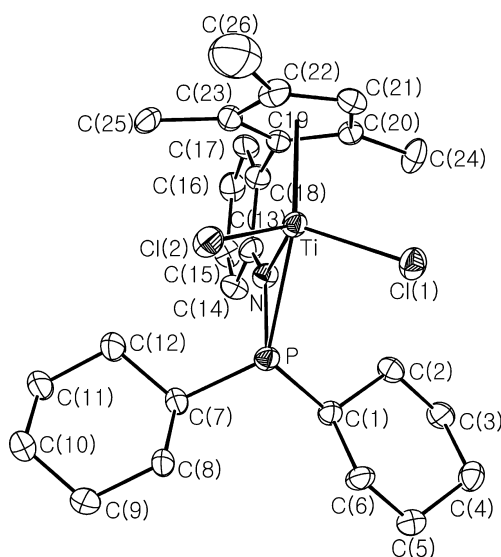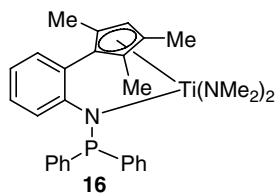Single crystals of the bis(dimethylamido)titanium complex **16** were obtained by recrystallization in pentane −30 °C. Fig. 3 shows its structure. The Ti–P separation (3.0343(12) Å) is significantly longer than those observed for **10** (2.6881(19) Å) and **14** (2.621(3) Å), and it is too large to be considered as a chemical bonding between these two atoms. Similar binding mode change by replacing the dimethylamide ligand with chloride was observed in dimethylsilylene bridged Me$_4$C$_5$/hydrazide ((η^5–C$_5$Me$_4$)SiMe$_2$(NNMe$_2$)) titanium complex [15]. Due to the absence of chemical bonding between the P and the Ti, the Ti–N–P angle increases to 108.49(13)° from those observed for the P-coordinated complexes **10** and **14** (95.93(15)° and 93.6(3)°, respectively) and inversely the C(13)–N–P angle decreases from 134.1(2)° and 135.6(6)° to 126.45(19)°. The Cp(cent)–Ti–N angle in **16** (104.08° is slightly larger than those in **10** and **14**. The nitrogen atom is trigonal and the sum of bond angle around the nitrogen is 359.5°. All the Ti, N, and P atoms are situated on the phenylene plane.

2.3. Polymerization studies

The newly prepared complexes are tested for ethylene and ethylene/1-hexene (co)copolymerization after activation with (Ph$_3$C)[B(C$_6$F$_5$)$_4$] and iBu$_3$Al (polymerization conditions: 30 mL toluene solution of 1-hexene (0.3 M), 0.50 μmol Ti, 2.0 μmol of [Ph$_3$C][B(C$_6$F$_5$)$_4$], 0.200 mmol of Al(iBu)$_3$, 60 psig ethylene, 90 °C, 10 min) or after activation with MMAO (polymerization conditions: 30 mL toluene solution of 1-hexene (0.3 M), 0.50 μmol Ti, Al/Ti, 5000, 60 psig ethylene, 90 °C, 10 min). All the complexes show negligible activity (<200 kg/molTi·h). Additional coordination of phosphorous might be attributed to the low activity [16]. Very low activities compared with the standard CGC were observed with the dimethylsilylene
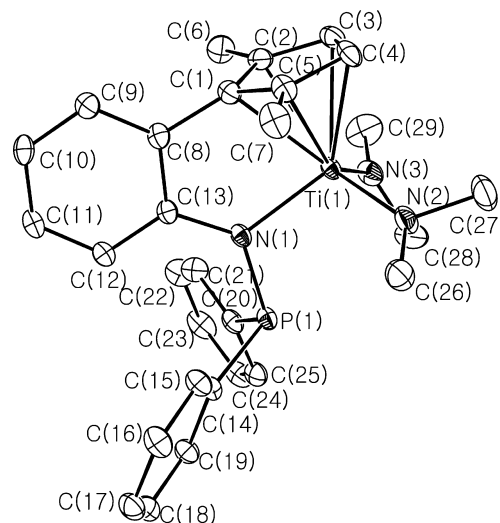

Fig. 2. Thermal ellipsoid plot (30% probability level) of **14**. Hydrogen atoms are omitted for clarity.

Fig. 3. Thermal ellipsoid plot (30% probability level) of **16**. Hydrogen atoms are omitted for clarity.

bridged Me$_4$C$_5$/hydrazide titanium complex [(η^5-C$_5$Me$_4$)SiMe$_2$(NNMe$_2$)]TiCl$_2$, where both nitrogens coordinate to the titanium. Activity of the unbridged Cp/phosphinoamide titanium complexes, Cp*TiCl$_2$(η^2–Ph$_2$PNR) is also low while the similar complexes constructed with monodentate ligand instead of the bidentate phosphinoamide ligand, Cp*TiCl$_2$(N = CNR2) or Cp*TiCl$_2$(OAr), show high activity [17].

3. Experimental section

3.1. General remarks

All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques. Toluene, pentane, and C$_6$D$_6$ were distilled from benzophenone ketyl. NMR spectra were recorded on a Varian Mercury plus 400. Elemental analyses were carried out on a Perkin-Elmer 2400 CHN microanalyzer. Preparation of the starting materials **1** and **2** was previously reported [6b].

3.2. Compound 3

To a flask containing 2-(Me$_2$C$_5$H$_3$)C$_6$H$_4$NH$_2$ (0.113 g, 0.61 mmol) in benzene (0.6 mL) was added pyridine (0.240 g, 3.04 mmol) and chlorodiphenylphosphine (0.134 g, 0.61 mmol). After the solution was stirred for 3 hours at room temperature, the generated white solid was filtered. All volatiles were removed to give a residue which was purified by recrystallization in pentane at -30 °C. White solid was isolated (0.144 g, 64%). ^{1}H NMR (C$_6$D$_6$): δ 1.68 (s, 3H, CH$_3$), 1.74 (d, J = 1.6 Hz, 3H, CH$_3$), 2.58 and 2.67 (AB, ^2J = 22 Hz, 2H, Cp–CH$_2$), 4.75 (d, J = 7.2 Hz, 1H, NH), 5.81 (d, J = 1.2 Hz, 1H, Cp–H), 6.79 (td, J = 1.2, 7.2 Hz, 1H, C$_6$H$_4$), 6.94–7.06 (m, 7H, C$_6$H$_4$, Ph), 7.09 (td, J = 1.2, 8.0 Hz, 1 H, C$_6$H$_4$), 7.34–7.42 (m, 4H, Ph), 7.65 (dd, J = 3.2, 8.0 Hz, 1H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR(C$_6$D$_6$): δ 14.89 (CH$_3$), 15.00 (CH$_3$), 44.55 (Cp–CH$_2$), 115.21 (d, $^3J_{CP}$ = 22 Hz, C$_6$H$_4$–C^6), 119.48 (C$_6$H$_4$–C^4), 124.82 (d, $^3J_{CP}$ = 4.0 Hz, C$_6$H$_4$–C^2), 125.27 (Cp–CH), 128.74 (d, $^3J_{CP}$ = 7 Hz, Ph-meta), 128.80 (C$_6$H$_4$–C$^{5\ or\ 3}$), 129.10 (d, $^3J_{CP}$ = 6 Hz, Ph-meta), 129.12 (Ph-para) 130.29 (C$_6$H$_4$–C$^{5\ or\ 3}$), 131.14 (d, $^2J_{CP}$ = 21 Hz, Ph-ortho), 131.30 (d, $^2J_{CP}$ = 21 Hz, Ph-ortho), 139.77 (Cp), 141.13 (d, $^1J_{CP}$ = 13 Hz), 141.52 (d, $^1J_{CP}$ = 13 Hz), 142.12 (Cp), 143.60 (Cp), 145.00 (d, $^2J_{CP}$ = 17 Hz, C$_6$H$_4$–C^1) ppm. ^{31}P NMR (C$_6$D$_6$): δ 45.56 ppm. Anal. Calc. (C$_{25}$H$_{24}$NP): C, 81.28; H, 6.55; N, 3.79. Found: C, 81.66; H, 6.31; N, 3.91%.

