Inorg. Chem. **2007**, *46*, 7199–7209

Synthesis and Reactivity of Metal Complexes Supported by the Tetradentate Monoanionic Ligand Bis(2-picolyl)(2-hydroxy-3,5-di-*tert*-butylbenzyl)amide (BPPA)

Wayne A. Chomitz, Stefan G. Minasian, Andrew D. Sutton, and John Arnold*

Department of Chemistry, University of California, Berkeley, California 94720-1460

Received April 23, 2007

Metal-halide complexes of Ti, V, Y, Zr, Al, Ga, and U supported by the tetradentate monoanionic (TDMA) ligand bis(2-picolyl)(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine, H(BPPA), were synthesized and spectroscopically characterized. In addition, the complexes (BPPA)$TiCl_2$, (BPPA)VBr_2, [(BPPA)YCl_2]$_2$, (BPPA)$AlCl_2$, (BPPA)$GaCl_2$, and (BPPA)UI_3 were characterized by single-crystal X-ray crystallography. In all cases the ligand is bound κ^4 to the metal center. All structurally characterized compounds are monomeric in the solid-state with the exception of [(BPPA)YCl_2]$_2$, which exists as a dimer in the solid-state. The metal–alkyl complexes (BPPA)$AlMe_2$ and (BPPA)$Zr(CH_2Ph)_3$ were also synthesized and characterized, and an X-ray structure of (BPPA)$Zr(CH_2Ph)_3$ was obtained. The transformation of BPPA from a monoanionic to a dianionic ligand via proton abstraction was observed and monitored by NMR spectroscopy.

Introduction

Group 3 and lanthanide complexes supported by cyclopentadienyl (Cp) ligands have been demonstrated as effective precatalysts for a variety of homogeneous processes.[1−5] These metals typically adopt the +3 oxidation state and are readily complexed by ligands incorporating hard σ donors such as oxygen and nitrogen. In addition to having suitable donor groups, an ideal ligand system from our perspective must also possess sufficient steric bulk to prevent unwanted aggregation and solvent ligation. Recent efforts by numerous research groups focusing on ligand design have sought to supplant the formerly ubiquitous Cp fragment.[6−9] A number of complexes of the general form $(LX)_2MR$[10] have been prepared, where LX is a bidentate monoanionic ligand and R is an alkoxy, alkyl, or amido group. A nonexhaustive list of examples of such bidentate ligands include benzamidinate,[11,12] guanidinate,[13] and mixed N, O donor sets such as bis(alkoxydimethylsilyl)amido frameworks[14] and bis(oxazolinates).[15] Alternatively, complexes of the general form $(L_2X_2)MR$, where L_2X_2 is a dianionic tetradentate ligand have also been studied. Many examples include bis(phenolates),[16−22] linked amidinates,[23] and porphyrin rings.[24−27]

Our interest lies in the comparatively understudied complexes of the general form $(L_3X)MR_2$, where L_3X is a

* To whom correspondence should be addressed. E-mail: arnold@berkeley.edu.

(1) Li, Y. W.; Fu, P. F.; Marks, T. J. *Organometallics* **1994**, *13*, 439−440.
(2) Gagne, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275−294.
(3) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103−8110.
(4) Mao, L. S.; Shen, Q.; Zue, M. Q.; Sun, J. *Organometallics* **1997**, *16*, 3711−3714.
(5) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291−1300.
(6) Piers, W. E.; Emslie, D. J. H. *Coord. Chem. Rev.* **2002**, *233*, 131−155.
(7) Bailey, P. J.; Pace, S. *Coord. Chem. Rev.* **2001**, *214*, 91−141.
(8) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447.
(9) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283−315.
(10) Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127−148.
(11) Duchateau, R.; Vanwee, C. T.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4931−4932.
(12) Hagadorn, J. R.; Arnold, J. *Organometallics* **1996**, *15*, 984−991.
(13) Lu, Z. P.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2001**, *20*, 706−712.
(14) Duchateau, R.; Tuinstra, T.; Brussee, E. A. C.; Meetsma, A.; vanDuijnen, P. T.; Teuben, J. H. *Organometallics* **1997**, *16*, 3511−3522.
(15) Gorlitzer, H. W.; Spiegler, M.; Anwander, R. *J. Chem. Soc. Dalton Trans.* **1999**, 4287−4288.
(16) Arnold, P. L.; Natrajan, L. S.; Hall, J. J.; Bird, S. J.; Wilson, C. *J. Organomet. Chem.* **2002**, *647*, 205−215.
(17) Ma, H. Y.; Spaniol, T. P.; Okuda, J. *Dalton Trans.* **2003**, 4770−4780.
(18) Yao, Y. M.; Ma, M. T.; Xu, X. P.; Zhang, Y.; Shen, Q.; Wong, W. T. *Organometallics* **2005**, *24*, 4014−4020.
(19) Xu, X. P.; Ma, M. T.; Yao, Y. M.; Zhang, Y.; Shen, Q. *Eur. J. Inorg. Chem.* **2005**, 676−684.
(20) O'Shaughnessy, P. N.; Knight, P. D.; Morton, C.; Gillespie, K. M.; Scott, P. *Chem. Commun.* **2003**, 1770−1771.
(21) Cai, C. X.; Amgoune, A.; Lehmann, C. W.; Carpentier, J. F. *Chem. Commun.* **2004**, 330−331.
(22) Cai, C. X.; Toupet, L.; Lehmann, C. W.; Carpentier, J. F. *J. Organomet. Chem.* **2003**, *683*, 131−136.

10.1021/ic700775k CCC: $37.00
Published on Web 07/26/2007

tetradentate monoanionic (TDMA) ligand.[28] Recently we reported the use of TDMA phenoxytriamine ligands supporting Group 3 metals in lactide polymerization.[29] The use of TDMA ligands opens up the possibility to study complexes of the general form $(L_3X)MR_2$. These coordinately saturated starting materials could provide a synthetic route to relatively rare trivalent $(L_3X)MR^+$ compounds,[30−32] thus allowing the opportunity to compare reactivity to related $(LX)_2MR$ and $(L_2X_2)MR$ systems. In addition, TDMA ligand systems could allow for the synthesis of a range of other trivalent main group and actinide metal complexes.

