

η^1 - and η^5 -Indenyl and Cyclopentadienyl Tri-*tert*-Butylphosphoraneiminatotitanium Complexes

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Received April 10, 2001

The compounds (indenyl)Ti(NP-*t*-Bu₃)Cl₂ (**4**), Cp₂Ti(NP-*t*-Bu₃)Cl (**6**), (indenyl)₂Ti(NP-*t*-Bu₃)Cl (**7**), Cp(indenyl)Ti(NP-*t*-Bu₃)Cl (**8**), Cp₃Ti(NP-*t*-Bu₃) (**9**), (indenyl)₃Ti(NP-*t*-Bu₃) (**10**), and Cp(indenyl)₂Ti(NP-*t*-Bu₃) (**11**) are readily derived from reaction with (dme)NaCp or Li(indenyl) with CpTi(NP-*t*-Bu₃)Cl₂ (**1**) or **4** in the appropriate stoichiometry. X-ray crystallography studies of (indenyl)Ti(NP-*t*-Bu₃)Me₂ (**5**) and **7–11** are reported. In the case of **6** and **9** two cyclopentadienyl rings are bound to the metal in a η^5 -bonding mode, whereas in **7**, **8**, **10**, and **11** one of the cyclopentadienyl or indenyl ligands is bound in an η^5 mode and the remainder in an η^1 -fashion. In the case of **10**, temperature-dependent ¹H NMR spectra infer a η^5 - η^1 ligand exchange process with an approximate barrier of 8–9 kcal/mol. Steric crowding appears to be the major factor determining the binding modes of the cyclopentadienyl and indenyl ligands. These structural data result in a view of the phosphoraneiminato ligand as a sterically demanding, four-electron donor ligand.

Introduction

A variety of alternatives to the traditional cyclopentadienyl ancillary ligands have been employed for the development of new polymerization catalyst systems in the recent literature. The research groups of Brookhart^{1–7} and Gibson^{8,9} have developed effective late metal olefin polymerization catalysts based on Schiff base complexes. For the early transition metals, elegant derivatization of the more traditional cyclopentadienyl ligands has permitted the specific control of the stereochemistry of the resulting polymers.¹⁰ In more exploratory efforts, McConville,^{11,12} Schrock,^{13–15} Bazan,^{16,17} and others^{18,19}

have developed new, active, nonmetallocene catalysts containing chelating amide ligands. In our own work, we have recently described a strategy for the ligand design for early metal catalysts based on the similarity of the steric and electronic characteristics of phosphoraneiminato ligands to those of the cyclopentadienyl ligand.^{20,21} This approach has led to the discovery of the highly effective catalysts of the form CpTi(NPR₃)X₂ and (R₃PN)₂TiX₂. The concept of ligands that offer a steric analogy to cyclopentadienyl groups was first described in the seminal work of Wolczanski et al. from 1984, in which they described the “tritox” (*t*-Bu₃)CO[−] ligand.²² The extensive studies of phosphoraneiminato derivatives by Dehnicke et al.^{23,24} have illustrated the potential of phosphoraneiminato ligands to act as 2–6

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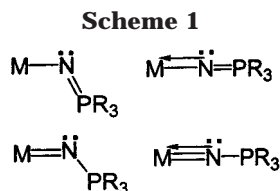
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electron donors. (Scheme 1). In this article, we examine attributes of these ligands via the study of the series of phosphoraneiminato complexes $(t\text{-Bu}_3\text{PN})\text{Ti}(\text{Cp})_n$ (indenyl) $_m\text{Cl}_{3-n-m}$ ($n, m = 0\text{--}3$). The subtle interplay of steric and electronic effects in these complexes is discussed. The implications regarding the nature and the utility of phosphoraneiminato groups as ancillary ligands are considered.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2 -free N_2 employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert atmosphere glovebox. Solvents were purified employing a Grubb's type column system manufactured by Innovative Technologies. All organic reagents were purified by conventional methods. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on Bruker Avance-300 and -500 operating at 300 and 500 MHz, respectively. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to SiMe_4 . ^{31}P NMR spectra were recorded on a Bruker Avance-300 and are referenced to 85% H_3PO_4 . Galbraith Laboratories Inc. Knoxville, TN, or Schwarzkopf Laboratories, Woodside, NY, performed combustion analyses. The compounds $\text{CpTi}(\text{NP-}t\text{-Bu}_3)\text{Cl}_2$ (**1**),²⁰ $\text{Me}_3\text{SiNP-}t\text{-Bu}_3$ (**2**)^{25,26} and (indenyl) TiCl_3 (**3**) were prepared by analogy with previously reported methods.²⁷