3.3. Compound 4

The compound was synthesized by the reaction of **2** and chlorodiphenylphosphine using same conditions and procedures as for **3**. White solid was isolated by recrystallization in pentane at −30 °C (58%). ^{1}H NMR (C$_6$D$_6$): δ

1.64 (s, 3H, CH$_3$), 1.74 (s, 3H, CH$_3$), 1.76 (s, 3H, CH$_3$), 2.53 and 2.60 (AB, J = 22 Hz, 2H, Cp-CH$_2$), 4.87 (d, J = 7.2 Hz, 1H, NH), 6.86 (td, J = 1.2, 7.6 Hz, 1H, C$_6$H$_4$), 6.98–7.08 (m, 6H, Ph), 7.11 (d, J = 7.2 Hz, 1 H, C$_6$H$_4$), 7.16 (td, J = 1.6, 7.6 Hz, 1H, C$_6$H$_4$), 7.38–7.48 (m, 4H, Ph), 7.70 (dd, J = 3.6, 8.0 Hz, 1H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR(C$_6$D$_6$): δ 12.09 (CH$_3$), 13.75 (CH$_3$), 14.60 (CH$_3$), 48.91 (Cp-CH$_2$), 115.26 (d, $^3J_{CP}$ = 21 Hz, C$_6$H$_4$-C^6), 119.48 (C$_6$H$_4$-C^4), 125.55 (d, $^3J_{CP}$ = 4.0 Hz, C$_6$H$_4$-C^2), 128.68 (d, $^3J_{CP}$ = 7 Hz, Ph-meta), 128.68 (C$_6$H$_4$-C$^{5\ or\ 3}$), 128.71 (d, $^3J_{CP}$ = 6 Hz, Ph-meta), 129.03 (Ph-para) 130.27 (C$_6$H$_4$-C$^{5\ or\ 3}$), 131.21 (d, $^2J_{CP}$ = 21 Hz, Ph-ortho), 131.30 (d, $^2J_{CP}$ = 21 Hz, Ph-ortho), 133.75 (Cp), 135 87 (Cp), 137.62 (Cp), 140.23 (Cp), 141.25 (d, $^1J_{CP}$ = 14 Hz), 141.64 (d, $^1J_{CP}$ = 13 Hz), 145.09 (d, $^2J_{CP}$ = 17 Hz, C$_6$H$_4$-C^1) ppm. ^{31}P NMR (C$_6$D$_6$): δ 45.78 ppm. Anal. Calc. (C$_{26}$H$_{26}$NP): C, 81.44; H, 6.86; N, 3.65. Found: C, 81.33; H, 7.01; N, 3.54%.

3.4. Compound 5

The compound was synthesized by the reaction of **1** and chlorodiisopropylphosphine using almost same conditions and procedures as for **3**. Excess chlorodiisopropylphosphine (1.3 equivalents) should be added to convert **1** completely to the desired product. The remained chlorodiisopropylphosphine could be removed by evacuation. Colorless oil was isolated in 75% yield. ^{1}H NMR (C$_6$D$_6$): δ 0.89 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 10 Hz, 3H, CH-CH$_3$), 0.91 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 10 Hz, 3H, CH-CH$_3$), 0.93 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 16 Hz, 3H, CH-CH$_3$), 0.95 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 16 Hz, 3H, CH-CH$_3$), 1.38–1.49 (m, 2H, CH), 1.82 (s, 3H, CH$_3$), 1.83 (q, J = 2.0 Hz, 3H, CH$_3$), 2.74–2.89 (m, 2H, Cp-CH$_2$), 4.01 (d, J = 10.8 Hz, 1H, NH), 5.93 (dd, J = 1.6, 3.2 Hz, 1H, Cp-CH), 6.76 (td, J = 1.2, 7.6 Hz, 1H, C$_6$H$_4$), 7.00 (dd, J = 1.6, 7.2 Hz, 1H, C$_6$H$_4$), 7.16 (td, J = 1.6, 7.6 Hz, 1H, C$_6$H$_4$), 7.73 (ddd, J = 1.2, 4.0, 8.4 Hz, 1H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR(C$_6$D$_6$): δ 14.93 (CH$_3$), 15.01 (CH$_3$), 17.04 (d, $^1J_{CP}$ = 8 Hz), 17.13 (d, $^1J_{CP}$ = 8 Hz), 19.17 (d, $^2J_{CP}$ = 20 Hz, PCHCH$_3$), 27.11 (d, $^2J_{CP}$ = 13 Hz, PCHCH$_3$), 27.26 (d, $^2J_{CP}$ = 13 Hz, PCHCH$_3$), 44.64 (Cp-CH$_2$), 114.69 (d, $^3J_{CP}$ = 22 Hz, C$_6$H$_4$-C^6), 118.14 (C$_6$H$_4$-C^4), 123.61 (d, presup3J_{CP} = 3.0 Hz, C$_6$H$_4$-C^2), 125.06 (Cp-CH), 128.71 (C$_6$H$_4$-C$^{5\ or\ 3}$), 130.02 (C$_6$H$_4$-C$^{5\ or\ 3}$), 140.40 (Cp), 141.68 (Cp), 143.87 (Cp), 147.12 (d, $^2J_{CP}$ = 16 Hz, C$_6$H$_4$-C^1) ppm. ^{31}P NMR (C$_6$D$_6$): δ 61.93 ppm. HRMS-EI m/z = M$^+$ Calcd. (C$_{19}$H$_{28}$NP): 301.1959. Found: 301.1958.