Our efforts to expand TDMA chemistry using phenoxytriamine ligands to other metals was hampered by the observation of low yields and intractable mixtures. The modular nature of the TDMA motif allows us to carry out simple modifications in order to test the resulting steric and electronic consequences on complex structure and reactivity. Here we examine the effects of replacing the two diethylamine donors with pyridines. This general ligand framework has previously been shown to bind to middle and late transition metals,[33−52] although its application to main group and early transition metals was unknown until recently, when Bercaw et al. described the synthesis and reactivity of a number of Group 3 complexes with BPPA.[53] Here we report the synthesis, coordination chemistry, and reactivity of a series of main group, transition metal, and actinide metal complexes supported by bis(2-picolyl)(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine, H(BPPA).

Experimental Section

Unless otherwise noted, all reactions were performed using standard Schlenk-line techniques or in an MBraun dry box under an atmosphere of nitrogen (<1 ppm O_2/H_2O). All glassware, cannulae, and Celite were stored in an oven at ca. 425 K. Pentane, toluene, methylene chloride, diethyl ether, DME, and THF were purified by passage through a column of activated alumina and degassed prior to use.[54] Pyridine was distilled from CaH_2. Deuterated solvents were vacuum-transferred from sodium/benzophenone (benzene, toluene, and THF) or calcium hydride (chloroform and pyridine). NMR spectra were recorded at ambient temperature on Bruker AV-300, AVQ-400, AVB-400, and DRX-500 spectrometers. ^1H and $^{13}C\{^1H\}$ chemical shifts are given relative to residual solvent peaks, and coupling constants (J) are given in Hz. ^{27}Al NMR chemical shifts are referenced to an external standard of 1 M $Al(NO_3)_3$ in H_2O/D_2O (0.0 ppm). Proton and carbon NMR assignments were routinely confirmed by $^1H-^1H$ (COSY) or $^1H-^{13}C$ (HMQC and HMBC) experiments. Infrared (IR) samples were prepared as Nujol mulls and were taken between KBr disks. Magnetic susceptibility (μ_{eff}) values were determined using the solution Evans' method.[55] Melting points were determined using sealed capillaries prepared under nitrogen and are uncorrected. The following chemicals were purified prior to use: AlI_3 (95%, Aldrich) was recrystallized from CS_2. $H[B(C_6F_5)_4 \cdot 2Et_2O]$,[56] $Zr(CH_2Ph)_4$,[57] $Y(CH_2SiMe_3)_3(THF)_2$,[58] $VBr_3(THF)_3$,[59] and $UI_3(THF)_4$[60] were prepared using the literature procedures, and unless otherwise noted, all reagents were acquired from commercial sources and used as received. Elemental analyses and mass spectral data were determined at the College of Chemistry, University of California, Berkeley. The X-ray structural determination was performed at CHEXRAY, University of California, Berkeley. Electrochemical measurements were performed using a BAS-100b electrochemical analyzer with a BAS C3 cell stand mounted on the bench top. Experiments were performed in dichloromethane with $[n\text{Bu}_4N][PF_6]$ (0.3 M) as the supporting electrolyte at ambient temperature

