Titanium Complexes of Sterically Demanding Cage-Phosphinimide Ligands

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The known ligand $PPh(C_6H_4O_3Me_4)$ (**1**) and its analogue $PCy(C_6H_4O_3Me_4)$ (**2**) have been prepared. In the latter synthesis the diphosphine species $(PCy)_2(C_6H_2O_3Me_4)$ (**3**) was also isolated as a minor product. Reaction of the cage phosphines **1** and **2** with Me_3SiN_3 effected oxidation to the corresponding (trimethylsilyl)phosphinimines $Me_3SiNPR(C_6H_4O_3Me_4)$ (R = Ph (**4**), Cy (**5**)). Subsequent reactions afforded the titanium complexes $CpTiCl_2(NPR(C_6H_4O_3Me_4))$ (R = Ph (**6**), Cy (**7**)) and $CpTiMe_2(NPR(C_6H_4O_3Me_4))$ (R = Ph (**8**), Cy (**9**)). Preliminary screening for catalytic activity in ethylene polymerization employing either methylalumoxane (MAO) or $[Ph_3C][B(C_6F_5)_4]$ as the activator showed minimal catalytic activity. These observations were probed via reactions of these complexes with $AlMe_3$, MAO, or $[Ph_3C][B(C_6F_5)_4]$. Reaction of **8** with $AlMe_3$ gave several products, one of which was fully characterized as the cage-rupture product $CpTiMe_2(NPCy(C_6H_4O_3Me_5)(\mu\text{-}AlMe_2)(AlMe_3))$ (**10**). A similar product is inferred by the spectroscopic monitoring of the reaction of **8** with MAO. In contrast, reaction of **2** with $AlMe_3$ resulted only in the formation of the adduct $Me_3AlPCy(C_6H_4O_3Me_4)$ (**11**). Structural data are reported for **2**, **3**, **8**, **10**, and **11**.

Introduction

A variety of approaches are being developed in the design of new homogeneous olefin polymerization catalysts.[1−5] Although recent efforts have broadened the range of metals to include group 5 and 6 metals, group 4 metals remain a focus due to the current commercial viability of these systems. It is the introduction of new ancillary ligands that offers complexes with the potential for enhanced reactivity. In this regard, Ti and Zr species containing diamides,[6−13] aryloxides,[14] borollide,[15] boratabenzenes,[16−23] borylamides,[24] trimethylenes,[15,17,25−27] cyclopentadienylborate,[28] and multidentate ligands[29] have drawn recent attention. In our own efforts, we have recently reported examinations of titanium phosphinimide complexes. Complexes of the form $CpTi(NPR_3)X_2$ have proven to be active single-site catalysts for the polymerization of ethylene,[30] while catalysts derived from $(R_3PN)_2TiX_2$ are highly active, exhibiting activity which exceeds that of the constrained-geometry catalysts under specific commercially relevant conditions.[31] An advantage to this family of catalysts is the ease with which modification of the steric and electronic properties of the ancillary phosphinimide ligands is achieved. In targeting new derivatives, the

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(1) Hlatky, G. G. *Coord. Chem. Rev.* **2000**, *199*, 235−329.

(2) Hlatky, G. G. *Coord. Chem. Rev.* **1999**, *181*, 243−296.

(3) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem.* **1999**, *112*, 1354−1356; *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447.

(4) Bochmann, M. *Chem. Commun.* **1996**, 255−270.

(5) Kaminsky, W. *Chem. Commun.* **1998**, 1413−1418.

(6) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L.-C.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 7822−7836.

(7) Schrock, R. R.; Schattenmann, F.; Aizenberg, M.; Davis, W. M. *Chem. Commun.* **1998**, 199−200.

(8) Baumann, R.; Davis, W., M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830−3831.

(9) Horton, A. D.; De With, J. *Chem. Commun.* **1996**, 1375−1376.

(10) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008−10009.

(11) Tinkler, S.; Deeth, R. J.; Duncalf, D. J.; McCamley, A. *Chem. Commun.* **1996**, *023*, 2623−2624.

(12) Nomura, K.; Naga, N.; Takaoki, K. *Macromolecules* **1998**, *31*, 8009−8015.

(13) Aoyagi, K.; Gantzel, P. K.; Kalai, K.; Tilley, T. D. *Organometallics* **1996**, *15*, 923−927.

(14) Nomura, K.; Naga, N.; Miki, M.; Yanagi, K.; Imai, A. *Organometallics* **1998**, *17*, 2152−2154.

(15) Bazan, G. C.; Donnelly, S. J.; Ridriguez, G. *J. Am. Chem. Soc.* **1995**, *117*, 2671−2672.

(16) Ashe, A. J. I.; Al-Ahmad, S.; Fang, X. *J. Organomet. Chem.* **1999**, *581*, 92−97.

(17) Sperry, C. K.; Bazan, G. C.; Cotter, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 1513−1523.

(18) Ashe, A. J., III; Al-Ahmad, S.; Fang, X.; Kampf, J. W. *Organometallics* **1998**, *17*, 3883−3888.

(19) Ashe, A. J., III; Al-Ahmad, S.; Kampf, J. W. *Organometallics* **1999**, *18*, 4234−4236.

(20) Bazan, G. C.; Rodriguez, G. *Organometallics* **1997**, *16*, 2492−2494.

(21) Herberich, G. E.; Englert, U.; Schmitz, A. *Organometallics* **1997**, *16*, 3751−3757.

(22) Rogers, J. S.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 1288−1298.

(23) Sperry, C. K. *J. Am. Chem. Soc.* **1997**, *119*, 9305−9306.