Synthesis of (Indenyl) $\text{Ti}(\text{NP-}t\text{-Bu}_3)\text{Cl}_2$ (4**).** Compound **2** (0.250 g; 0.864 mmol) was added to a toluene solution (50 mL) of **3** (0.230 g; 0.854 mmol). The solution was heated to 110 °C for 12 h. The volatile products were removed in vacuo to yield a bright yellow solid. The solid was washed with hexane (3×25 mL), filtered, and dried under vacuum (0.365 g; 0.810 mmol; 95%). ^1H NMR: δ 7.80 (m, 2H, indenyl), 7.19 (m, 2H, indenyl), 6.85 (t, 1H, indenyl), 6.60 (d, 2H, indenyl), 1.15 (d, $J_{\text{PH}} = 13.7$ Hz, 27H, P-*t*-Bu₃). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 129.07, 125.64, 125.29, 115.98, 105.21, 42.00 (d, $^1J_{\text{PC}} = 44.5$ Hz, PCMe₃), 29.41. $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 46.12. Anal. Calcd for $\text{C}_{21}\text{H}_{36}\text{Cl}_2\text{NPTi}$: C, 55.86; H, 8.04; N, 3.10. Found: C, 55.64; H, 7.78; N, 2.98.

Synthesis of (Indenyl) $\text{Ti}(\text{NP-}t\text{-Bu}_3)\text{Me}_2$ (5**).** To a diethyl ether solution (25 mL) of complex **4** (0.250 g; 0.555 mmol) was added an excess of MeMgBr (0.42 mL; 3.0 M; 1.25 mmol) at room temperature. The solution was stirred for 12 h. The solvent was removed under vacuum and the solid extracted with hexane (3×25 mL). The volume of the solvent was reduced to 10 mL, and the solution was left to crystallize overnight. Light yellow crystalline **5** was isolated by filtration and dried under vacuum (0.195 g; 0.476 mmol; 86%). ^1H NMR: δ 7.67 (m, 2H, indenyl), 7.20 (m, 2H, indenyl), 6.85 (d, 2H, indenyl), 6.01 (t, 1H, indenyl), 1.20 (d, $^3J_{\text{PH}} = 13.0$ Hz, 27H, P^{*t*}Bu₃), 0.16 (s, 6H, TiMe₂). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 126.54, 125.02, 123.48, 112.71, 100.62, 42.86 (TiMe₂), 41.30 (d, $^1J_{\text{PC}} = 46.1$ Hz, PCMe₃), 29.57. $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 31.93. Anal. Calcd for $\text{C}_{23}\text{H}_{42}\text{NPTi}$: C, 67.15; H, 10.22; N, 3.41. Found: C, 67.01; H, 10.04; N, 3.21.