(23) Bambirra, S.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2001**, *20*, 782−785.
(24) Schaverien, C. J. Organometallic chemistry of the lanthanides. *Adv. Organomet. Chem.* **1994**, *36*, 283−362.
(25) Schaverien, C. J.; Orpen, A. G. *Inorg. Chem.* **1991**, *30*, 4968−4978.
(26) Brand, H.; Arnold, J. *Coord. Chem. Rev.* **1995**, *140*, 137−168.
(27) Arnold, J.; Hoffman, C. G.; Dawson, D. Y.; Hollander, F. J. *Organometallics* **1993**, *12*, 3645−3654.
(28) For representative examples of metal complexes with related L_2X tripodal ligand systems, see: (a) Hammes, B. S.; Carrano, C. J. *Inorg. Chem.* **1999**, *38*, 3562−3568. (b) Milione, S.; Bertolasi, V.; Cuenca, T.; Grassi, A. *Organometallics* **2005**, *24*, 4915-4925. (c) Whited, M. T.; Rivard, E.; Peters, J. C. *Chem. Comm.* **2006**, 1613−1615.
(29) Westmoreland, I.; Arnold, J. *Dalton Trans.* **2006**, 4155−4163.
(30) Bambirra, S.; Bouwkamp, M. W.; Meetsma, A.; Hessen, B. *J. Am. Chem. Soc.* **2004**, *126*, 9182−9183.
(31) Bambirra, S.; Meetsma, A.; Hessen, B.; Bruins, A. P. *Organometallics* **2006**, *25*, 3486−3495.
(32) Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J. *Chem. Rev.* **2006**, *106*, 2404−2433.
(33) Vaidyanathan, M.; Viswanathan, R.; Palaniandavar, M.; Balasubramanian, T.; Prabhaharan, P.; Muthiah, T. P. *Inorg. Chem.* **1998**, *37*, 6418−6427.
(34) Velusamy, M.; Mayilmurugan, R.; Palaniandavar, M. *Inorg. Chem.* **2004**, *43*, 6284−6293.
(35) Viswanathan, R.; Palaniandavar, M.; Balasubramanian, T.; Muthiah, T. P. *Inorg. Chem.* **1998**, *37*, 2943−2951.
(36) Yan, S. P.; Que, L.; Taylor, L. F.; Anderson, O. P. *J. Am. Chem. Soc.* **1988**, *110*, 5222−5224.
(37) Trosch, A.; Vahrenkamp, H. *Eur. J. Inorg. Chem.* **1998**, 827−832.
(38) Trosch, A.; Vahrenkamp, H. *Inorg. Chem.* **2001**, *40*, 2305−2311.
(39) Sarkar, S.; Mondal, A.; Ribas, J.; Drew, M. G. B.; Pramanik, K.; Rajak, K. K. *Eur. J. Inorg. Chem.* **2004**, 4633−4639.
(40) Shimazaki, Y.; Huth, S.; Hirota, S.; Yamauchi, O. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1187−1195.
(41) Shimazaki, Y.; Huth, S.; Karasawa, S.; Hirota, S.; Naruta, Y.; Yamauchi, O. *Inorg. Chem.* **2004**, *43*, 7816−7822.
(42) Rajendran, U.; Viswanathan, R.; Palaniandavar, M.; Lakshminarayanan, M. *J. Chem. Soc. Dalton Trans.* **1992**, 3563−3564.
(43) Reddig, N.; Pursche, D.; Kloskowski, M.; Slinn, C.; Baldeau, S. M.; Rompel, A. *Eur. J. Inorg. Chem.* **2004**, 879−887.
(44) Reddig, N.; Pursche, D.; Krebs, B.; Rompel, A. *Inorg. Chim. Acta* **2004**, *357*, 2703−2712.
(45) Reddig, N.; Pursche, D.; Rompel, A. *Dalton Trans.* **2004**, 1474−1480.
(46) Olmstead, M. M.; Patten, T. E.; Troeltzsch, C. *Inorg. Chim. Acta* **2004**, *357*, 619−624.
(47) Koval, I. A.; Huisman, M.; Stassen, A. F.; Gamez, P.; Lutz, M.; Spek, A. L.; Reedijk, J. *Eur. J. Inorg. Chem.* **2004**, 591−600.
(48) Ito, S.; Nishino, S.; Itoh, H.; Ohba, S.; Nishida, Y. *Polyhedron* **1998**, *17*, 1637−1642.
(49) de Oliveira, M. C. B.; Scarpellini, M.; Neves, A.; Terenzi, H.; Bortoluzzi, A. J.; Szpoganics, B.; Greatti, A.; Mangrich, A. S.; de Souza, E. M.; Fernandez, P. M.; Soares, M. R. *Inorg. Chem.* **2005**, *44*, 921−929.
(50) Adams, H.; Bailey, N. A.; Campbell, I. K.; Fenton, D. E.; He, Q. Y. *J. Chem. Soc., Dalton Trans.* **1996**, 2233−2237.
(51) Adams, H.; Fenton, D. E.; McHugh, P. E. *Polyhedron* **2003**, *22*, 75−81.
(52) Goodwin, J. M.; Olmstead, M. M.; Patten, T. E. *J. Am. Chem. Soc.* **2004**, *126*, 14352−14353.
(53) Marinescu, S. C.; Agapie, T.; Day, M. W.; Bercaw, J. E. *Organometallics* **2007**, *26*, 1178−1190.
(54) Alaimo, P. J.; Peters, D. W.; Arnold, J.; Bergman, R. G. *J. Chem. Educ.* **2001**, *78*, 64−64.
(55) Piguet, C. *J. Chem. Educ.* **1997**, *74*, 815−816.
(56) Jutzi, P.; Muller, C.; Stammler, A.; Stammler, H. G. *Organometallics* **2000**, *19*, 1442−1444.
(57) Zucchini, U.; Albizzat. E; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357.
(58) Hultzsch, K. C.; Voth, P.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 228−243.
(59) Davies, S. C.; Durrant, M. C.; Hughes, D. L.; Le Floc'h, C.; Pope, S. J. A.; Reid, G.; Richards, R. L.; Sanders, J. R. *J. Chem. Soc., Dalton Trans.* **1998**, 2191−2198.
(60) Clark, D. L.; Sattelberger, A. P. *Inorg. Synth.* **1997**, *31*, 307−315.

(22 °C) under N_2. A three-electrode setup was implemented with a glassy carbon working electrode, platinum auxiliary electrode, and a Ag/AgCl reference electrode. All potentials are reported relative to the Fc/Fc^+ couple as an internal standard.

Crystallographic Analysis. Single crystals of **4**−**6** and **12**−**14** were coated in Paratone-N oil, mounted on a Kaptan loop, transferred to a Siemens SMART diffractometer or a Bruker APEX CCD area detector,[61] centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that has been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrices and cell constants were determined by collection of 60 30 s frames, followed by spot integration and least-squares refinement. An arbitrary hemisphere of data was collected, and the raw data were integrated using SAINT.[62] Cell dimensions reported were calculated from all reflections with $I > 10\sigma$. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Data were analyzed for agreement and possible absorption using XPREP.[63] An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.[64] The structure was solved and refined with the teXsan software package.[65] Thermal parameters for all non-hydrogen atoms were refined anisotropically, except in solvent molecules disordered over multiple partially occupied positions. ORTEP diagrams were created using the ORTEP-3 software package.[66]

Single-crystal diffraction data for **10** were collected using synchrotron radiation at the Advanced Light Source at Lawrence Berkeley National Laboratory. A crystal was coated in Paratone-N oil and mounted on a Kaptan loop, transferred to a Bruker D8 controller, and cooled in a dinitrogen stream. Data were collected using a Bruker Platinum 200 with an APEX2 v1.0-27 detector. Initial lattice parameters were obtained from a least-squares analysis of more than 30 centered reflections; these parameters were later refined against all data. A full hemisphere of data was collected. Data were integrated using Bruker SAINT version 7.06 and corrected for Lorentz and polarization effects using SADABS. Space group assignments were made on the basis of systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined against all data using the SHELXTL 5.0 software package. Thermal parameters for all non-hydrogen atoms were refined anisotropically, except in solvent molecules disordered over multiple partially occupied positions. A summary of the X-ray diffraction data is presented in the Supporting Information.