(24) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 308−321.

(25) Kowal, C. M.; Bazan, G. C. *J. Am. Chem. Soc.* **1996**, *118*, 10317−10318.

(26) Quan, R. W.; Bazan, G. C.; Kiely, A. F.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4489−4490.

(27) Sperry, C. K.; Cotter, W. D.; Lee, R. A.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *121*, 7791−7805.

(28) Sun, Y.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1997**, *16*, 2509−2513.

(29) Fokken, S.; Spaniol, T. P.; Kang, H.-C.; Massa, W.; Okuda, J. *Organometallics* **1996**, *15*, 5069−5072.

(30) Stephan, D. W.; Stewart, J. C.; Guerin, F.; Spence, R. E. v.; Xu, W.; Harrison, D. G. *Organometallics* **1999**, *17*, 1116−1118.

(31) Stephan, D. W.; Guerin, F.; Spence, R. E. v.; Koch, L.; Gao, X.; Brown, S. J.; Swabey, J. W.; Wang, Q.; Xu, W.; Zoricak, P.; Harrison, D. G. *Organometallics* **1999**, *17*, 2046−2048.

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steric bulk of the phosphinimide ligand was proposed as an important asset, as it could offer protection of the Ti−N bond in the derived catalyst. Focusing on bulky phosphine precursors, we noted the recent work of Pringle et al.,[32,33] who have reported a new class of bulky bidentate phosphine ligands where the P atoms are incorporated in a sterically demanding adamantane-like cage. The structural characterization of Pd derivatives of these ligands revealed the very large ligand cone angles. Herein, we have adopted related ligands for the synthesis of new titanium phosphaadamantyl−phosphinimide derivatives. Reactions of these species with Lewis acids are investigated, and the implications for the design of new single-site olefin polymerization catalysts 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 type column system manufactured by Innovative Technology. All organic reagents were purified by conventional methods. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Bruker Avance 300 and 500 spectrometers 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 referenced to 85% H_3PO_4. Guelph Chemical Laboratory (Guelph, Ontario, Canada) performed combustion analyses. The ligand $PPh(C_6H_4O_3Me_4)$ (**1**) was prepared as reported in the literature.[35]

Synthesis of $PCy(C_6H_4O_3Me_4)$ (2) and $(PCy)_2(C_6H_2O_3Me_4)$ (3). To 200 mL of a stirred 5 M solution of HCl was added 20 g of 2,4-pentanedione (0.2 mol), 20 mL of MeOH, and 3 g (25.8 mmol) of $CyPH_2$. After the mixture was stirred for 24 h, the volatiles were removed in vacuo and the resulting orange oil was triturated with 200 mL of water to give a pale yellow solid that was recrystallized from MeCN to give 4.6 g (60%) of the white crystalline product **2**. Successive recrystallization from the mother liquor yielded a small crop of crystals of **3** suitable for X-ray crystallography. **2**: ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, δ) −12.6 (s); ^{1}H NMR (C_6D_6, 25 °C, δ) 1.89 (m, 1H), 1.68 (br m, 1H), 1.54−1.68 (m, 7H), 1.11−1.33 (m, 18H); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, δ) 97.6 (s, quat), 95.9 (s, quat), 73.1 (d, $|J_{C-P}| = 26$ Hz, quat), 72.4 (d, $|J_{C-P}| = 13$ Hz, quat), 45.6 (d, $|J_{C-P}| = 11$ Hz, CH_2), 38.5 (s, CH_2), 33.5 (d, $|J_{C-P}| = 22$ Hz, CH_2), 31.9 (d, $|J_{C-P}| = 24$ Hz, CH_3), 30.1 (d, $|J_{C-P}| = 7$ Hz, CH_2), 29.6 (d, $|J_{C-P}| = 22$ Hz, CH_3), 28.3 (d, $|J_{C-P}| = 11$ Hz, CH), 28.0 (s, CH_3), 27.6 (s, CH_3), 26.9 (d, $|J_{C-P}| = 7$ Hz, CH_2), 26.3 (d, $|J_{C-P}| = 13$ Hz, CH_3), 26.0 (s, CH_2). Anal. Calcd for $C_{16}H_{27}O_3P$: C, 64.41; H, 9.12. Found: C, 64.30; H, 9.01. **3**: ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, δ) 0.6; ^{1}H NMR (C_6D_6, 25 °C, δ) 0.87−2.5 (br, m).