3.5. Compound 6

The compound was synthesized by the reaction of **2** and chlorodiisopropylphosphine using almost same conditions and procedures as for **5**. Colorless oil was isolated in 52% yield. ^{1}H NMR (C$_6$D$_6$): δ 0.92 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 10 Hz, 3H, CH-CH$_3$), 0.94 (dd, $^3J_{HH}$ = 6.8 Hz,

$^3J_{PH} = 16$ Hz, 3H, CH-CH_3), 0.95 (dd, $^3J_{HH} = 6.8$ Hz, $^3J_{PH} = 10$ Hz, 3H, CH-CH_3), 0.98 (dd, $^3J_{HH} = 6.8$ Hz, $^3J_{PH} = 16$ Hz, 3H, CH-CH_3), 1.38–1.52 (m, 2H, CH), 1.74 (s, 3H, CH$_3$), 1.85 (s, 6H, CH$_3$), 2.69 and 2.79 (AB, $J = 22.4$ Hz, 2H, Cp-CH$_2$), 4.12 (d, $J = 10.8$ Hz, 1H, NH), 6.81 (t, $J = 7.2$ Hz, 1H, C$_6$H$_4$), 7.07 (d, $J = 7.2$ Hz, 1 H, C$_6$H$_4$), 7.20 (t, $J = 7.6$ Hz, 1H, C$_6$H$_4$), 7.80 (dd, $J = 4.0$, 8.0 Hz, 1H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR(C$_6$D$_6$): δ 12.15 (CH$_3$), 13.85 (CH$_3$), 14.67 (CH$_3$), 17.07 (d, $^1J_{CP} = 7$ Hz), 17.13 (d, $^1J_{CP} = 7$ Hz), 19.13 (d, $^2J_{CP} = 20$ Hz, PCHCH_3), 19.20 (d, $^2J_{CP} = 20$ Hz, PCHCH_3), 27.10 (d, $^2J_{CP} = 13$ Hz, PCHCH_3), 27.20 (d, $^2J_{CP} = 13$ Hz, PCHCH_3), 49.00 (Cp-CH$_2$), 114.64 (d, $^3J_{CP} = 21$ Hz, C$_6$H$_4$-C^6), 118.12 (C$_6$H$_4$-C^4), 124.26 (d, $^3J_{CP} = 3.0$ Hz, C$_6$H$_4$-C^2), 128.58 (C$_6$H$_4$-C$^{5 \text{ or } 3}$), 130.06 (C$_6$H$_4$-C$^{5 \text{ or } 3}$), 133.57 (Cp), 136.04 (Cp), 137.21 (Cp), 140.81 (Cp), 147.14 (d, $^2J_{CP} = 16$ Hz, C$_6$H$_4$-C^1) ppm. ^{31}P NMR (C$_6$D$_6$): δ 61.77 ppm. HRMS-EI m/z = M$^+$ Calcd. (C$_{20}$H$_{30}$NP): 315.2116. Found: 315.2118.

3.6. Compound 7

The compound was synthesized by the reaction of **1** and chlorodicyclohexylphosphine using almost same conditions and procedures as for **3**. Excess chlorodicyclohexylphosphine (1.3 equivalents) should be added to convert **1** completely to the desired product. The remained chlorodicyclohexylphosphine could not be removed from the product by evacuation, The product was obtained contaminated with some chlorodicyclohexylphosphine in 82% yield, which is used for the next reaction without further purification. ^{1}H NMR (C$_6$D$_6$): δ 1.06–1.78 (m, 22H, Cy), 1.88 (s, 3H, CH$_3$), 1.90 (q, $J = 2.0$ Hz, 3H, CH$_3$), 2.79–2.90 (m, 2H, Cp-CH$_2$), 4.11 (d, $J = 10.4$ Hz, 1H, NH), 5.96 (t, $J = 2.0$ Hz, 1H, Cp-H), 6.81 (td, $J = 1.2$, 7.6 Hz, 1H, C$_6$H$_4$), 7.06 (dd, $J = 1.2$, 7.6 Hz, 1H, C$_6$H$_4$), 7.22 (td, $J = 1.6$, 7.6 Hz, 1H, C$_6$H$_4$), 7.80 (ddd, $J = 0.8$, 4.0, 8.0 Hz, 1H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 15.02 (CH$_3$), 15.07 (CH$_3$), 27.1–27.7 (m, P-Cy), 29.54 (d, $^2J_{CP} = 18$ Hz, PCHCH_2), 29.59 (d, $^2J_{CP} = 18$ Hz, PCHCH_2), 37.00 (d, $^1J_{CP} = 13$ Hz), 37.13 (d, $^1J_{CP} = 13$ Hz), 44.71 (Cp-CH$_2$), 114.83 (d, $^3J_{CP} = 21$ Hz, C$_6$H$_4$-C^6), 118.04 (C$_6$H$_4$-C^4), 123.62 (d, $^3J_{CP} = 3.0$ Hz, C$_6$H$_4$-C^2), 125.07 (Cp-CH), 128.63 (C$_6$H$_4$-C$^{5 \text{ or } 3}$), 129.96 (C$_6$H$_4$-C$^{5 \text{ or } 3}$), 140.58 (Cp), 141.61 (Cp), 143.90 (Cp), 147.39 (d, $^2J_{CP} = 16$ Hz, C$_6$H$_4$-C^1) ppm. ^{31}P NMR (C$_6$D$_6$): δ 56.32 ppm. HRMS-EI m/z = M$^+$ Calcd. (C$_{25}$H$_{36}$NP): 381.2585. Found: 381.2585.

3.7. Compound 8

The compound was synthesized by the reaction of **2** and chlorodicyclohexylphosphine using almost same conditions and procedures as for **7**. The product was obtained contaminated with some chlorodicyclohexylphosphine in 75% yield, which is used for the next reaction without further purification. ^{1}H NMR (C$_6$D$_6$): δ 1.02–1.72 (m, 22H, Cy),

1.74 (s, 3H, CH$_3$), 1.86 (s, 3H, CH$_3$), 1.87 (s, 3H, CH$_3$), 2.71 and 2.80 (AB, $J = 22.4$ Hz, 2H, Cp-CH$_2$), 4.16 (d, $J = 10.8$ Hz, 1H, NH), 6.81 (td, $J = 0.8$, 7.6 Hz, 1 H, C$_6$H$_4$), 7.06 (d, $J = 6.4$ Hz, 1H, C$_6$H$_4$), 7.21 (td, $J = 1.6$, 8.0 Hz, 1H, C$_6$H$_4$), 7.75 (dd, $J = 4.0$, 8.0 Hz, 1H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR(C$_6$D$_6$): δ 12.19 (CH$_3$), 13.83 (CH$_3$), 14.72 (CH$_3$), 26.8–27.8 (m, P-Cy), 29.54 (d, $^2J_{CP} = 18$ Hz, PCHCH_2), 29.57 (d, $^2J_{CP} = 18$ Hz, PCHCH_2), 36.97 (d, $^1J_{CP} = 13$ Hz), 37.16 (d, $^1J_{CP} = 13$ Hz), 49.07 (Cp-CH$_2$), 114.90 (d, $^3J_{CP} = 22$ Hz, C$_6$H$_4$-C^6), 118.07 (C$_6$H$_4$-C^4), 124.38 (C$_6$H$_4$-C^2), 128.54 (C$_6$H$_4$-C$^{5 \text{ or } 3}$), 129.97 (C$_6$H$_4$-C$^{5 \text{ or } 3}$), 133.60 (Cp), 136.15 (Cp), 137.12 (Cp), 141.04 (Cp), 147.41 (d, $^2J_{CP} = 17$ Hz, C$_6$H$_4$-C^1) ppm. ^{31}P NMR (C$_6$D$_6$): δ 56.77 ppm. HRMS-EI m/z = M$^+$ Calcd. (C$_{26}$H$_{38}$NP): 395.2742. Found: 395.2741.