H(BPPA). A modified literature procedure was used.[37] To a suspension of 2-pyridinecarboxaldehyde (10.4 g, 96.7 mmol) in 200 mL of absolute ethanol was added a solution of 2-(aminomethyl)-pyridine (10.5 g, 97.1 mmol) in 200 mL of absolute ethanol dropwise at 0 °C. After 4 h, the solution was cooled to 0 °C and sodium borohydride (7.26 g, 192 mmol) was added in small portions. After the reaction was stirred for 12 h at room temperature, 240 mL of aqueous hydrochloric acid (5 M) was added slowly and stirred for 1 h. A 2 M aqueous solution of sodium hydroxide was then added until a pH of 11 was reached. The mixture was extracted with methylene chloride (6 × 100 mL), dried over sodium sulfate, and then filtered. Removal of volatiles afforded 17.1 g (89% yield) of analytically pure di-(2-picolyl)amine (DPA) as a brown oil.

A flask containing 17.1 g (86.0 mmol) of DPA and 2.71 g (86.0 mmol) of paraformaldehyde was heated at 80 °C for 1 h. To the resulting paste was added 2,4-di-*tert*-butylphenol (17.7 g, 86.0 mmol) and 60 mL of methanol, and the reaction mixture was heated at reflux for 24 h. The solvent was removed under vacuum, leaving a brown oil. Analytically pure product was collected as a yellow solid (27.9 g, 77.6% yield) after crystallization from pentane at −40 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 1.36 (s, 9 H, *t*-Bu); 1.77 (s, 9 H, *t*-Bu); 3.67 (s, 2 H, $-CH_2-$); 3.81 (s, 4 H, $-CH_2-$); 6.53 (m, 2 H, py-H); 6.97 (d, J_{HH} = 6.3 Hz, 2 H, py-H); 7.01 (m, 2 H, py-H); 8.42 (d, J_{HH} = 4.8 Hz, 2 H, py-H).

K(BPPA) (1). A solution of H(BPPA) (7.0 g, 17 mmol) in 50 mL of THF was added to a suspension of potassium hydride (1.35 g, 33.6 mmol) in 70 mL of THF at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 12 h. After removal of volatiles under vacuum, the crude material was extracted with toluene and filtered through a bed of Celite. The solvent was removed under vacuum, and the crude product was washed with cold pentane (2 × 30 mL) leaving analytically pure product as an off-white solid (7.1 g, 93%). Colorless crystals were grown from toluene at −40 °C overnight. ^{1}H NMR (400 MHz, C_6D_6): δ 1.63 (s, 9 H, *t*-Bu); 1.82 (s, 9 H, *t*-Bu); 3.58 (s, 4 H, -CH_2-); 3.93 (s, 2 H, -CH_2-); 6.30 (m, 2 H, py-H); 6.55 (d, J_{HH} = 7.8 Hz, 2 H, py-H); 6.78 (m, 2 H, py-H); 7.35 (d, J_{HH} = 2.4 Hz, 1 H, Ar−H); 7.62 (d, J_{HH} = 2.4 Hz, 1 H, Ar−H); 8.26 (d, J_{HH} = 4.2 Hz, 1 H, py-H). IR (cm^{-1}): 1593 (s); 1570 (m); 1323 (s); 1260 (w); 1234 (w); 1200 (w); 1155 (w); 1125 (w); 1073 (s); 1000 (m); 967 (w); 952 (w); 905 (w); 875 (m); 828 (m); 791 (w); 765 (s); 694 (w); 672 (w); 624 (m); 500 (m). Anal. Calcd for $C_{27}H_{34}N_3$-OK: C, 71.15; H, 7.53; N, 9.22. Found: C, 71.60; H, 7.92; N, 8.63. mp = 150−151 °C.

Li(BPPA) (2). To a solution of H(BPPA) (1.0 g, 2.4 mmol) in 40 mL of pentane at 0 °C was added a solution of lithium hexamethyldisilazide (0.39 g, 2.4 mmol) in 20 mL of pentane. The reaction mixture was allowed to warm to room temperature and was stirred for 4 h. The solvent was removed under vacuum, and the crude product was washed with pentane. Colorless crystals were grown from toluene at −40 °C overnight (0.53 mg, 52% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 1.43 (s, 9 H, *t*-Bu); 1.81 (s, 9 H, *t*-Bu); 3.17 (s, 1 H, $-CH_2-$); 3.18 (s, 1 H, $-CH_2-$); 3.77 (s, 2 H, $-CH_2-$); 4.41 (s, 1 H, $-CH_2-$); 4.71 (s, 1 H, $-CH_2-$); 6.15 (s, 1 H, py-H); 6.36 (s, 2 H, py-H); 6.72 (s, 1 H, py-H); 6.84 (s, 1 H, py-H); 6.92 (d, J_{HH} = 2.4 Hz, 1 H, Ar−H); 7.26 (d, J_{HH} = 2.4 Hz, 1 H, Ar−H); 8.30 (s, 1 H, py-H); 8.59 (s, 1 H, py-H). IR (cm^{-1}): 1601 (m); 1318 (m); 1299 (w); 1262 (w); 1235 (w); 1199 (w); 1050 (w); 1008 (w); 949 (w); 870 (m); 834 (m); 806 (w); 749 (m); 576 (m); 542 (m). Anal. calcd for $C_{27}H_{34}N_3OLi$: C, 76.55; H, 8.11; N, 9.92. Found: C, 76.24; H, 8.39; N, 9.71. mp (dec) = 210 °C.

Na(BPPA) (3). A solution of H(BPPA) (1.0 g, 2.4 mmol) in 10 mL of THF was added to a suspension of sodium hydride (0.15 g, 6.0 mmol) in 30 mL of THF at 0 °C. The reaction mixture was allowed to stir for 4 h at room temperature. The solvent was removed under vacuum, and the crude material was washed with pentane. Colorless crystals were grown from toluene at −40 °C overnight (460 mg, 47% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 1.55 (s, 9 H, *t*-Bu); 1.90 (s, 9 H, *t*-Bu); 3.21 (s, 3 H, $-CH_2-$); 3.60 (s, 2 H, $-CH_2-$); 4.72 (s, 1 H, $-CH_2-$); 6.35 (s, 2 H, py-H); 6.41 (s, 2 H, py-H); 6.79 (m, 2 H, py-H); 7.11 (d, J_{HH} = 2.4 Hz, 1 H, Ar−H); 7.41 (d, J_{HH} = 2.4 Hz, 1 H, Ar−H); 8.32 (br s, 2 H,