Synthesis of $Me_3SiNPR(C_6H_4O_3Me_4)$ (R = Ph (4), Cy (5)). These compounds were prepared in a similar manner, and thus only one preparation is detailed. To 1.38 g (4.72 mmol) of **1** was added 652 mg (5.67 mmol) of $(CH_3)_3SiN_3$ to form a pale yellow slush. Heating for 3 h melted the mixture to give a clear, brown liquid, which was cooled to give 1.5 g (85%) of the waxy, brown solid product **4**. **4**: ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, δ) −12.1 (s); ^{1}H NMR (C_6D_6, 25 °C, δ) 8.34 (m, 2H, Ph), 7.24 (m, 3H, Ph), 2.81 (dd, $|^2J_{H-H}| = 12.4$ Hz, $|^3J_{H-P}| = 2.8$ Hz, 1H, CH_2), 1.91 (dd, $|^2J_{H-H}| = 12.5$ Hz, $|^3J_{H-P}| = 2.7$ Hz, 1H, CH_2), 1.77 (m, 1H, CH_2), 1.77 (m, 1H, CH_2), 1.70 (m, 1H, CH_2), 1.56 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.40 (d, $|^3J_{H-P}| = 12.6$ Hz, 3H, CH_3), 1.22 (d, $|J^3{}_{H-P}| = 12.6$ Hz, 3H, CH_3), 0.52 (s, 9H, $Si(CH_3)_3$); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, δ) 134.3 (d, $|^2J_{C-P}| = 8$ Hz, Ph), 131.6 (d, $|^4J_{C-P}| = 3$ Hz, Ph), 130.4 (d, $|^1J_{C-P}| = 76$ Hz, Ph), 128.9 (d, $|^3J_{C-P}| = 11$ Hz, Ph), 97.2 (s, quat), 96.7 (s, quat), 75.4 (d, $|^1J_{C-P}| = 75$ Hz, quat), 74.0 (d, $|^1J_{C-P}| = 65$ Hz, quat), 43.4 (d, $|J_{C-P}| = 5$ Hz, CH_2), 40.9 (s, CH_2), 28.2 (s, CH_3), 28.0 (s, CH_3), 21.8 (s, CH_3), 21.2 (s, CH_3), 4.9 (s, $Si(CH_3)_3$). Anal. Calcd for $C_{19}H_{30}NO_3PSi$: C, 60.13; H, 7.97; N, 3.69. Found: C, 59.95; H, 7.81; N, 3.42. **5**: yield 82%; ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, δ) −2.7 (s); ^{1}H NMR (C_6D_6, 25 °C, δ): 2.58 (dd, $|^2J_{H-H}| = 12.8$ Hz, $|^3J_{H-P}| = 5.0$ Hz, 1H, CH_2), 1.93 (2H), 1.41−1.73 (m, 10H), 1.42 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.26 (d, $|^3J_{H-P}| = 12.6$ Hz, 3H, CH_3), 1.23 (d, $|^3J_{H-P}| = 11.6$ Hz, 3H, CH_3), 1.07 (m, 2H), 0.39 (s, 9H, $Si(CH_3)_3$); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, δ) 96.4 (s, quat), 96.0 (s, quat), 74.9 (d, $|^1J_{C-P}| = 33$ Hz, quat), 74.1 (d, $|^1J_{C-P}| = 27$ Hz, quat), 43.9 (d, $|J_{C-P}| = 5$ Hz, CH_2), 40.5 (s), 34.7 (s), 33.9 (s), 29.3 (s), 28.1 (s), 28.0 (s), 27.9 (s), 27.4 (d, $|J_{C-P}| = 12$ Hz), 26.7 (d, $|J_{C-P}| = 12$ Hz), 26.3 (s), 23.0 (d, $|J_{C-P}| = 4$ Hz), 4.9 (s, $Si(CH_3)_3$). Anal. Calcd for $C_{19}H_{36}NO_3PSi$: C, 59.19; H, 9.41; N, 3.63. Found: C, 59.01; H, 9.11; N, 3.45.

Synthesis of $CpTiCl_2(NPR(C_6H_4O_3Me_4))$ (R = Ph (6), Cy (7)). These compounds were prepared in a similar manner, and thus only one preparation is detailed. To 311 mg (1.42 mmol) of $CpTiCl_3$ and 537 mg (1.42 mmol) of **4** was added 50 mL of benzene to give a cloudy yellow mixture. Heating for 3 h at 80 °C gave a clear deep yellow solution. Cooling and removal of volatiles gave 635 mg (91%) of the yellow solid product **6**. **6**: ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, δ) −8.3 (s); ^{1}H NMR (C_6D_6, 25 °C, δ) 8.22 (m, 2H, Ph), 7.67 (m, 3H, Ph), 6.54 (s, 5H, Cp), 2.82 (dd, $|^2J_{H-H}| = 14.0$ Hz, $|^3J_{H-P}| = 2.8$ Hz, CH_2), 1.68 (d, $|^2J_{H-H}| = 13.9$ Hz, CH_2), 1.61 (d, $|^2J_{H-H}| = 13.9$ Hz, CH_2), 1.45 (m, 1H, CH_2), 1.42 (s, 3H, CH_3), 1.34 (d, $|^3J_{H-P}| = 9.7$ Hz, CH_3), 1.20 (s, 3H, CH_3), 1.10 (d, 3H, $|^3J_{H-P}| = 13.5$ Hz); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, δ) 134.3 (d, $|^2J_{C-P}| = 7$ Hz, Ph), 133.5 (s, Ph), 129.5 (d, $|^2J_{C-P}| = 11$ Hz), 124.9 (s, Ph), 116.4 (s, Cp), 97.6 (s, quat), 96.9 (s, quat), 75.9 (d, $|^1J_{C-P}| = 11$ Hz, quat), 75.2 (s, quat), 42.2 (d, $|J_{C-P}| = 6$ Hz, CH_2), 40.9 (s, CH_2), 27.8 (s, CH_3), 27.6 (s, CH_3), 22.3 (s, CH_3), 21.4 (s, CH_3). Anal. Calcd for $C_{21}H_{26}Cl_2NO_3PTi$: C, 51.45; H, 5.35; N, 2.86. Found: C, 51.05; H, 5.11; N, 2.52. **7**: yield 91%; ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, δ) 4.1 (s); ^{1}H NMR (C_6D_6, 25 °C, δ) 6.50 (s, 5H, Cp), 2.73 (dd, $|^2J_{H-H}| = 13.7$ Hz, $|^3J_{H-P}| = 2.6$ Hz, CH_2), 2.1 (m, 1H), 1.96 (m, 2H), 1.43−1.59 (m, 3H), 1.39 (d, $|^3J_{H-P}| = 13.1$ Hz, CH_3), 1.37 (s, 3H, CH_3), 1.26 (d, $|^3J_{H-P}| = 12.2$ Hz, CH_3), 1.18 (s, 3H, CH_3), 0.89−1.13 (m, 4H); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, δ) 115.8 (s, Cp), 96.9 (s, quat), 96.2 (s, quat), 75.5 (d, $|^1J_{C-P}| = 13$ Hz, quat), 75.1 (d, $|^1J_{C-P}| = 22$ Hz, quat), 43.4 (d, $|J_{C-P}| = 5$ Hz, CH_2), 40.6 (s, CH_2), 35.7 (d, $|J_{C-P}| = 50$ Hz, CH), 28.9 (d, $|J_{C-P}| = 4$ Hz, CH_2), 28.2 (d, $|J_{C-P}| = 4$ Hz, CH_2), 27.6 (s, CH_3), 27.4 (s, CH_3), 27.1 (d, $|J_{C-P}| = 13$ Hz, CH_2), 26.6 (d, $|J_{C-P}| = 12$ Hz, CH_2), 25.8 (s, CH_2), 23.8 (s, CH_3), 23.6 (s, CH_3). Anal. Calcd for $C_{21}H_{32}Cl_2NO_3PTi$: C, 50.83; H, 6.50; N, 2.82. Found: C, 50.35; H, 6.21; N, 2.42.