3.8. Compound 9

Compound**3** (0.144 g, 0.39 mmol), Ti(NMe$_2$)$_4$(0.092 g, 0.041 mmol) and benzene (1.5 mL) were added into a sealable tube. The solution was stirred overnight at 80 °C. Removal of solvent gave red solid which was pure by the NMR analysis. Single crystals of the bis(dimethylamido)titanium complex were obtained by recrystallization in pentane at −30 °C. ^{1}H NMR (C$_6$D$_6$): δ 1.97 (s, 6H, CH$_3$), 3.19 (s, 6H, NCH$_3$), 3.20 (s, 6H, NCH$_3$), 5.81 (s, 2H, Cp-CH), 6.70–6.82 (m, 3H), 7.02–7.08 (m, 2H), 7.09–7.18 (m, 5H, ph-H), 7.62–7.72 (m, 4H) ppm. ^{13}C{^{1}H} NMR(C$_6$D$_6$): δ 13.37 (CH$_3$), 50.21 (NCH$_3$), 50.26 (NCH$_3$), 110.24 (C$_6$H$_4$-C^4), 119.57 (d, $^3J_{CP} = 6$ Hz, C$_6$H$_4$-C^6), 119.79 (Cp-CH), 127.26 (Cp-CCH$_3$), 127.71 (C$_6$H$_4$-C$^{5 \text{ or } 3}$), 127.71 (C$_6$H$_4$-C$^{5 \text{ or } 3}$), 128.11 (d, $^3J_{CP} = 7$ Hz, Ph-*meta*), 128.55 (Ph-*para*), 129.08 (d, $^3J_{CP} = 6$ Hz, C$_6$H$_4$-C^2), 131.07 (d, $^2J_{CP} = 18$ Hz, Ph-*ortho*), 137.13 (Cp-C^{bridgehead}), 140.19 (d, $^1J_{CP} = 33$ Hz), 161.38 (d, $^2J_{CP} = 10$ Hz, C$_6$H$_4$-C^1) ppm. ^{31}P NMR (C$_6$D$_6$): δ 40.67 ppm. To a flask containing the resulting bis(dimethylamido)titanium complex in benzene (1.5 mL) was added Me$_2$SiCl$_2$(0.14 mL, 1.2 mmol). After the solution was stirred for 3 hours at room temperature, all volatiles were removed under vacuum to give a yellow residue. The residue was dissolved in CHCl$_3$ and filtered over Celite. After removing solvent, the residue was triturated in pentane to give brownish red solid (0.14 g, 72%). ^{1}H NMR (CDCl$_3$): δ 2.03 (s, 6H, CH$_3$), 6.46 (d, $J = 8.0$ Hz, 1H, C$_6$H$_4$), 6.83 (s, 2H, Cp-CH), 7.15 (t, $J = 7.2$ Hz, 1H, C$_6$H$_4$), 7.20 (t, $J = 7.6$ Hz, 1H, C$_6$H$_4$), 7.36–7.48 (m, 7H, C$_6$H$_4$and Ph), 7.57–7.63 (m, 4H, ph-CH) ppm. ^{13}C{^{1}H} NMR(CDCl$_3$): δ 14.96 (CH$_3$), 114.69 (C$_6$H$_4$-C^4), 121.01 (d, $^3J_{CP} = 3$ Hz, C$_6$H$_4$-C^6), 124.44 (Cp-CH), 128.44 (C$_6$H$_4$-C$^{5 \text{ or } 3}$), 128.54 (d, $^3J_{CP} = 8$ Hz, Ph-*meta*), 129.96 (Ph-*para*), 130.29 (d, $^1J_{CP} = 6$ Hz), 130.61 (d, $^3J_{CP} = 7$ Hz, C$_6$H$_4$-C^2), 132.11 (d, $^2J_{CP} = 14$ Hz, Ph-*ortho*), 139.98 (Cp-CCH$_3$), 142.34 (Cp-C^{bridgehead}), 161.25 (d, $^2J_{CP} = 8$ Hz, C$_6$H$_4$-C^1) ppm. ^{31}P NMR (CDCl$_3$): δ 7.73 ppm. Anal. Calc. (C$_{25}$H$_{22}$Cl$_2$NPTi): C, 61.76; H, 4.56; N, 2.88. Found: C, 61.97; H, 4.43; N, 3.21%.