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Synthesis of $\text{Cp}_2\text{Ti}(\text{NP-}t\text{-Bu}_3)\text{Cl}$ (6**), (Indenyl) $_2\text{Ti}(\text{NP-}t\text{-Bu}_3)\text{Cl}$ (**7**), $\text{Cp}(\text{Indenyl})\text{Ti}(\text{NP-}t\text{-Bu}_3)\text{Cl}$ (**8**), $\text{Cp}_3\text{Ti}(\text{NP-}t\text{-Bu}_3)$ (**9**), and (Indenyl) $_3\text{Ti}(\text{NP-}t\text{-Bu}_3)$ (**10**).** These compounds were prepared in a similar manner employing the indicated starting materials. Thus, only one representative preparation is described in detail. To a THF solution (10 mL) of complex **1** (0.250 g; 0.625 mmol) was added 1 equiv of (dme)NaCp (0.100 g; 0.625 mmol) at 20 °C. The yellow solution turned dark red within minutes. The solution was stirred for 12 h. The solvent was removed under vacuum to yield a dark red solid. The solid was extracted with hot benzene (3×25 mL). The volume of the filtrate was reduced to 10 mL and the solution left to crystallize for 12 h. Dark red crystalline **6** was isolated by filtration and dried under vacuum (0.251 g; 0.584 mmol; 93%). ^1H NMR: δ 6.21 (s, 10H, Cp), 1.17 (d, $^3J_{\text{PH}} = 13.1$ Hz, 27H, P-*t*-Bu₃). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 115.06, 41.80 (d, $^1J_{\text{PC}} = 45.9$ Hz, PCMe₃), 29.99. $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 39.45. Anal. Calcd for $\text{C}_{22}\text{H}_{37}\text{ClNPTi}$: C, 61.54; H, 8.62; N, 3.26. Found: C, 61.33; H, 8.46; N, 3.01. **7**: Starting materials: **4**, Li(indenyl). Yield: 86%. ^1H NMR: δ 7.53 (m, 2H, indenyl), 7.32 (m, 2H, indenyl), 7.24 (m, 4H, indenyl), 6.45 (br m, 2H, indenyl), 6.44 (m, 2H, indenyl), 6.14 (br, 2H, indenyl), 1.18 (d, $^3J_{\text{PH}} = 11.9$ Hz, 27H, P-*t*-Bu₃). Partial $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 41.50 (d, $^1J_{\text{PC}} = 44.1$ Hz, PCMe₃), 29.53. $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 44.08. Anal. Calcd for $\text{C}_{30}\text{H}_{45}\text{ClNPTi}$: C, 67.51; H, 8.50; N, 2.62. Found: C, 67.23; H, 8.29; N, 2.33. **8**: Starting materials: **4**, (dme)NaCp or **1**, Li(indenyl). Yield: 88%. ^1H NMR: δ 8.04 (d, 1H, indenyl), 7.72 (d, 1H, indenyl), 7.32 (m, 2H, indenyl), 6.85 (m, 2H, indenyl), 6.24 (d, 1H, indenyl), 5.68 (s, 5H, Cp), 1.16 (d, $^3J_{\text{PH}} = 13.4$ Hz, 27H, P^{*t*}Bu₃). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 147.73, 142.44, 133.19, 124.65, 122.28, 122.13, 120.97, 115.35, 113.69, 93.77, 41.55 (d, $^1J_{\text{PC}} = 44.1$ Hz, PCMe₃), 29.52. $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 44.44. Anal. Calcd for $\text{C}_{26}\text{H}_{41}\text{ClNPTi}$: C, 64.86; H, 8.52; N, 2.91; Found: C, 64.61; H, 8.21; N, 2.80. **9**: Starting materials: **1**, (dme)NaCp. Yield: 89%. ^1H NMR δ 6.03 (s, 15H, Cp), 1.13 (d, $^3J_{\text{PH}} = 13.1$ Hz, 27H, P^{*t*}Bu₃). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 114.57, 42.00 (d, $^1J_{\text{PC}} = 46.6$ Hz, PCMe₃), 30.50. $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 37.48. Anal. Calcd for $\text{C}_{27}\text{H}_{42}\text{NPTi}$: C, 70.54; H, 9.21; N, 3.05. Found: C, 70.33; H, 9.07; N, 2.95. **10**: Starting materials: **4**, Li(indenyl). Yield: 95%. ^1H NMR: δ 7.45 (broad m, 6H, indenyl), 7.18 (m, 6H, indenyl), 6.29 (t, 3H, indenyl), 5.53 (broad, 6H, indenyl), 0.95 (d, $^3J_{\text{PH}} = 13.5$ Hz, 27H, P^{*t*}Bu₃). Partial $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 41.35 (d, $^1J_{\text{PC}} = 44.0$ Hz, PCMe₃), 15.53. $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 44.08. Anal. Calcd for $\text{C}_{39}\text{H}_{54}\text{NPTi}$: C, 76.10; H, 8.78; N, 2.28. Found: C, 75.89; H, 8.63; N, 2.11.