Synthesis of $CpTiMe_2(NPR(C_6H_4O_3Me_4))$ (R = Ph (8), Cy (9)). These compounds were prepared in a similar manner, and thus only one preparation is detailed. To a stirred solution of 100 mg (0.204 mmol) of **6** in 5 mL of Et_2O was added dropwise 0.34 mL (1.021 mmol) of a 3.0 M ether solution of MeMgBr. After 1 h the solvent was evacuated, leaving a pale beige solid which was extracted with 3 × 10 mL of hexane. The extracts were filtered and pumped dry, yielding 77 mg (84%) of the pale yellow solid product. **8**: ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, δ) −18.1 (s); ^{1}H NMR (C_6D_6, 25 °C, δ) 8.36 (m, 2H, Ph), 7.11 (m, 3H, Ph), 6.26, (s, 5H, Cp), 2.83 (dd, $|^2J_{H-H}| = 13.5$ Hz, $|^3J_{H-P}| = 2.9$ Hz, CH_2), 1.65 (m, 3H, CH_2), 1.46 (s, CH_3), 1.38 (d, $|^3J_{H-P}| = 13.2$ Hz, CH_3), 1.31 (s, CH_3), 1.17 (d, $|^3J_{H-P}| = 12.8$ Hz, CH_3), 0.88 (s, 3H, $TiCH_3$), 0.82 (s, 3H, $TiCH_3$); ^{13}C-

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(32) Gee, V.; Orpen, A. G.; Phetmung, H.; Pringle, P. G.; Pugh, R. I. *Chem. Commun.* **1999**, 901−902.

(33) Budzelaar, P. H.; Drent, E.; Pringle, P. G. Eur. Patent p 97302079, 1996.

Table 1. Crystallographic Parameters[a]

	2	3	8	10	11
formula	$C_{16}H_{27}O_3P$	$C_{22}H_{32}O_2P_2$	$C_{23}H_{32}NO_3PTi$	$C_{29}H_{56}Al_2NO_3PTi$	$C_{19}H_{36}AlO_3P$
fw	298.35	390.42	449.37	599.58	370.43
a, Å	17.746(3)	8.3606(2)	15.967(3)	18.8861(5)	9.2469(2)
b, Å	10.070(3)	14.4883(3)	14.966(5)	19.0758(4)	11.9776(4)
c, Å	9.139(2)	18.3934(4)	20.101(4)	10.0047(3)	19.9925(6)
β, deg	91.56(2)	90	90	90	102.1940(10)
V, Å^3	1632.6(6)	2228.01(9)	4803(2)	3604.37(16)	2164.32(11)
cryst syst	monoclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$Pbca$	$Pnn2$	$P2_1/n$
d(calcd) g cm^{-3}	1.214	1.164	1.243	1.105	1.137
Z	4	4	8	4	4
μ, mm^{-1}	0.174	0.208	0.445	0.357	0.181
no. of data collected	8105	11 461	22 635	16 188	10 630
no. of data used	2844	3888	4212	6173	3761
no. of variables	181	191	262	334	217
R, %	0.0342	0.0856	0.0683	0.0854	0.0480
R_w, %	0.1193	0.2221	0.1822	0.2000	0.1227
goodness of fit	1.026	1.633	1.260	1.118	0.879

[a] All data collected at 24 °C with Mo Kα radiation ($\lambda = 0.710\,69$ Å). $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