3.9. Compound 10

The complex was synthesized from **4** using same conditions and procedures as for **9**. Overall yield from **4** was 86%. The NMR data for the bis(dimethylamido)titanium complex: ^{1}H NMR (C$_6$D$_6$): δ 1.82 (s, 3H, CH$_3$), 1.93 (s, 6H,CH$_3$), 2.90 (s, 6H, NCH$_3$), 3.42 (s, 6H, NCH$_3$), 5.90 (s, 1H, Cp-CH), 6.62–6.74 (m, 2H), 7.02–7.14 (m, 8 H), 7.52–7.58 (m, 2H), 7.66–7.72 (m, 2H) ppm. ^{13}C{^{1}H} NMR(C$_6$D$_6$): δ 11.90 (CH$_3$), 12.68 (CH$_3$), 12.92 (CH$_3$), 48.07 (NCH$_3$), 52.08 (NCH$_3$), 52.18 (NCH$_3$), 114.60 (C$_6$H$_4$-C^4), 119.61 (Cp-CCH$_3$), 119.71 (Cp-CCH$_3$), 119.72 (Cp-CH), 120.06 (d, $^3J_{CP}$ = 3 Hz, C$_6$H$_4$-C^6), 124.40 (Cp-CCH$_3$), 127.31 (C$_6$H$_4$-C$^{5\,or\,3}$), 127.47 (C$_6$H$_4$-C$^{5\,or\,3}$), 128.30 (d, $^3J_{CP}$ = 8 Hz, Ph-*meta*), 128.34 (d, $^3J_{CP}$ = 8 Hz, Ph-*meta*), 128.72 (Ph-*para*), 129.65 (d, $^3J_{CP}$ = 6 Hz, C$_6$H$_4$-C^2), 130.55 (d, $^2J_{CP}$ = 17 Hz, Ph-*ortho*), 131.27 (d, $^2J_{CP}$ = 19 Hz, Ph-*ortho*), 136.92 (Cp-C^{bridgehead}), 140.47 (d, $^1J_{CP}$ = 34 Hz), 141.40 (d, $^1J_{CP}$ = 34 Hz), 161.84 (d, $^2J_{CP}$ = 10 Hz, C$_6$H$_4$-C^1) ppm. ^{31}P NMR (C$_6$D$_6$): δ 42.21 ppm. Single crystals of **10** were obtained by vapor-phase addition of pentane to a benzene solution. The analytical data for **10**: ^{1}H NMR (C$_6$D$_6$): δ 1.75 (s, 3H, CH$_3$), 1.92 (s, 3H, CH$_3$), 2.27 (s, 3H, CH$_3$), 6.32 (s, 1H, Cp-H), 6.53 (d, J = 7.6 Hz, 1H, C$_6$H$_4$), 6.82 (td, J = 1.6, 7.6 Hz, 1H, C$_6$H$_4$), 6.86 (t, J = 7.2 Hz, 1H, C$_6$H$_4$), 6.92–7.04 (m, 4H, Ph), 7.09 (d, J = 6.8 Hz, 1H, C$_6$H$_4$), 7.47–7.66 (m, 6H, Ph) ppm. ^{13}C{^{1}H} NMR(C$_6$D$_6$): δ 12.69 (CH$_3$), 14.40 (CH$_3$), 15.23 (CH$_3$), 115.15 (C$_6$H$_4$-C^4), 121.58 (d, $^3J_{CP}$ = 6 Hz, C$_6$H$_4$-C^6), 124.39 (Cp-CH), 128.73 (C$_6$H$_4$-C$^{5\,or\,3}$), 128.83 (d, $^3J_{CP}$ = 8 Hz, Ph-*meta*), 128.87 (d, $^3J_{CP}$ = 8 Hz, Ph-*meta*), 128.93 (C$_6$H$_4$-C$^{5\,or\,3}$), 129.98 (Ph-*para*), 130.11 (Ph-*para*), 131.51 (d, $^1J_{CP}$ = 8 Hz), 131.51 (d, $^1J_{CP}$ = 8 Hz), 131.58 (d, $^3J_{CP}$ = 6 Hz, C$_6$H$_4$-C^2), 131.81 (Cp-CCH$_3$), 132.42 (d, $^2J_{CP}$ = 15 Hz, Ph-*ortho*), 132.65 (d, $^2J_{CP}$ = 15 Hz, Ph-*ortho*), 139.13 (Cp-CCH$_3$), 139.40 (Cp-CCH$_3$), 142.24 (Cp-C^{bridgehead}), 162.19 (d, $^2J_{CP}$ = 8 Hz, C$_6$H$_4$-C^1) ppm. ^{31}P NMR (C$_6$D$_6$): δ 6.33 ppm. Anal. Calc. (C$_{26}$H$_{24}$Cl$_2$NPTi): C, 62.43 ; H, 4.84; N, 2.80. Found: C, 62.11; H, 5.11; N, 2.88%.

3.10. Compound 11

The complex was synthesized from **5** using same conditions and procedures as for **9**. Overall yield from **5** was 75%. The NMR data for the bis(dimethylamido)titanium complex:^{1}H NMR (C$_6$D$_6$): δ 0.99 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 10 Hz, 6H, CH-CH_3), 1.21 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 18 Hz, 6H, CH-CH$_3$), 1.84 (s, 6H, CH$_3$), 2.48 (septet, J = 6.8 Hz, 2H, CH), 3.15 (s, 6H, N-CH$_3$), 3.16 (s, 6H, N-CH$_3$), 5.67 (s, 2H, Cp-H), 6.84 (d, J = 8.4 Hz, 1H, C$_6$H$_4$), 6.88 (td, J = 1.2, 7.6 Hz, 1H, C$_6$H$_4$), 7.14 (dd, J = 2.0, 7.2 Hz, 1 H, C$_6$H$_4$), 7.18 (ddd, J = 1.6, 7.2, 8.0 Hz, 1H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR(C$_6$D$_6$): δ 13.38 (CH$_3$), 20.57 (d, $^1J_{CP}$ = 9 Hz), 22.15 (d, $^2J_{CP}$ = 33 Hz, PCHCH_3), 28.48 (d, $^2J_{CP}$ = 27 Hz, PCHCH_3), 51.00 (NCH$_3$), 51.07 (NCH$_3$), 110.42 (C$_6$H$_4$-C^4), 116.90 (d,

$^3J_{CP}$ = 5 Hz, C$_6$H$_4$-C^6), 119.39 (Cp-CH), 127.49 (Cp-CCH$_3$), 128.05 (C$_6$H$_4$-C$^{5\,or\,3}$), 128.60 (d, $^3J_{CP}$ = 8 Hz, C$_6$H$_4$-C^2), 128.96 (C$_6$H$_4$-C$^{5\,or\,3}$), 137.22 (Cp-C^{bridgehead}), 164.30 (d, $^2J_{CP}$ = 9 Hz, C$_6$H$_4$-C^1) ppm. ^{31}P NMR (C$_6$D$_6$): δ 63.21 ppm. The analytical data for **11**: ^{1}H NMR (CDCl$_3$): δ 0.96 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 14 Hz, 6H, CH-CH_3), 1.22 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 20 Hz, 6H, CH-CH$_3$), 1.81 (s, 6H, CH$_3$), 2.28 (septet, J = 6.8 Hz, 2H, CH), 6.34 (d, J = 8.0 Hz, 1H, C$_6$H$_4$), 6.51 (s, 2H, Cp-H), 6.94 (t, J = 7.2 Hz, 1 H, C$_6$H$_4$), 7.03 (d, J = 7.6 Hz, 1H, C$_6$H$_4$), 7.08 (td, J = 1.6, 8.0 Hz, 1H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR(CDCl$_3$): δ 14.69 (CH$_3$), 19.26 (d, $^1J_{CP}$ = 3 Hz), 21.03 (d, $^2J_{CP}$ = 20 Hz, PCHCH_3), 30.46 (d, $^2J_{CP}$ = 14 Hz, PCHCH_3), 113.81 (C$_6$H$_4$-C^4), 121.90 (d, $^3J_{CP}$ = 3 Hz, C$_6$H$_4$-C^6), 124.34 (Cp-CH), 128.96 (C$_6$H$_4$-C$^{5\,or\,3}$), 128.99 (C$_6$H$_4$-C$^{5\,or\,3}$), 130.87 (d, $^3J_{CP}$ = 6 Hz, C$_6$H$_4$-C^2), 137.78 (Cp-CCH$_3$), 141.14 (Cp-C^{bridgehead}), 163.31 (d, $^2J_{CP}$ = 8 Hz, C$_6$H$_4$-C^1) ppm. ^{31}P NMR (CDCl$_3$): δ 28.53 ppm. Anal. Calc. (C$_{19}$H$_{26}$Cl$_2$NPTi): C, 54.57; H, 6.27; N, 3.35. Found: C, 54.72; H, 6.43; N, 3.12%.