Generation of $\text{Cp}(\text{Indenyl})_2\text{Ti}(\text{NP-}t\text{-Bu}_3)$ (11**).** Reaction of complex **1** with 2 equiv of Li(indenyl) generated a solution containing a mixture of products. All attempts to purify the products were unsuccessful, although a couple of single crystals of **11** were obtained in one case. The inability to obtain **11** cleanly in bulk precluded the report of spectral data.

X-ray Data Collection and Reduction. X-ray quality crystals of **5** and **7–11** were obtained directly from the preparation as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2 -free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer collecting a hemisphere of data in 1329 frames with 10 s exposure times. Crystal data are summarized in Table 1. The observed extinctions were consistent with the space groups in each case. The data sets were collected ($4.5^\circ < 2\theta < 45\text{--}50.0^\circ$). A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing package. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package operating on a SGI Challenge mainframe

Table 1. Crystallographic Parameters^a

	5	7	8	9	10	11
formula	C ₂₃ H ₄₀ NPTi	C ₃₃ H ₂₂ CINPTi	C ₃₅ H ₄₅ CINPTi	C ₅₄ H ₈₄ N ₂ P ₂ Ti ₂	C ₇₈ H ₉₆ N ₂ P ₂ Ti ₂	C ₇₀ H ₉₂ N ₂ P ₂ Ti
fw	409.43	546.84	594.04	918.97	1219.31	1119.20
a, Å	8.3256(11)	10.299(2)	12.857(22)	11.190(3)	12.858(7)	12.658(3)
b, Å	9.9880(10)	12.155(3)	14.456(16)	14.763(2)	15.930(9)	19.658(4)
c, Å	29.100(5)	15.071(3)	15.027(23)	16.157(3)	18.006(10)	12.716(4)
α, deg	90.00	68.101(15)	90.00	16.157(3)	73.45(5)	90.00
β, deg	90.00	77.06(2)	111.97(11)	73.01(2)	73.73(3)	99.97(2)
γ, deg	90.00	77.06(2)	90.00	82.94(2)	82.41(6)	90.00
V (Å ³)	2419.8(6)	1592.9(6)	2590.2(66)	2530.3(9)	3388.2(32)	3116.4(14)
space group	P2 ₁ 2 ₁ 2 ₁	P1	P2 ₁ /c	P1	P1	Pn
d(calc), g cm ⁻³	1.124	1.140	1.523	1.206	1.195	1.193
Z	2	2	4	2	2	2
μ, cm ⁻¹	0.426	0.422	0.525	0.415	0.327	0.349
no. of data collected	12 714	8253	12 696	13 084	14 934	11 368
no. of data used	4238	5379	4483	8536	9672	6009
no. of variables	235	327	271	541	757	359
R (%)	0.0285	0.0525	0.0655	0.0396	0.0856	0.0938
R _w (%)	0.0870	0.1550	0.1633	0.1223	0.1788	0.1935
goodness of fit	0.752	1.238	1.198	1.014	1.115	0.991

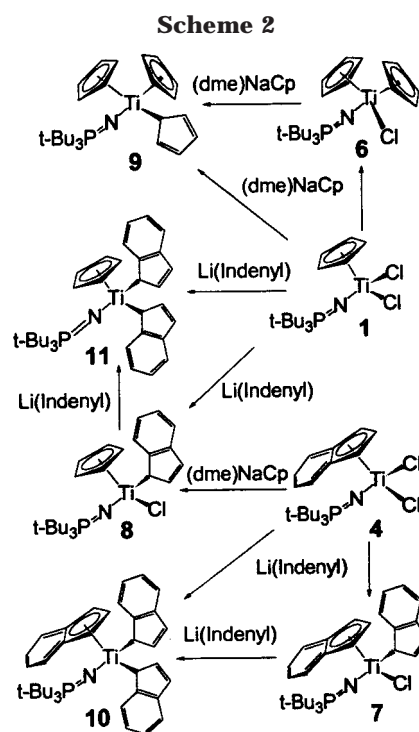
^a All data collected at 24 °C with Mo Kα radiation ($\lambda = 0.71069$ Å), $R = \sum(|F_o| - |F_c|)/\sum|F_o|$, $R_w = [\sum(|F_o| - |F_c|)^2/\sum|F_o|^2]^{0.5}$.

computer with remote X-terminals or PC employing X-emulation. The reflections with $F_o^2 > 3\sigma F_o^2$ were used in the refinements.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.²⁸ The heavy atom positions were determined using direct methods employing either the SHELXTL or direct methods routines. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F , minimizing the function $w(|F_o| - |F_c|)^2$ where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information.