(61) *SMART: Area-Detector Software Package*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2001−2003.
(62) *SAINT: SAX Area-Detector Integration Program, V6.40*; Bruker Analytical X-ray Systems Inc.: Madison, WI, 2003.
(63) *XPREP*; Bruker Analytical X-ray Systems Inc.: Madison, WI, 2003.
(64) *SADABS: Bruker-Nonius Area Detector Scaling and Absorption v. 2.05*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2003.
(65) *teXsan: Cystal Structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1992.
(66) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

py-H). IR (cm^{-1}): 1594 (s); 1571 (m); 1358 (w); 1328 (m); 1300 (m); 1258 (w); 1232 (w); 1197 (w); 1148 (m); 1131 (m); 1049 (w); 1003 (m); 988 (w); 937 (w); 871 (m); 830 (m); 804 (w); 766 (s); 745 (s); 636 (m); 502 (m). Anal. Calcd for $C_{27}H_{34}N_3ONa$: C, 73.76; H, 7.81; N, 9.56. Found: C, 73.30; H, 7.82; N, 9.39. mp = 235−237 °C.

(BPPA)TiCl$_2$ (4). To a suspension of $TiCl_3$ (0.51 g, 3.3 mmol) in 30 mL of THF was added a solution of K(BPPA) (1.5 g, 3.3 mmol) in 20 mL of THF at room temperature. The dark red reaction mixture was allowed to stir for 12 h. The solvent was removed under vacuum, and the crude product was washed with diethyl ether. The resultant solid was extracted with methylene chloride (50 mL) and filtered through a bed of Celite. Concentration and cooling to −40 °C led to the formation of red, blade-like crystals overnight (0.97 g, 55% yield). IR (cm^{-1}): 1607 (s); 1570 (w); 1338 (w); 1304 (m); 1269 (s); 1239 (m); 1204 (w); 1171 (m); 1131 (w); 1096 (m); 1054 (m); 1023 (m); 981 (w); 916 (w); 856 (s); 762 (s); 648 (m); 606 (m); 576 (s); 517 (w); 482 (m). Anal. Calcd for $C_{27}H_{34}N_3OTiCl_2$: C, 60.56; H, 6.41; N, 7.85. Found: C, 60.28; H, 6.47; N, 7.65. mp = 304−306 °C. μ_{eff} = 1.71 μ_B.

(BPPA)VBr$_2$ (5). To a slurry of $VBr_3(THF)_3$ (0.60 g, 1.2 mmol) in 20 mL of THF was added a solution of K(BPPA) (0.54 g, 1.2 mmol) in 10 mL of THF at room temperature. The dark purple-red reaction mixture was stirred for 12 h. The volatiles were removed under vacuum, and the crude product was washed with diethyl ether and subsequently extracted with methylene chloride (50 mL). The solution was filtered through a bed of Celite and concentrated. Red blade-like crystals were obtained after cooling to −40 °C overnight (0.53 g, 71% yield). IR (cm^{-1}): 1608 (s); 1358 (m); 1308 (w); 1259 (s); 1238 (m); 1206 (w); 1169 (m); 1110 (m); 1086 (m); 1055 (w); 1022 (s); 934 (w); 837 (m); 809 (w); 762 (m); 723 (w); 650 (m); 611 (m); 575 (w). Anal. Calcd for $C_{27}H_{34}N_3OVBr_2$: C, 51.69; H, 5.47; N, 6.70. Found: C, 51.30; H, 5.36; N, 6.59. mp (dec) = 190 °C. μ_{eff} = 2.67 μ_B.

[(BPPA)YCl$_2$]$_2$ (6). To a suspension of YCl_3 (0.37 g, 1.9 mmol) in 40 mL of THF was added a solution of K(BPPA) (0.87 g, 1.9 mmol) in 35 mL of THF at room temperature. After stirring the yellow reaction mixture for 24 h, the solvent was removed under vacuum. The resultant solid was washed with diethyl ether before extraction with methylene chloride and filtration through Celite. The product was isolated as colorless crystals from THF after storage at −40 °C overnight (0.67 g, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (s, 9 H, *t*-Bu); 1.41 (s, 9 H, *t*-Bu); 3.71 (s, 2 H, $-CH_2-$); 4.02 (d, J_{HH} = 13.5 Hz, 2 H, $-CH_2-$); 4.88 (d, J_{HH} = 13.5 Hz, 2 H, $-CH_2-$); 6.61 (s, 1 H, Ar−H); 6.70 (s, 1 H, Ar−H); 7.07 (m, 2 H, py-H); 7.19 (m, 2 H, py-H); 7.58 (m, 2 H, py-H); 9.50 (s, 2 H, py-H). ^{13}C{^{1}H} NMR (125 MHz, C_5D_5N): δ 25.10, 29.57, 31.41, 33.26, 33.99, 61.89, 67.12, 125.01, 127.96, 128.70, 136.08, 138.10, 157.43, 160.87. IR (cm^{-1}): 1605 (s); 1570 (m); 1299 (s); 1238 (w); 1203 (w); 1167 (w); 1131 (w); 1099 (m); 1056 (w); 1013 (m); 838 (m); 805 (w); 758 (m); 636 (w); 533 (w). Anal. Calcd for $C_{27}H_{34}N_3OYCl_2$: C, 56.25; H, 5.96; N, 7.29. Found: C, 55.93; H, 5.84; N, 7.17. mp (dec) = 278−279 °C.