3.11. Compound 12

The complex was synthesized from **6** using same conditions and procedures as for **9**. Overall yield from **6** was 67%. The NMR data for the bis(dimethylamido)titanium complex: ^{1}H NMR (C$_6$D$_6$): δ 0.81 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 10 Hz, 3H, CH-CH_3), 1.19 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 10 Hz, 3H, CH-CH_3), 1.19 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 18 Hz, 3H, CH-CH_3), 1.24 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 18 Hz, 3H, CH-CH$_3$), 1.79 (s, 3H, CH$_3$), 1.82 (s, 3H, CH$_3$), 1.88 (s, 3H, CH$_3$), 2.50 (septet, J = 6.8 Hz, 2H, CH), 2.94 (s, 6H, NCH3), 3.43 (s, 6H, NCH$_3$), 5.91 (s, 1H, Cp-H), 6.89 (d, J = 8.4 Hz, 1H, C$_6$H$_4$), 6.90 (t, J = 7.6 Hz, 1H, C$_6$H$_4$), 7.17 (d, J = 8.4 Hz, 1 H, C$_6$H$_4$), 7.20 (t, J = 8.0 Hz, 1H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR(C$_6$D$_6$): δ 11.59 (CH$_3$), 12.67 (CH$_3$), 12.71 (CH$_3$), 19.84 (d, $^1J_{CP}$ = 9 Hz), 21.02 (d, $^1J_{CP}$ = 9 Hz), 21.29 (d, $^2J_{CP}$ = 33 Hz, PCHCH_3), 23.14 (d, $^2J_{CP}$ = 37 Hz, PCHCH_3), 27.50(d, $^2J_{CP}$ = 26 Hz, PCHCH_3), 29.60 (d, $^2J_{CP}$ = 30 Hz, PCHCH_3), 44.24 (NCH$_3$), 48.16 (NCH$_3$), 53.50 (NCH$_3$), 53.62 (NCH$_3$), 114.76 (C$_6$H$_4$-C^4), 117.00 (d, $^3J_{CP}$ = 6 Hz, C$_6$H$_4$-C^6), 119.13 (Cp-CH), 119.68 (Cp-CCH$_3$), 122.95 (Cp-CCH$_3$), 127.04 (Cp-CCH$_3$), 128.96 (C$_6$H$_4$-C$^{5\,or\,3}$), 136.93 (Cp-C^{bridgehead}), 164.80 (d, $^2J_{CP}$ = 9 Hz, C$_6$H$_4$-C^1) ppm. ^{31}P NMR (C$_6$D$_6$): δ 65.77 ppm. The analytical data for **12**: ^{1}H NMR (C$_6$D$_6$): δ 0.94 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 14 Hz, 3H, CHCH_3), 0.98 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 14 Hz, 3H, CHCH_3), 1.23 (dd, J = 6.8, 20 Hz, 6H, CHCH_3), 1.62 (s, 3H, CH$_3$), 1.85 (s, 3H, CH$_3$), 2.26 (s, 3H, CH$_3$), 2.34 (septet, J = 6.8 Hz, 2H, CH), 6.30 (s, 1H, Cp-H), 6.40 (d, J = 7.6 Hz, 1H, C$_6$H$_4$), 7.02 (t, J = 7.2 Hz, 1 H, C$_6$H$_4$), 7.13 (d, J = 6.8 Hz, 1H, C$_6$H$_4$), 7.18 (t, J = 7.6 Hz, 1H, C$_6$H$_4$) ppm.^{13}C{^{1}H} NMR(C$_6$D$_6$): δ 12.29 (CH$_3$), 14.13 (CH$_3$), 14.92 (CH$_3$), 19.27 (d, $^1J_{CP}$ = 5 Hz), 19.31 (d,

$^1J_{CP} = 3$ Hz), 21.10 (d, $^2J_{CP} = 20$ Hz, PCHCH_3), 30.30 (d, $^2J_{CP} = 15$ Hz, PCHCH_3), 30.39 (d, $^2J_{CP} = 14$ Hz, PCHCH_3), 113.84 (C_6H_4-C^4), 122.27 (d, $^3J_{CP} = 3$ Hz, C_6H_4-C^6), 124.30 (Cp-CH), 129.00 (C_6H_4-$C^{5\ or\ 3}$), 129.09 (C_6H_4-$C^{5\ or\ 3}$), 131.01 (Cp-CCH$_3$), 131.43 (d, $^3J_{CP} = 7$ Hz, C_6H_4-C^2), 137.47 (Cp-CCH$_3$), 137.81 (Cp-CCH$_3$), 141.20 (Cp-$C^{bridgehead}$), 163.56 (d, $^2J_{CP} = 9$ Hz, C_6H_4-C^1) ppm. ^{31}P NMR (C_6D_6): δ 26.04 ppm. Anal. Calc. ($C_{20}H_{28}Cl_2$-NPTi): C, 55.58; H, 6.53; N, 3.24. Found: C, 55.82; H, 6.39; N, 3.37%.

3.12. Compound 13

The complex was synthesized from **7** using same conditions and procedures as for **9**. Overall yield from **7** was 56%. The analytical data for **13**: ^{1}H NMR (CDCl$_3$): δ 1.1–2.6 (m, 22H, Cy), 1.88 (s, 6H, CH$_3$), 6.67 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.70 (s, 2H, Cp-H), 7.23 (t, $J = 7.2$ Hz, 1H, C_6H_4), 7.39 (td, $J = 1.6$, 7.6 Hz, 1H, C_6H_4), 7.42 (d, $J = 7.2$ Hz, 1H, C_6H_4) ppm. ^{13}C{^{1}H} NMR(CDCl$_3$): δ 14.64 (CH$_3$), 25.82 (Cy), 27.04 (Cy), 27.15 (d, $^1J_{CP} = 7$ Hz, Cy), 27.92 (Cy), 31.17 (d, $^2J_{CP} = 15$ Hz, Cy), 40.17 (d, $^2J_{CP} = 14$ Hz, Cy), 113.42 (C_6H_4-C^4), 121.70 (d, $^3J_{CP} = 3$ Hz, C_6H_4-C^6), 124.22 (Cp-CH), 128.66 (C_6H_4-$C^{5\ or\ 3}$), 128.83 (C_6H_4-$C^{5\ or\ 3}$), 130.27 (d, $^3J_{CP} = 7$ Hz, C_6H_4-C^2), 138.14 (Cp-CCH$_3$), 141.15 (Cp-$C^{bridgehead}$), 163.29 (d, $^2J_{CP} = 8$ Hz, C_6H_4-C^1) ppm. ^{31}P NMR (CDCl$_3$): δ 19.49 ppm. Anal. Calc. ($C_{25}H_{34}Cl_2$-NPTi): C, 60.26; H, 6.88; N, 2.81. Found: C, 60.44; H, 6.63; N, 2.95%.