Results and Discussion

Synthetic routes to the species described herein are summarized in Scheme 2. We have previously described the facile synthesis of CpTi(NP-*t*-Bu₃)Cl₂ (**1**).²⁰ In a similar manner reaction of Me₃SiNP-*t*-Bu₃ (**2**) and (indenyl)TiCl₃ (**3**) affords the species (indenyl)Ti(NP-*t*-Bu₃)Cl₂ (**4**) in 95% isolated yield. This species is readily converted to (indenyl)Ti(NP-*t*-Bu₃)Me₂ (**5**) in 86% yield via reaction with methyl Grignard. This light yellow crystalline product exhibits methyl resonances in the ¹H NMR spectrum at 0.16 ppm. Compound **5** was also characterized by X-ray crystallography (Figure 1). These data reveal Ti–methyl carbon distances of 2.128(4) Å (av) with a C–Ti–C angle of 99.50(13)°. The phospho-



raneiminato ligand geometry is typical of that seen in CpTi-phosphoraneiminato complexes.²⁴ The Ti–N and P–N distances in **5** are 1.782(2) and 1.585(2) Å, respectively, with a P–N–Ti angle approaching linearity (178.38(11)°).

Reaction of **1** with 1 equiv of (dme)NaCp affords the dark red product Cp₂Ti(NP-*t*-Bu₃)Cl (**6**) in 93% isolated yield. The ¹H NMR spectrum of **6** shows a single resonance at 6.21 ppm attributable to the cyclopentadienyl protons. The spectral features are temperature invariant, thus inferring that both cyclopentadienyl rings are bound to the metal in a η^5 bonding mode. In a similar synthetic procedure, reaction of **5** with Li(indenyl) yields the complex (indenyl)₂Ti(NP-*t*-Bu₃)Cl (**7**) in 86% isolated yield. The ¹H NMR data infer the presence of both an η^5 - and an η^1 -bound indenyl ligand, as the overlapping resonances accounting for 14 protons give rise to six signals. These NMR features of **7** are invariant with temperature, even on heating solutions

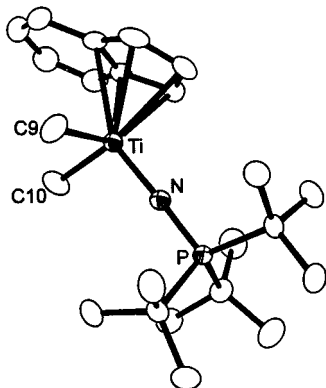


Figure 1. ORTEP drawings of **5**, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Ti–N 1.782(2) Å; Ti–C(10) 2.123(3) Å; Ti–C(9) 2.133(3) Å; P–N 1.585(2) Å; N–Ti–C(10) 103.78(10)°; N–Ti–C(9) 101.83(9)°; C(10)–Ti–C(9) 99.50(13)°; P–N–Ti 178.38(11)°.

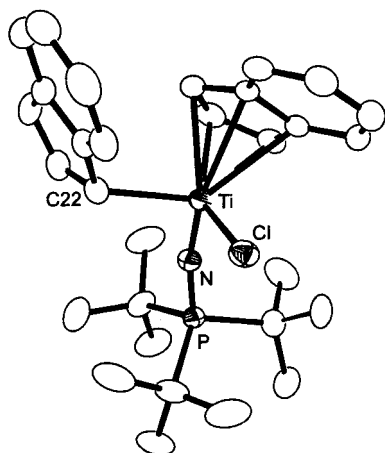


Figure 2. ORTEP drawings of **7**, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Ti–N 1.775(2) Å; Ti–C(22) 2.229(3) Å; Ti–Cl 2.2947(10) Å; P–N 1.609(3) Å; N–Ti–C(22) 99.17(12)°; N–Ti–Cl 104.63(9)°; C(22)–Ti–Cl 97.10(10)°; P–N–Ti 167.4(2)°.