{^{1}H} NMR (C_6D_6, 25 °C, δ) 134.3 (d, $|^2J_{C-P}| = 9$ Hz, Ph), 132.4 (s, Ph), 129.6 (d, $|^2J_{C-P}| = 11$ Hz), 124.9 (s, Ph), 113.6 (s, Cp), 97.4 (s, quat), 96.8 (s, quat), 75.9 (d, $|^1J_{C-P}| = 32$ Hz, quat), 75.1 (d, $|^1J_{C-P}| = 30$ Hz, quat), 42.8 (d, $|J_{C-P}| = 6$ Hz, CH_2), 40.9 (s, CH_2), 32.3 (s, TiCH_3), 30.5 (s, TiCH_3), 28.0 (s, CH_3), 27.8 (s, CH_3), 22.3 (s, CH_3), 21.1 (s, CH_3). **9**: yield 91%; ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, δ) −7.6 (s); ^{1}H NMR (C_6D_6, 25 °C, δ) 6.35 (s, 5H, Cp), 2.79 (dd, $|^2J_{H-H}| = 13.2$ Hz, $|^3J_{H-P}| = 2.7$ Hz, $\mathrm{C}H_2$), 2.03−2.33 (m, 3H, CH_2), 1.45−1.83 (m, 10H), 1.50 (s, 3H, CH_3), 1.43 (d, $|^2J_{H-P}| = 11.3$ Hz, $\mathrm{C}H_3$), 1.38 (d, $|^3J_{H-P}| = 11.7$ Hz, $\mathrm{C}H_3$), 1.37 (s, 3H, CH_3), 0.96−1.31 (m, 4H), 0.87 (s, 3H, Ti$\mathrm{C}H_3$), 0.84 (s, 3H, Ti$\mathrm{C}H_3$); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, δ) 111.5 (s, Cp), 96.8 (s, quat), 96.3 (s, quat), 75.3 (d, $|^1J_{C-P}| = 36$ Hz, quat), 75.0 (d, $|^1J_{C-P}| = 23$ Hz, quat), 43.4 (s, CH_2), 42.5 (s, TiCH_3), 42.4 (s, TiCH_3), 40.6 (s, CH_2), 35.3 (d, $|J_{C-P}| = 53$ Hz, CH), 29.5 (s, CH_2), 28.3 (d, $|J_{C-P}| = 4$ Hz, CH_2), 28.1 (s, CH_3), 28.0 (s, CH_3), 27.5 (d, $|J_{C-P}| = 12$ Hz, CH_2), 26.9 (d, $|J_{C-P}| = 12$ Hz, CH_2), 23.9 (s, CH_3), 23.5 (s, CH_3).

Synthesis of CpTiMe$_2$(NPCy($C_6H_4O_3Me_5$)(μ-AlMe$_2$)(AlMe$_3$)) (10). To a solution of 80 mg (0.178 mmol) of **9** in 1 mL of hexane was added dropwise 0.3 mL (0.6 mmol) of a 2.0 M heptane solution of Al$(CH_3)_3$. The solution was filtered and placed in an NMR tube. After 16 h, crystals suitable for X-ray crystallography had formed. ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, δ): 46.4 (br s), minor impurity at 45.1. ^{1}H NMR (C_6D_6, 25 °C, δ): 6.11, (s, 5H, Cp), 2.86 (m, 1H), 2.46 (m, 2H), 2.20 (m, 1H), 1.94 (m, 2H), 1.69 (m, 2H), 1.41−1.59 (m, 5H), 1.39 (s, 1H), 1.28 (s, 3H), 0.79−1.23 (m, 14H), −0.07 (br s, 9H, Al$(\mathrm{C}H_3)_3$), −0.25 (s, 6H, Al$(\mathrm{C}H_3)_3$).

Synthesis of Cy(cage)PAlMe$_3$. To a stirred benzene (5 mL) solution of **2** (93 mg, 0.31 mmol) was added dropwise with stirring 0.60 mL (1.2 mmol) of a 2.0 M heptane solution of AlMe$_3$. After the mixture was stirred for 3 h, a white precipitate was formed, which was filtered and dried to give 107 mg (93%) of the product. Recrystallization from benzene gave crystals suitable for X-ray crystallography. ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, δ): −17.9 (s). ^{1}H NMR (C_6D_6, 25 °C, δ): 2.00 (dd, $|^2J_{H-H}| = 13.3$ Hz, $|^3J_{H-P}| = 5.1$ Hz, $\mathrm{C}H_2$), 1.89 (m, 2H), 1.72 (m, 1H), 1.27−1.57 (m, 8H), 1.38 (d, $|^3J_{H-P}| = 12.3$ Hz, $\mathrm{C}H_3$), 1.35 (s, 3H, $\mathrm{C}H_3$), 1.28 (d, $|^3J_{H-P}| = 11.1$ Hz, $\mathrm{C}H_3$), 1.26 (s, 3H, $\mathrm{C}H_3$), 1.04 (m, 1H), 0.95 (m, 2H), −0.22 (s, 9H, Al$(\mathrm{C}H_3)_3$). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, δ): 96.7 (s, quat), 96.3 (s, quat), 73.3 (s, quat), 72.8 (d, $|^1J_{C-P}| = 8$ Hz, quat), 44.4 (d, $|^2J_{C-P}| = 5$ Hz, CH_2), 39.5 (s, CH_2), 32.8 (d, $|^2J_{C-P}| = 10$ Hz, CH_3), 32.5 (s, CH_2), 29.3 (s, CH), 28.9 (d, $|J_{C-P}| = 11$ Hz, CH_3), 28.3 (s, CH_2), 27.8 (s, CH_3), 27.7 (d, $|J_{C-P}| = 13$ Hz, CH_2), 27.0 (d, $|J_{C-P}| = 13$ Hz, CH_2), 26.3 (s, CH_2), −5.3 (s, Al$(CH_3)_3$). Anal. Calcd for $C_{19}H_{26}O_3PAl$: C, 59.07; H, 8.37; Found: C, 58.85; H, 8.22.