(BPPA)ZrCl$_3$ (7). To a suspension of $ZrCl_4$ (1.2 g, 3.3 mmol) in 40 mL of THF was added a solution of K(BPPA) (1.5 g, 3.3 mmol) in 20 mL of THF at −70 °C. The yellow reaction mixture was stirred for 12 h at room temperature. After removal of volatiles under vacuum, the crude product was washed with diethyl ether, extracted with methylene chloride, and filtered through a bed of Celite. Removal of solvent under vacuum left analytically pure compound (1.3 g, 64% yield). Colorless crystals of **7** were grown from a concentrated pyridine solution at −15 °C overnight. ^{1}H NMR (400 MHz, C_5D_5N): δ 1.18 (s, 9 H, *t*-Bu); 1.68 (s, 9 H, *t*-Bu); 3.68 (s, 2 H, $-CH_2-$); 4.26 (d, J_{HH} = 15 Hz, 2 H, $-CH_2-$); 5.50 (d, J_{HH} = 15.3 Hz, 2 H, $-CH_2-$); 6.71 (d, J_{HH} = 2.1 Hz, 1 H, Ar−H); 7.14 (d, J_{HH} = 2.4 Hz, 1 H, Ar−H); 7.17 (m, 2 H, py-H); 7.35 (d, J_{HH} = 7.8 Hz, 2 H, py-H); 7.68 (m, 2 H, py-H); 10.27 (d, J_{HH} = 5.1 Hz, 2 H, py-H). ^{13}C{^{1}H} NMR (125 MHz, C_5D_5N): δ 17.06, 31.07, 31.99, 34.62, 35.56, 62.98, 65.76, 104.23, 117.02, 125.16, 140.58, 142.94, 153.75, 158.06, 158.39. IR (cm^{-1}): 1608 (s); 1572 (m); 1533 (w); 1360 (m); 1293 (m); 1255 (s); 1204 (w); 1158 (m); 1129 (w); 1092 (m); 1060 (m); 1013 (s); 978 (w); 915 (m); 847 (s); 812 (w); 760 (s); 732 (s); 682 (w); 639 (m); 603 (m); 552 (m); 471 (m). Anal. Calcd for $C_{27}H_{34}N_3OZrCl_3$: C, 52.79; H, 5.59; N, 6.84. Found: C, 52.80; H, 5.48; N, 6.97. mp (dec) = 170 °C

(BPPA)AlMe$_2$ (8). To a solution of H(BPPA) (1.0 g, 2.4 mmol) in 5 mL of toluene at −78 °C was added $AlMe_3$ (1.2 mL, 2.0 M in hexanes, 2.4 mmol) by syringe, and the reaction mixture was stirred for 6 h at 0 °C. After evaporation of volatiles under vacuum and trituration with pentane, the product was obtained as an off-white solid (2.1 g, 92%). The crude product was of sufficient purity for subsequent reactions; however, it must be stored as a solid below 0 °C to avoid thermal decomposition. ^{1}H NMR (500 MHz, C_6D_6): δ −0.11 (s, 6 H, $AlMe_2$), 1.44 (s, 9 H, *t*-Bu), 1.91 (s, 9 H, *t*-Bu), 3.62 (s, 2 H, $-CH_2-$), 3.90 (br s, 4 H, $-CH_2-$), 6.54 (d, J_{HH} = 7.5 Hz, 2 H, py-H), 6.54 (m, 3 H, Ar−H + py-H), 6.90 (dt, J_{HH} = 7.6 Hz, J_{HH} = 1.5 Hz, 2 H, py-H), 7.63 (d, J_{HH} = 2.5 Hz, 1 H, Ar−H), 8.34 (d, J_{HH} = 4.5 Hz, 2 H, py-H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 30.37, 32.26, 34.18, 35.58, 54.88, 59.46, 119.60, 122.95, 124.04, 124.57, 125.12, 135.74, 136.66, 137.61, 147.89, 153.69, 160.16. ^{27}Al NMR (500 MHz, $CDCl_3$): no signal detected.

(BPPA)AlI$_2$ (9). Method A. To a solution of freshly prepared **8** (17.0 g, 35.9 mmol) in 70 mL of toluene was added a solution of I_2 (18.2 g, 71.8 mmol) in 150 mL of toluene dropwise *via* cannula at −78 °C. The bright purple solution was stirred for 16 h. Following filtration and crystallization from methylene chloride (200 mL), the product was obtained as light orange plates (8.07 g, 32.2%).

Method B. To a suspenstion of AlI_3 (0.893 g, 0.219 mmol) in 30 mL of toluene was added a solution of K(BPPA) (0.100 g, 0.219 mmol) in 20 mL of toluene at −78 °C. The reaction mixture was stirred for 16 h, forming a thick white suspension. Following removal of solvent under vacuum, the product was extracted with methylene chloride (75 mL) and the solvent removed under vacuum to yield the crude product. (0.106 g, 69.6%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.18 (s, 9 H, *t*-Bu), 1.32 (s, 9 H, *t*-Bu), 4.07 (s, 2 H, $-CH_2-$), 4.74 (d, J_{HH} = 16.5 Hz, 2 H, $-CH_2-$), 5.24 (br s, 2 H, $-CH_2-$), 6.87 (s, 1 H, Ar−H), 7.11 (s, 1 H, Ar−H), 7.69 (t, J_{HH} = 6.5 Hz, 2 H, py-H), 7.81 (s, 2 H, Ar−H), 8.18 (s, 2 H, py-H), 9.78 (s, 2 H, py-H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 29.76. 31.72, 34.25, 34.91, 53.62, 58.02, 60.69, 118.94, 124.30, 125.23, 125.29, 138.59, 141.13, 144.05, 150.10, 154.43. ^{27}Al NMR (500 MHz, $CDCl_3$): no signal detected. IR (cm^{-1}): 1615 (m), 1569 (m), 1390 (m), 1360 (m), 1320 (m), 1300 (m), 1285 (m), 1267 (m), 1239 (m), 1204 (w), 1172 (w), 1158 (w), 1131 (w), 1118 (w), 1103 (w), 1059 (s), 1029 (m), 959 (w), 861 (s), 836 (s), 813 (w), 767 (s), 749 (m), 727 (m), 661 (m), 618 (m), 577 (m), 566 (m), 489 (w). Anal. Calcd for $C_{27}H_{34}ON_3AlI_2 \cdot CH_2Cl_2$: C, 42.99; H, 4.64; N, 5.37. Found: C, 43.33; H, 4.58; N, 5.38. mp (dec) = 145 °C.