of **7** to 80 °C. A crystallographic study of **7** (Figure 2) confirmed the interpretation of the NMR data and the presence of η^5 - and η^1 -bound indenyl ligands. The Ti–N and Ti–Cl distances in **7** are 1.775(2) and 2.2947(10) Å, respectively. The Ti–C distance for the η^1 -indenyl ligand is 2.229(3) Å. This distance is slightly longer than the σ -Ti–C found in **5**, consistent with the greater steric demands of the indenyl ligands.

The mixed cyclopentadienyl–indenyl species Cp(indenyl)Ti(NP-*t*-Bu₃)Cl (**8**) can be prepared via the two obvious pathways. Either reaction of **4** with 1 equiv of (dme)NaCp or reaction of **1** with Li(indenyl) affords dark red crystalline of **8**. Regardless of the synthetic route, ¹H and ¹³C{¹H} NMR data confirm that the product **8** contains an η^5 -cyclopentadienyl group and an η^1 -indenyl fragment. This view was also affirmed by the results of an X-ray crystallographic study (Figure 3). While most of the metric parameters within **8** are similar to those seen in **7**, it is noteworthy that the lesser steric congestion in **8** results in a shorter Ti–C bond of 2.198(5) Å. The synthesis of **8** from **1** involves a facile nucleophilic substitution. In contrast, the path to **8** from **4** requires an η^5 - η^1 -indenyl ring-slippage. Such processes are well documented for other systems and have been

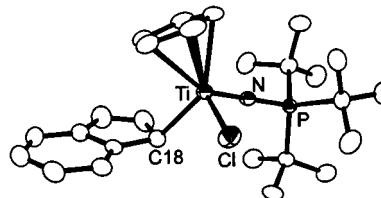


Figure 3. ORTEP drawings of **8**, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Ti–N 1.773(4) Å; Ti–C(18) 2.198(5) Å; Ti–Cl 2.299(2) Å; P–N 1.604(4) Å; N–Ti–C(18) 98.9(2)°; N–Ti–Cl 103.03(14)°; C(18)–Ti–Cl 99.8(2)°; P–N–Ti 169.1(2)°.

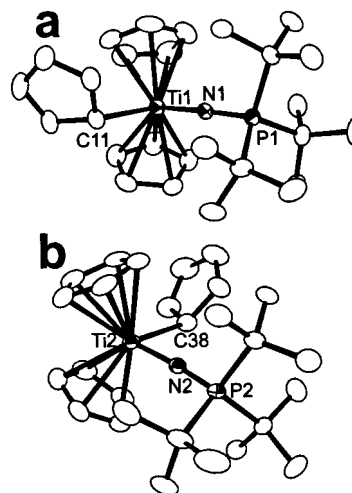


Figure 4. ORTEP drawing of the two independent molecules (a) and (b) of **9** in the asymmetric unit, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Ti(1)–N(1) 1.844(2) Å; Ti(1)–C(11) 2.378(2) Å; Ti(2)–N(2) 1.850(2) Å; Ti(2)–C(38) 2.355(2) Å; P(1)–N(1) 1.590(2) Å; P(2)–N(2) 1.590(2) Å; N(1)–Ti(1)–C(11) 92.71(7)°; N(2)–Ti(2)–C(38) 92.79(7)°; P(1)–N(1)–Ti(1) 175.56(9)°; P(2)–N(2)–Ti(2) 175.43(9)°.

implicated in the chemistry of other group 4 metal complexes.^{29,30}

Complex **1** reacts with 2 equiv of (dme)NaCp to give the dark red crystalline product **9** formulated as Cp₂Ti(NP-*t*-Bu₃) in 89% yield. ¹H and ¹³C{¹H} NMR spectra show single resonances at 6.03 and 114.57 ppm, respectively, attributable to the cyclopentadienyl ligands. Cooling to –80 °C reveals no change in these resonances, suggesting a rapid process of site exchange. It should be noted that the presence of three η^5 -cyclopentadienyl ligands cannot specifically be excluded, although this proposition is unlikely for both steric and electronic reasons. An X-ray crystallographic analysis of **9** (Figure 4) reveals that the molecule contains two η^5 - and one η^1 -cyclopentadienyl group in the solid state. This geometry results in a relatively electron rich metal center in **9** compared to **5**, **7**, and **8**. The dramatic lengthening of the Ti–N to 1.844(2) Å and the Ti–C σ -bonds to 2.366(4) Å supports this view.