Ethylene Polymerization. A solution of 6−10 μmol of **6** or **7** in 2.0 mL of dry toluene was added to a flask containing 2.0 mL of dry toluene. A 500 equiv amount of a 10 wt % toluene solution of methylaluminoxane (MAO) was added to the flask. Alternatively, the compound **8** or **9** was combined with [Ph$_3$C][B$(C_6F_5)_4$] under an ethylene atmosphere at 25 °C. The flask was attached to a Schlenk line with a cold trap, a stopwatch was started, and the flask was three times evacuated for 5 s and refilled with predried 99.9% ethylene gas. The solution was rapidly stirred under 1 atm of ethylene at room temperature. The polymerization was stopped by the injection of a 1.0 M HCl/methanol solution, the total reaction time was noted, and the polymer was isolated.

X-ray Data Collection and Reduction. X-ray-quality crystals of **2**, **3**, **8**, **10**, and **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° < 2θ < 45−50.0°). A measure of decay was obtained by recollecting 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 TEXSAN solution package operating on a SGI Indy computer. 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.[34] The heavy-atom positions were determined using direct methods employing either the SHELX or SHELXTL direct-methods routine. 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

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[34] Cromer, D. T.; Mann, J. B. *Acta Crystallogr. Sect. A: Cryst. Phys., Theor. Gen. Crystallogr.* **1968**, *A24*, 390.

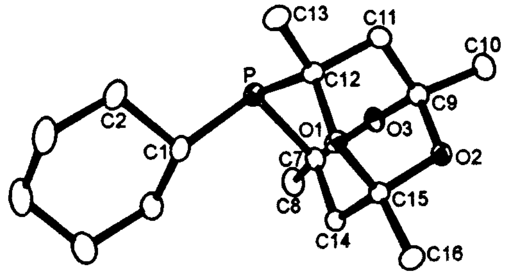
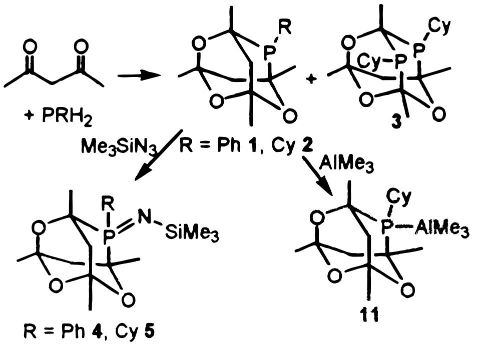


Figure 1. ORTEP drawing of **2**. Thermal ellipsoids of 30% probability are shown; all but the bridging methyl hydrogen atoms are omitted for clarity.

Scheme 1



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. In the cases where the space group is acentric, model inversion and re-refinement was employed to determine the correct enantiomorph. 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

Epstein and Buckler[35] showed in 1961 that the reaction of $PhPH_2$ with 2,4-pentanedione affords the "cage-phosphine" $PPh(C_6H_4O_3Me_4)$ (**1**). In the corresponding reaction of $CyPH_2$, they described only the isolation of the diphosphine species, formulated as $(PCy)_2(C_6H_2O_3Me_4)$ (**3**) (Scheme 1). While we have reproduced the preparation of **1** using their method, we have also isolated the phosphine $PCy(C_6H_4O_3Me_4)$ (**2**) as a white crystalline product in 60% yield from the analogous reaction of $CyPH_2$. In addition, the species **3** was isolated as a minor product. The formulations of these compounds were confirmed by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Compounds **2** and **3** were also characterized by X-ray crystallography (Figures 1 and 2). Compound **2** was confirmed as the trioxaphosphaadamantyl species. In the case of **3**, the X-ray data confirmed that the only isomer formed was the 1,3-diphosphine cage. This preference can be explained via the mechanistic considerations described by Bekiaris et al.[36] in studies of closely related systems.

Heating these phosphaadamantyl ligands, **1** and **2**, in the presence of a slight excess of Me_3SiN_3 effected oxidation to the corresponding (trimethylsilyl)phosphinimines $Me_3SiNPR(C_6H_4O_3Me_4)$ (R = Ph (**4**), Cy (**5**)) as confirmed by ^1H, ^{31}P, and ^{13}C NMR spectroscopy. These products were isolated in 85 and 82% yields, respectively. Analogous attempts to oxidize the even more sterically demanding phosphaadamantyl ligand derived from hexafluoroacetylacetone, $PPh(C_6H_4O_3(CF_3)_4)$, failed. No reaction between the phosphine with Me_3SiN_3 was observed, even under reflux conditions in xylene for 14 days.

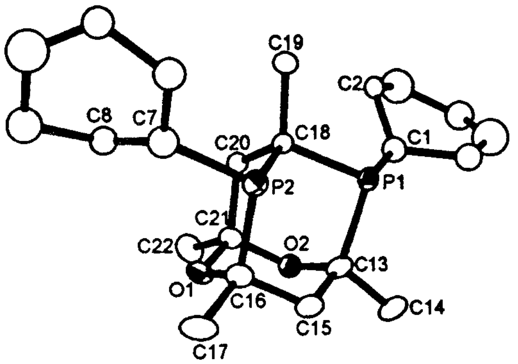
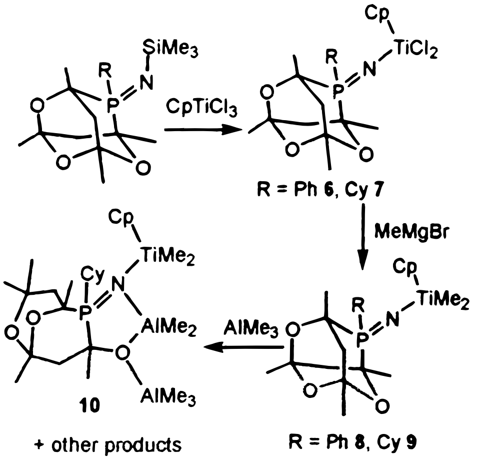


Figure 2. ORTEP drawing of **3**. Thermal ellipsoids of 30% probability are shown; all but the bridging methyl hydrogen atoms are omitted for clarity.