(BPPA)AlCl$_2$ (10). To a suspension of $AlCl_3$ (1.46 g, 11.0 mmol) in 50 mL of toluene was added a solution of K(BPPA) (5.00 g, 11.0 mmol) in 50 mL of toluene at −78 °C. The reaction mixture was stirred for 16 h, forming a thick white suspension. Following removal of solvent under vacuum, the product was extracted with

methylene chloride (200 mL), filtered through Celite, and stored at −10 °C for 3 days, resulting in the formation of colorless needles (2.35 g, 41.6%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.14 (s, 9 H, *t*-Bu), 1.28 (s, 9 H, *t*-Bu), 3.90 (br s, 2 H, $-CH_2-$), 4.46 (br s, 2 H, $-CH_2-$), 4.75 (d, 2 H, $-CH_2-$), 6.69 (s, 1 H, Ar−H), 6.91 (d, J_{HH} = 2.0 Hz, 1 H, Ar−H), 7.18 (br s, 2 H, py-H), 7.32 (m, 2 H, py-H), 7.71 (s, 2 H, py-H), 9.36 (d, J_{HH} = 5 Hz, 2 H, py-H). ^{13}C-{^{1}H} NMR (125 MHz, $CDCl_3$): δ 30.19, 31.91, 33.98, 34.92, 53.64, 63.51, 120.07, 124.33, 137.59, 140.13, 147.72, 152.73. ^{27}Al NMR (500 MHz, $CDCl_3$): δ 31.5. IR (cm^{-1}): 1612 (m), 1572 (w), 1481 (s), 1459 (m), 1423 (w), 1306 (m), 1284 (m), 1239 (w), 1203 (w), 1155 (w), 1090 (w), 1057 (w), 1027 (w), 930 (w), 878 (m), 842 (m), 777 (m), 760 (m), 737 (m), 647 (m), 612 (w), 576 (w), 559 (w), 521 (w), 494 (w). Anal. Calcd for $C_{27}H_{34}ON_3AlCl_2{\cdot}CH_2Cl_2$: C, 56.11; H, 6.05; N, 7.01. Found: C, 57.03; H, 6.11; N, 7.06. mp (dec) = 221 °C.

(BPPA)AlBr$_2$ (11). 11 was prepared in an analogous manner to **10** with $AlBr_3$ (2.93 g, 11.0 mmol). The product was obtained as colorless needles after crystallization from methylene chloride (2.34 g, 35.4%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.12 (s, 9 H, *t*-Bu), 1.30 (s, 9 H, *t*-Bu), 3.94 (s, 2 H, $-CH_2-$), 4.51 (d, J_{HH} = 15.5 Hz, 2 H, $-CH_2-$), 5.06 (d, J_{HH} = 15.5 Hz, 2 H, $-CH_2-$), 6.72 (d, J_{HH} = 2.5 Hz, 1 H, Ar−H), 6.92 (d, J_{HH} = 2.5 Hz, 1 H, Ar−H), 7.31 (m, 4 H, py-H), 7.74 (m, 2 H, py-H), 9.48 (d, J_{HH} = 5.0 Hz, 2 H, py-H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 30.24, 31.83, 33.98, 34.84, 53.63, 60.94, 63.11, 120.09, 122.73, 123.38, 124.26, 124.50, 128.39, 129.19, 137.66, 138.41, 140.79, 147.61, 152.97, 158.43. ^{27}Al NMR (500 MHz, $CDCl_3$): δ 29.2. IR (cm^{-1}): 1613 (s), 1571 (m), 1377 (m), 1361 (m), 1295 (m), 1275 (m), 1238 (m), 1204 (w), 1169 (w), 1157 (m), 1133 (m), 1088 (m), 1057 (m), 1027 (m), 981 (w), 929 (w), 913 (w), 879 (m), 840 (s), 810 (w), 777 (s), 735 (s), 657 (m), 612 (m), 577 (m), 561 (m), 521 (w), 495 (w), 468 (w), 449 (w). Anal. Calcd for $C_{27}H_{34}ON_3AlBr_2{\cdot}0.5CH_2Cl_2$: C, 51.14; H, 5.46; N, 6.51. Found: C, 50.68; H, 5.29; N, 6.59. mp (dec) = 220 °C.

(BPPA)GaCl$_2$ (12). To a suspension of $GaCl_3$ (2.96 g, 16.8 mmol) in 100 mL of toluene (100 mL) at −78 °C was added a solution of K(BPPA) (7.65 g, 16.8 mmol) in 200 mL of toluene. The solution was then allowed to warm to room temperature and was stirred for 16 h, forming a thick white suspension. Following evaporation of volatiles under vacuum, the residue was triturated with pentane, extracted with methylene chloride (200 mL), and filtered through Celite. Colorless needles formed after storage at −10 °C for 7 days (1.59 g, 17.2%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.11 (s, 9 H, *t*-Bu), 1.32 (s, 9 H, *t*-Bu), 3.83 (br s, 2 H, $-CH_2-$), 4.36 (br s, 2 H, $-CH_2-$), 4.84 (br s, 2 H, $-CH_2-$), 6.64 (s, 1 H, Ar−H), 6.87 (s, 1 H, Ar−H), 7.19 (br s, 2 H, py-H), 7.40 (br s, 2 H, py-H), 7.77 (s, 2 H, py-H), 9.22 (s, 2 H, py-H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 30.31, 31.92, 33.96, 35.04, 53.64, 59.77, 66.46, 119.85, 122.77, 123.77, 124.55, 124.74, 137.70, 138.21, 140.47, 146.75, 151.26, 160.86. IR (cm^{-1}): 1608 (m), 1574 (w), 1422 (s), 1377 (m), 1361 (m), 1394 (m), 1279 (s), 1238 (m), 1203 (w), 1167 (w), 1155 (w), 1096 (w), 1054 (m), 1023 (w), 981 (w), 929 (m), 878 (w), 833 (m), 776 (s), 759 (m), 736 (s), 646 (w), 536 (w), 512 (w), 430 (w). Anal. Calcd for $C_{27}H_{34}ON_3GaCl_2{\cdot}CH_2Cl_2$: C, 52.37; H, 5.65; N, 6.54. Found: C, 53.04; H, 5.53; N, 6.57. mp (dec) = 259 °C.