The analogous species (indenyl)₃Ti(NP-*t*-Bu₃) (**10**) is obtained from the reaction of **4** with excess Li(indenyl).

(29) Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *J. Chem. Soc. (D)* **1980**, 962–972.

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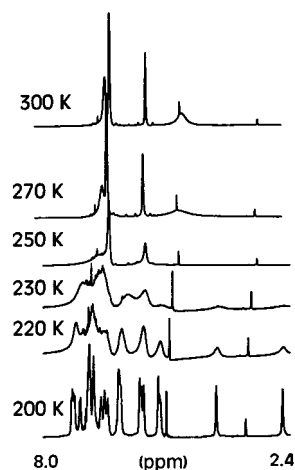


Figure 5. Variable-temperature ^1H NMR spectra for **10**.

This results in the dark red crystalline product **10** in 95% yield. The ^1H NMR data show four resonances at 25 $^\circ\text{C}$, which sharpen on heating, inferring an η^5 - η^1 -site exchange process. On cooling to -80 $^\circ\text{C}$, 18 resonances are observed, inferring the presence of inequivalent η^5 - and η^1 -indenyl rings (Figure 5). The precise assessment of the exchange barrier is a complicated issue, as the exchange process appears to involve three sites for each of seven protons. Consequently, the coalescence of resonances cannot be unambiguously observed, although it appears that coalescence of the resonances in the ^1H NMR spectra of **10** occurs at approximately -25 $^\circ\text{C}$. This infers an approximate barrier to η^5 - and η^1 -indenyl site exchange of 8–9 kcal/mol.

An X-ray crystallographic study of **10** confirmed that this species in the solid state contains a single η^5 - and two η^1 -indenyl ligands (Figure 6). The Ti–N_{av} (1.780(6) Å) in **10** are similar to those seen in **5**, **7**, and **8**, while the Ti–C are slightly longer (Ti–C_{av} 2.215(7) Å), although not as long as those seen in the more electron rich species **9**. It is presumably the greater steric demands of the indenyl ligands that preclude the binding of two of such ligands in a η^5 -manner.

The one remaining complex containing Cp and indenyl ligands, i.e., Cp(indenyl)₂Ti(NP-*t*Bu₃) (**11**), proved synthetically illusive. In the reaction of **1** with excess Li(indenyl) or reaction of **7** with (dme)NaCp, only an inseparable mixture of products was obtained. Despite the inability to obtain a pure bulk sample of **11**, a couple X-ray quality crystals were obtained from one attempted synthesis. The structure (Figure 7) confirmed the presence of an η^5 -cyclopentadienyl and two η^1 -indenyl ligands. The metric parameters of **11** are unexceptional, as they mimic those observed for **5**, **7**, **8**, and **10**.

In the series of compounds described herein, it is clear that steric crowding is a major factor determining the binding modes of the cyclopentadienyl and indenyl ligands. The steric demands of the larger indenyl ligand and its extended π -system facilitate ring slippage and thus favor η^1 -binding. While the geometries of the phosphoraneiminato ligands are relatively constant, with only minor changes in the P–N distances and Ti–N–P angles, there is a clear effect of the electronic environment at the metal center on the Ti–N bond distance. In the formally 18-electron species **9**, the Ti–N is lengthened to 1.844(2) Å. In contrast, in **5**, **7**, **8**, **10**, and **11** the electron count is formally 14 and the Ti–N