Scheme 2



Reaction of **4** and **5** with 1 equiv of $CpTiCl_3$ in refluxing benzene for 3 h afforded yellow products in greater than 90% yields. These products were formulated as $CpTiCl_2(NPR(C_6H_4O_3Me_4))$ (R = Ph (**6**), Cy (**7**)) (Scheme 2) on the basis of NMR data. Subsequent reaction of **6** and **7** with excess MeMgBr in diethyl ether gave pale beige solids in 84% and 91% yields, respectively. These species were formulated as the complexes $CpTiMe_2(NPR(C_6H_4O_3Me_4))$ (R = Ph (**8**), Cy (**9**)). NMR data supported these formulations, and in the case of **8**, this was confirmed crystallographically (Figure 3). The metric parameters of **8** are unexceptional.[30,31,37] As in previously reported species, the Ti−N−P vector is approximately linear (171.3(2)°), while the Ti−N bond distance of 1.806(3) Å is also typical.

Preliminary screening (1 atm, 25 °C) for catalytic activity in ethylene polymerization was performed for

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(35) Epstein, M.; Buckler, S. A. *J. Am. Chem. Soc.* **1961**, *83*, 3279.

(36) Bekiaris, G.; Lork, E.; Offermann, W.; Roeshenthaler, G. V. *Chem. Ber.* **1997**, *130*, 1547−1550.

(37) Dehnicke, K.; Kreiger, M.; Massa, W. *Coord. Chem. Rev.* **1999**, *182*, 19−65.

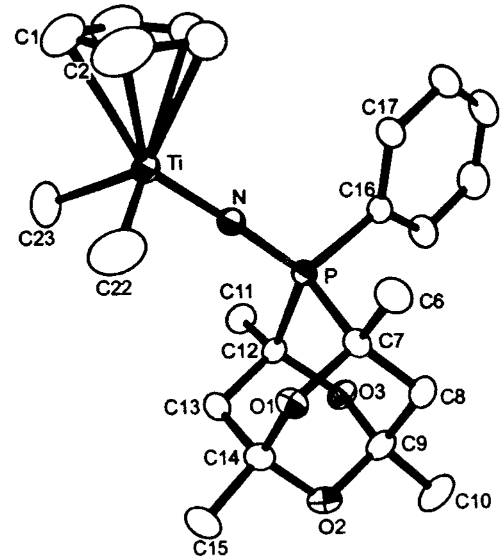

Figure 3. ORTEP drawing of **8**. Thermal ellipsoids of 30% probability are shown; all but the bridging methyl hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Ti(1)−N(1), 1.806(3); Ti(1)−C(23), 2.162(5); Ti(1)−C(22), 2.165(6); P(1)−N(1), 1.565(3); N(1)−Ti(1)−C(23), 103.3(2); N(1)−Ti(1)−C(22), 102.0(2); C(23)−Ti(1)−C(22), 99.7(3); P(1)−N(1)−Ti(1), 171.3(2).

compounds **6** and **7** in the presence of 500 equiv of methylalumoxane (MAO). Alternatively, the compounds **8** and **9** were combined with $[Ph_3C][B(C_6F_5)_4]$ under an ethylene atmosphere at 25 °C. In all cases, only a minimal amount of polymer was observed under these conditions. These low activities (<10 g of PE/(mmol/h)) stand in marked contrast to our previous reports of active olefin polymerization catalysts derived from the complexes $(Cp^{\ddagger})TiX_2(NPR_3)$ ($Cp^{\ddagger}$ = Cp, *t*-BuCp; X = Cl, Me; R = *t*-Bu, *i*-Pr, Cy) and $(R_3PN)_2TiX_2$.[30,31]

The interaction of the complexes of these cage-phosphinimides with aluminum reagents was investigated. Initially, reaction of **8** with $AlMe_3$ was used as a model for the interaction with MAO. Monitoring by $^{31}P\{^1H\}$ NMR spectroscopy revealed the formation of two products, a major species exhibiting a resonance at 46.4 ppm and a minor impurity at 45.1 ppm. The ^1H NMR spectrum was complex and precluded structural formulation of the products. Fortunately, crystals of the major product **10** were isolated upon standing. An X-ray diffraction study provided the unequivocal identification of **10** as $CpTiMe_2(NPCy(C_6H_4O_3Me_5)(\mu\text{-}AlMe_2)(AlMe_3))$ (Figure 4). In this species, the phosphaadamantyl cage has been split open by the transfer of a methyl group from $AlMe_3$ to one of the quaternary carbons with cleavage of the adjacent C−O bond. The resulting oxygen atom bridges $AlMe_2$ and $AlMe_3$ groups, while the $AlMe_2$ is also bound to the phosphinimide nitrogen atom. The reduced P−N and Ti−N bond strengths in **10** compared to **8** are reflected in the corresponding distances of 1.997(5) and 1.624(5) Å, respectively.

In contrast to the reaction of **8**, reaction of the free phosphine **2** with $AlMe_3$ resulted only in the formation of the adduct $Me_3AlPCy(C_6H_4O_3Me_4)$ (**11**). The formulation of this white solid, isolated in 93% yield, was confirmed by X-ray crystallography (Figure 5). The Al−P bond length in the phosphine−alane adduct is 2.5526(11) Å.