3.13. Compound 14

The complex was synthesized from **8** using same conditions and procedures as for **9**. Overall yield from **8** was 78%. Single crystals of **14** were obtained by vapor-phase addition of pentane to a benzene solution. The analytical data for **14**: ^{1}H NMR (C_6D_6): δ 1.1–2.6 (m, 22H, Cy), 1.67 (s, 3H, CH$_3$), 1.90 (s, 3H, CH$_3$), 2.29 (s, 3H, CH$_3$), 6.32 (s, 1H, Cp-H), 6.49 (d, $J = 7.6$ Hz, 1H, C_6H_4), 6.96 (t, $J = 7.6$ Hz, 1H, C_6H_4), 7.08–7.20 (m, 2H, C_6H_4) ppm. ^{13}C{^{1}H} NMR(C_6D_6): δ 12.35 (CH$_3$), 14.10 (CH$_3$), 14.99 (CH$_3$), 26.26 (Cy), 27.41 (Cy), 27.53 (d, $^1J_{CP} = 5$ Hz, Cy), 28.36 (Cy), 31.53 (d, $^2J_{CP} = 17$ Hz, Cy), 40.42 (d, $^2J_{CP} = 15$ Hz, Cy), 40.48 (d, $^2J_{CP} = 15$ Hz, Cy), 113.68 (C_6H_4-C^4), 122.40 (d, $^3J_{CP} = 3$ Hz, C_6H_4-C^6), 124.12 (Cp-CH), 128.93 (C_6H_4-$C^{5\ or\ 3}$), 129.09 (C_6H_4-$C^{5\ or\ 3}$), 131.00 (Cp-CCH$_3$), 131.45 (d, $^3J_{CP} = 7$ Hz, C_6H_4-C^2), 137.20 (Cp-CCH$_3$), 137.54 (Cp-CCH$_3$), 141.01 (Cp-$C^{bridgehead}$), 164.22 (d, $^2J_{CP} = 8$ Hz, C_6H_4-C^1) ppm. ^{31}P NMR (C_6D_6): δ 17.26 ppm. Anal. Calc. ($C_{26}H_{36}Cl_2$NPTi): C, 60.95; H, 7.08; N, 2.73. Found: C, 60.78; H, 7.17; N, 2.99%.

3.14. Compound 15

The complex was synthesized by the reaction **4** and Zr(NMe$_2$)$_4$ using same conditions and procedures as for

9. Overall yield from **4** was 83%. The NMR data for the bis(dimethylamido)zirconium complex: ^{1}H NMR (C_6D_6): δ 0.80 (dd, $^3J_{HH} = 6.8$ Hz, $^3J_{PH} = 12$ Hz, 3H, CH-CH_3), 1.07 (dd, $^3J_{HH} = 6.8$ Hz, $^3J_{PH} = 12$ Hz, 3H, CH-CH_3), 1.09 (dd, $^3J_{HH} = 6.8$ Hz, $^3J_{PH} = 18$ Hz, 3H, CH-CH_3), 1.14 (dd, $^3J_{HH} = 6.8$ Hz, $^3J_{PH} = 18$ Hz, 3H, CH-CH_3), 1.82 (s, 3H, CH$_3$), 1.90 (s, 3H, CH$_3$), 1.98 (s, 3H, CH$_3$), 2.34–2.48 (m, 2H, CH), 2.87 (6H, NCH$_3$), 3.14 (6H, NCH$_3$), 5.87 (s, 1H, Cp-H), 6.72 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.89 (td, $J = 1.2$, 7.2 Hz, 1H, C_6H_4), 7.16 (td, $J = 1.6$, 7.6 Hz, 1H, C_6H_4), 7.21 (dd, $J = 1.2$, 7.2 Hz, 1H, C_6H_4) ppm. ^{31}P NMR (C_6D_6): δ 44.47 ppm. The analytical data for **15**: ^{1}H NMR (C_6D_6): δ 0.94 (dd, $^3J_{HH} = 7.2$ Hz, $^3J_{PH} = 14$ Hz, 3H, CHCH_3), 0.97 (dd, $^3J_{HH} = 7.2$ Hz, $^3J_{PH} = 14$ Hz, 3H, CHCH_3), 1.10 (dd, $^3J_{HH} = 7.2$ Hz, $^3J_{PH} = 20$ Hz, 3H, CHCH_3), 1.11 (dd, $^3J_{HH} = 7.2$ Hz, $^3J_{PH} = 20$ Hz, 3H, CHCH_3), 1.68 (s, 3H, CH$_3$), 1.89 (s, 3H, CH$_3$), 2.18 (s, 3H, CH$_3$), 2.20–2.32 (m, 2H, CH), 6.08 (s, 1H, Cp-H), 6.44 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.94 (td, $J = 0.8$, 7.2 Hz, 1 H, C_6H_4), 7.08–7.14 (m, 2H, C_6H_4) ppm. ^{13}C{^{1}H} NMR(C_6D_6): δ 11.26 (CH$_3$), 13.24 (CH$_3$), 13.63 (CH$_3$), 19.15 (d, $^1J_{CP} = 3$ Hz), 19.20 (d, $^1J_{CP} = 3$ Hz), 20.53 (d, $^2J_{CP} = 19$ Hz, PCHCH_3), 28.25 (d, $^2J_{CP} = 11$ Hz, PCHCH_3), 28.32 (d, $^2J_{CP} = 11$ Hz, PCHCH_3), 115.90 (C_6H_4-C^4), 116.56 (d, $^3J_{CP} = 3$ Hz, C_6H_4-C^6), 122.93 (Cp-CH), 126.12 (Cp-CCH$_3$), 129.02 (C_6H_4-$C^{5\ or\ 3}$), 129.81 (C_6H_4-$C^{5\ or\ 3}$), 130.41 (d, $^3J_{CP} = 7$ Hz, C_6H_4-C^2), 131.03 (Cp-CCH$_3$), 131.20 (Cp-CCH$_3$), 136.73 (Cp-$C^{bridgehead}$), 160.31 (d, $^2J_{CP} = 10$ Hz, C_6H_4-C^1) ppm. ^{31}P NMR (C_6D_6): δ 34.12 ppm. Anal. Calc. ($C_{20}H_{28}Cl_2$NPZr): C,

Table 2
Crystallographic Parameters of 10, 14 and 16

	10	14	16
Formula	$C_{26}H_{24}Cl_2NPTi$	$C_{26}H_{36}Cl_2NPTi$	$C_{29}H_{34}N_3PTi$
F_w	500.23	512.33	503.46
Size (mm^3)	$0.1 \times 0.1 \times 0.3$	$0.15 \times 0.15 \times 0.5$	$0.2 \times 0.15 \times 0.05$
a (Å)	10.777(8)	10.205(3)	9.655(3)
b (Å)	13.924(16)	17.172(6)	15.373(7)
c (Å)	16.261(17)	14.795(5)	17.746(7)
α (°)	90	90	90
β (°)	90	103.857(11)	98.110(14)
γ (°)	90	90	90
V (Å^3)	2440(4)	2517.3(15)	2607.6(18)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
D (calc), gcm^{-1}	1.362	1.352	1.282
Z	4	4	4
μ, mm^{-1}	0.649	0.630	0.412
Number of data collected	22465	23058	23913
Number of unique data	5523	5633	5858
Number of variables	377	425	447
R (%)	0.0510	0.0952	0.0641
R_w (%)	0.1302	0.2580	0.1746
Goodness of fit	1.002	1.019	1.083

Data collected at 150(2) K with Mo Kα radiation (λ(Kα) = 0.7107 Å), $R(F) = \sum ||F_o| - |F_c||/\sum |F_o|$ with $F_o > 2.0\sigma(I)$, $R_w = [\sum [w(F_o^2 - F_c^2)^2]/ \sum [w(F_o)^2]^2]^{1/2}$ with $F_o > 2.0\sigma(I)$.