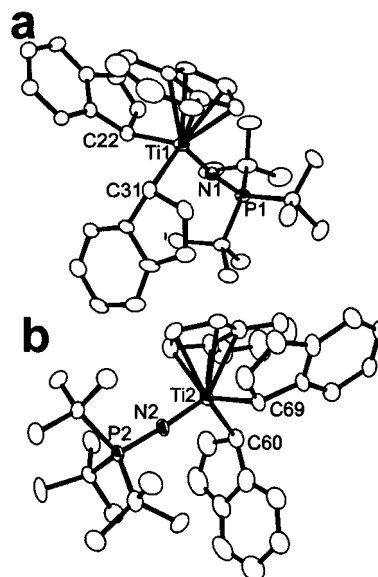


Figure 6. ORTEP drawing of the two independent molecules (a) and (b) of **10** in the asymmetric unit, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Ti(1)–N(1) 1.786(5) Å; Ti(1)–C(22) 2.212(7) Å; Ti(1)–C(31) 2.217(7) Å; Ti(2)–N(2) 1.774(5) Å; Ti(2)–C(69) 2.205(7) Å; Ti(2)–C(60) 2.221(8) Å; P(1)–N(1) 1.613(5) Å; P(2)–N(2) 1.627(5) Å; N(1)–Ti(1)–C(22) 100.1(2) $^\circ$; N(1)–Ti(1)–C(31) 108.1(3) $^\circ$; C(22)–Ti(1)–C(31) 98.0(3) $^\circ$; N(2)–Ti(2)–C(69) 99.3(3) $^\circ$; N(2)–Ti(2)–C(60) 108.1(3) $^\circ$; C(69)–Ti(2)–C(60) 98.2(3) $^\circ$; P(1)–N(1)–Ti(1) 171.6(4) $^\circ$; P(2)–N(2)–Ti(2) 175.2(4) $^\circ$.

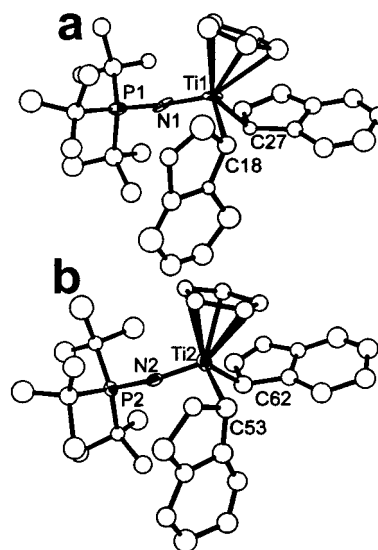


Figure 7. ORTEP drawing of the two independent molecules (a) and (b) of **11** in the asymmetric unit, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Ti(1)–N(1) 1.77(2) Å; Ti(1)–C(27) 2.26(2) Å; Ti(1)–C(18) 2.27(2) Å; Ti(2)–N(2) 1.80(2) Å; Ti(2)–C(62) 2.18(2) Å; Ti(2)–C(53) 2.19(2) Å; P(1)–N(1) 1.61(2) Å; P(2)–N(2) 1.62(2) Å; N(1)–Ti(1)–C(27) 100.9(7) $^\circ$; N(1)–Ti(1)–C(18) 108.3(8) $^\circ$; C(27)–Ti(1)–C(18) 95.1(8) $^\circ$; N(2)–Ti(2)–C(62) 100.4(8) $^\circ$; N(2)–Ti(2)–C(53) 107.8(9) $^\circ$; C(62)–Ti(2)–C(53) 99.2(9) $^\circ$; P(1)–N(1)–Ti(1) 174.5(11) $^\circ$; P(2)–N(2)–Ti(2) 172.3(12) $^\circ$.

is strengthened and shortens to about 1.77 Å. An alternative view proposed by a reviewer suggests that the phosphoraneiminato ligand is a six-electron donor and proposes a Cp[−][TiCp₂(NPR₃)⁺ ion pair for **9**.

It is our view that the above electron-counting formalisms as well as the structural data support the view that the phosphoraneiminato ligands are similar to a sterically demanding, four-electron-donating, "imide" ligand. This view is consistent with the electrophilicity and reactivity that phosphoraneiminato ligand complexes exhibit. It is the chemistry of such electron-deficient, phosphoraneiminato complexes that is the subject of ongoing study.

Acknowledgment. Financial support from NSERC of Canada and NOVA Chemicals Corporation is gratefully acknowledged.

Supporting Information Available: Crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM010298H