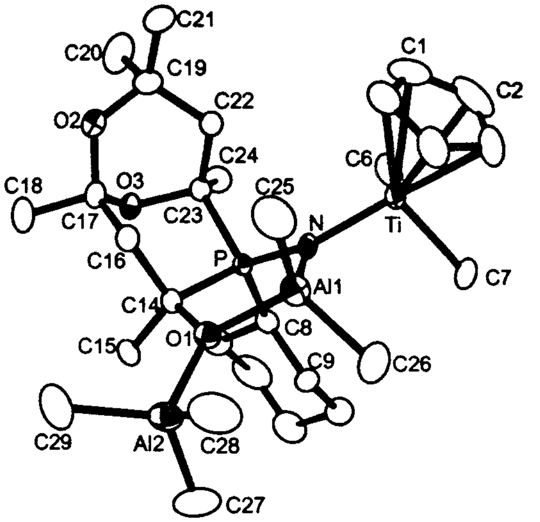

Figure 4. ORTEP drawing of **10**. Thermal ellipsoids of 30% probability are shown; all but the bridging methyl hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Ti(1)−N(1), 1.997(5); Ti(1)−C(7), 2.132(8); Ti(1)−C(6), 2.124(10); Al(1)−O(1), 1.886(5); Al(1)−N(1), 1.972(6); Al(1)−C(26), 1.970(10); Al(1)−C(25), 1.996(10); Al(2)−O(1), 1.953(5); Al(2)−C(27), 1.991(10); Al(2)−C(29), 2.025(11); Al(2)−C(28), 2.035(12); P(1)−N(1), 1.624(5); N(1)−Ti(1)−C(7), 105.3(3); N(1)−Ti(1)−C(6), 108.0(3); C(7)−Ti(1)−C(6), 92.6(5); O(1)−Al(1)−N(1), 94.6(2); O(1)−Al(1)−C(26), 110.9(4); N(1)−Al(1)−C(26), 110.3(4); O(1)−Al(1)−C(25), 107.8(4); N(1)−Al(1)−C(25), 113.6(4); C(26)−Al(1)−C(25), 117.2(5); O(1)−Al(2)−C(27), 104.0(4); O(1)−Al(2)−C(29), 111.8(4); C(27)−Al(2)−C(29), 114.6(6); O(1)−Al(2)−C(28), 104.9(4); C(27)−Al(2)−C(28), 113.0(6); C(29)−Al(2)−C(28), 108.1(6); P(1)−N(1)−Al(1), 109.6(3); P(1)−N(1)−Ti(1), 132.1(3); Al(1)−N(1)−Ti(1), 118.1(3); Al(1)−O(1)−Al(2), 120.1(3).

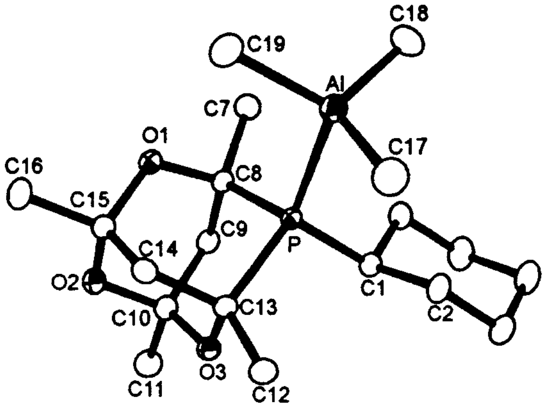

Figure 5. ORTEP drawing of **11**. Thermal ellipsoids of 30% probability are shown; all but the bridging methyl hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Al(1)−C(17), 1.971(3); Al(1)−C(19), 1.975(3); Al(1)−C(18), 1.973(3); Al(1)−P(1), 2.5526(11); C(17)−Al(1)−C(19), 114.0(2); C(17)−Al(1)−C(18), 115.3(2); C(19)−Al(1)−C(18), 115.1(2); C(17)−Al(1)−P(1), 103.87(10); C(19)−Al(1)−P(1), 104.18(11); C(18)−Al(1)−P(1), 102.09(11); C(1)−P(1)−Al(1), 114.77(9).

Monitoring of the reaction of **8** with MAO directly by ^{31}P NMR spectroscopy revealed the presence of several products with resonances around 45 ppm. The similarity of this chemical shift range to that seen for the reaction with $AlMe_3$ suggests that cage rupture may have occurred under polymerization conditions. It is interesting that the $AlMe_3$ does not effect cage rupture of ligand **2**; rather, **11** is formed cleanly. These observations suggest that an interaction of Al with the Ti-bound phosphinimide N atom may be involved in the initiation of the process of cage rupture. Reactions of **8** and **9** with $[Ph_3C][B(C_6F_5)_4]$ were also monitored by $^{31}P\{^1H\}$ NMR spectroscopy, revealing the formation of a handful of products, none of which could be fully characterized. Although unconfirmed, we speculate that ligand rupture is also effected by the Lewis acidic reagent $[Ph_3C][B(C_6F_5)_4]$.

In summary, titanium derivatives of the sterically demanding cage-phosphinimide ligands have been synthesized. The corresponding Ti complexes react with Lewis acids to effect ligand cage rupture, affording a mixture of Ti products, observations that do not augur well for single-site catalysis. Current efforts are focused on ligand modifications that provide enhanced Ti−N bond stability and are suited to the generation of a single active center.

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

Supporting Information Available: Tables giving X-ray data for **2**, **3**, **8**, **10**, and **11**; data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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