50.51 ; H, 5.93; N, 2.95%. Found: C, 50.33 ; H, 5.69 ; N, 3.29%.

3.15. X-ray crystallography

Crystals of **10** , **14**, and **16** coated with grease (Apiezon N) were mounted onto a thin glass fiber with epoxy glue and placed in a cold nitrogen stream at 150(2) K on Rigaku single crystal X-ray diffractometer. The structures were solved by direct methods (SHELXL-97) and refined against all F^2 data (SHELXL-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions. The crystal data and refinement results are summarized in Table 2.

4. Supplementary material

CCDC 615699, 615700 and 615701 contain the supplementary crystallographic data for **10**, **14** and **16**. These data can be obtained free of charge via http://www.ccdc.cam. ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ ccdc.cam.ac.uk.

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References

[1] (a) A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587;
(b) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283.

[2] (a) Review: H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem., Int. Ed. Engl. 34 (1995) 1143;
(b) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem., Int. Ed. Eng. 38 (1999) 429;
(c) H.G. Alt, A. Köpple, Chem. Rev. 100 (2000) 1205;
(d) G.W. Coates, Chem. Rev. 100 (2000) 1223;
(e) L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 100 (2000) 1253;
(f) E.Y.–X. Chen, T.J. Marks, Chem. Rev. 100 (2000) 1391;
(g) H.G. Alt, Dalton Trans. (2005) 3271.

[3] (a) L.J. Irwin, S.A. Miller, J. Am. Chem. Soc. 127 (2005) 9972;
(b) C. Grandini, I. Camurati, S. Guidotti, N. Mascellani, L. Resconi, I.E. Nifant'ev, I.A. Kashulin, P.V. Ivchenko, P. Mercandelli, A. Sironi, Organometallics 23 (2004) 344;

(c) C. De Rosa, F. Auriemma, O. Ruiz de Ballesteros, L. Resconi, A. Fait, E. Ciaccia, I. Camurati, J. Am. Chem. Soc. 125 (2003) 10913;
(d) J. Klosin, W.J. Kruper Jr., P.N. Nickias, G.R. Roof, P. De Waele, K.A. Abboud, Organometallics 20 (2001) 2663.

[4] G. Altenhoff, S. Bredeau, G. Erker, G. Kehr, O. Kataeva, R. Frohlich, Organometallics 21 (2002) 4084.

[5] (a) K. Kunz, G. Erker, S. Doring, R. Frohlich, G. Kehr, J. Am. Chem. Soc. 123 (2001) 6181;
(b) C. Wang, G. Erker, G. Kehr, K. Wedeking, R. Frohlich, Organometallics 24 (2005) 4760;
(c) T.H. Kim, Y.C. Won, B.Y. Lee, D.M. Shin, Y.K. Chung, Eur. J. Inorg. Chem. (2004) 1522;
(d) D. van Leusen, D.J. Beetstra, B. Hessen, J.H. Teuben, Organometallics 19 (2000) 4084.

[6] (a) D.J. Cho, C.J. Wu, S, S, W.-S. Han, S.O. Kang, B.Y. Lee, Organometallics 25 (2006) 2133;
(b) D.J. Cho, C.J. Wu, T. Bok, E.J. Lee, C.H. Lee, W.-S. Han, S.O. Kang, B.Y. Lee, Dalton Trans. (2006) 4056.

[7] D.W. Carpenetti, L. Kloppenburg, J.T. Kupec, J.L. Petersen, Organometallics 15 (1996) 1572.

[8] (a) Z. Fei, P.J. Dyson, Coord. Chem. Rev. 249 (2005) 2056;
(b) Z. Fei, R. Scopelliti, P.J. Dyson, Eur. J. Inorg. Chem. (2003) 3527;
(c) N. Poetschke, M. Nieger, M.A. Khan, E. Niecke, M.T. Ashby, Inorg. Chem. 36 (1997) 4087;
(d) Z. Fei, R. Scopelliti, P.J. Dyson, Inorg. Chem. 42 (2003) 2125;
(e) H. Nagashima, T. Sue, T. Oda, A. Kanemitsu, T. Matsumoto, Y. Motoyama, Y. Sunada, Organometallics 25 (2006) 1987;
(f) Y. Sunada, T. Sue, T. Matsumoto, H. Nagashima, J. Organomet. Chem. 691 (2006) 3176.

[9] O. Kühl, T. Koch, F.B. Somoza Jr., P.C. Junk, E. Hey-Hawkins, D. Plat, M.S. Eisen, J. Organomet. Chem. 604 (2000) 116.

[10] C. Qi, S. Zhang, J. Sun, J. Organomet. Chem. 690 (2005) 2941.

[11] P. Jutzi, Chem. Rev. 86 (1986) 983.

[12] D.G. Gorenstein, Phosphorous-31 spin-spin coupling constants: principles and applications, in: D.G. Gorenstein (Ed.), Phosphorous-31 NMR: Principles and Applications, Academic Press, 1984, pp. 37–53.

[13] B.Y. Lee, J.W. Han, I.S. Lee, Y.K.J. Chung, Organomet. Chem. 627 (2001) 233.

[14] (a) W.-Q. Hu, X.-L. Sun, C. Wang, Y. Gao, Y. Tang, et al., Organometallics 23 (2004) 1684;
(b) C.A. Willoughby, R.R. Duff Jr., W.M. Davis, S.L. Buchwald, Organometallics 15 (1996) 472.

[15] (a) J.T. Park, S.C. Yoon, B.-J. Bae, W.S. Seo, I.-H. Suh, T.K. Han, J.R. Park, Organometallics 19 (2000) 1269;
(b) S.C. Yoon, B.-J. Bae, I.-H. Suh, J.T. Park, Organometallics 18 (1999) 2049.

[16] F. Amor, A. Butt, K.E. du Plooy, T.P. Spaniol, J. Okuda, Organometallics 17 (1998) 5836.

[17] (a) K. Nomura, W. Wang, M. Fujiki, J. Liu, Chem. Commun. (2006) 2659;
(b) W. Wang, M. Fujiki, K. Nomura, J. Am. Chem. Soc. 127 (2005) 4582, and references therein.