(BPPA)UI$_3$ (13). To a solution of $UI_3(THF)_4$ (0.903 g, 1.0 mmol) in 25 mL of diethyl ether at 0 °C was added a solution of K(BPPA) (0.455 g, 1.0 mmol) in 25 mL of diethyl ether. The resulting dark brown solution was allowed to warm to room temperature and was stirred overnight. The solvent was removed under vacuum, and the resulting dark solid was extracted with methylene chloride. The resultant dark green solution was filtered and concentrated affording emerald green, X-ray quality crystals of **13** after storage for 24 h at −40 °C (0.181 g, 18%). ^{1}H NMR (300 MHz, $CDCl_3$): δ −22.1 (br, s); −14.9 (br, s); −9.5 (br, s); −4.4 (br, s); 12.8 (br, s); 24.3 (br, s); 32.1 (br, s); 46.8 (br, s); 50.7 (br, s). IR (cm^{-1}): 1603 (s), 1323 (m), 1302 (m), 1261 (m), 1224 (m), 1201 (m), 1167 (m), 1126 (m), 1100 (m), 1084 (m), 1056 (m), 1012 (s), 967 (w) 947 (w), 915 (m), 847 (s), 831 (s), 809 (s), 751 (m), 724 (s), 669 (m), 638 (m), 595 (s), 464 (w). Calc for $C_{27}H_{34}I_3N_3O_1U_1$: C, 31.32; H, 3.31; N, 4.06. Found: C, 31.20; H, 3.64; N, 3.83%. mp = 176−179 °C.

(BPPA)Zr(CH$_2$Ph)$_3$ (14). To a solution of $Zr(CH_2Ph)_4$ (1.51 g, 3.32 mmol) in 50 mL of diethyl ether was added a solution of H(BPPA) (1.39 g, 3.32 mmol) in 50 mL of diethyl ether at −40 °C. After 3 h, the cold bath was removed, and the solvent was removed under vacuum leaving a bright orange powder that was extracted with DME ensuring the temperature was maintained below 0 °C. The solution was quickly filtered and concentrated, yielding large orange parallelograms (0.96 g, 36%) after cooling overnight at −40 °C. ^{1}H NMR (300 MHz, THF-d_8): δ 1.25 (s, 9 H, *t*-Bu); 1.55 (s, 9 H, *t*-Bu); 2.60 (br s, 6 H, C*H*$_2$Ph); 3.11 (s, 2 H, CH_2); 3.15 (d, J_{HH} = 15.9 Hz, 2 H, $-CH_2-$); 3.35 (d, J_{HH} = 16.2 Hz, 2 H, $-CH_2-$); 6.66 (d, J_{HH} = 2.4 Hz, 1 H, Ar−H); 6.92 (d, J_{HH} = 7.8 Hz, 2 H, py-H); 7.06 (d, J_{HH} = 2.4 Hz, 1 H, Ar−H); 7.41 (m, 2 H, py-H); 7.67 (m, 2 H, py-H); 9.00 (d, J_{HH} = 5.1 Hz, 2 H, py-H). ^{13}C{^{1}H} NMR (125 MHz, THF-d_8): δ 29.43, 29.54, 30.13, 30.97, 31.11, 33.51, 34.56, 12208, 123.02, 123.35, 123.59, 124.36, 124.99, 126.26, 126.54, 127.34, 127.86, 128.08, 128.63, 134.84, 136.60, 138.16, 149.11, 156.68. IR (cm^{-1}): 1590 (s); 1414 (w); 1304 (m); 1273 (m); 1239 (w); 1205 (s); 1173 (m); 1090 (m); 1009 (m); 976 (s); 842 (m); 800 (m); 745 (s); 699 (s); 612 (w); 543 (m). mp (dec) = 180−185 °C.

[(BPPA)Zr(CH$_2$Ph)$_2$][B(C$_6$F$_5$)$_4$] (16). To an NMR tube containing (BPPA)$Zr(CH_2Ph)_3$ (0.010 g, 0.013 mmol) and $H[B(C_6F_5)_4{\cdot}2Et_2O]$ (0.011 g, 0.013 mmol) was added C_6D_5Cl. The resulting yellow-orange solution was analyzed by NMR spectroscopy. ^{1}H NMR (400 MHz, C_6D_5Cl): δ 1.21 (s, 9 H, *t*-Bu); 1.33 (s, 9 H, *t*-Bu); 3.07 (br s, 2 H, $-CH_2-$); 3.42 (d, J_{HH} = 16.4 Hz, 2 H, $-CH_2-$); 3.90 (d, J_{HH} = 16.4 Hz, 2 H, $-CH_2-$); 6.59 (d, J_{HH} = 7.6 Hz, 2 H, py-H); 6.68 (br s, 2 H, py-H); 6.76 (m, 2 H, py-H); 7.25 (d, J_{HH} = 2.4 Hz, 1 H, Ar−H); 8.26 (d, J_{HH} = 5.2 Hz, 2 H, py-H). ^{19}F NMR (400 MHz, C_6D_5Cl): δ −130.92 (s); −161.18 (t, J_{FF} = 24 Hz); −165.12 (m).

Results and Discussion

Ligand Synthesis and Characterization. H(BPPA) was synthesized by a two-step reaction. A solution of 2-(aminomethyl)pyridine was treated with 2-pyridinecarboxaldehyde in ethanol followed by reduction with $NaBH_4$. This simple procedure afforded DPA in high yield. Subsequent reaction of DPA with paraformaldehyde, followed by 2,4-di-*tert*-butylphenol in refluxing methanol for 24 h yielded H(BPPA), which was obtained in high yield as a crystalline solid.

The reaction of H(BPPA) with excess KH resulted in the isolation of the alkali metal salt **1** in high yield after filtration and evaporation of solvent under vacuum. The salt can be used without further purification or can be crystallized from toluene at −40 °C. The Li (**2**) and Na (**3**) analogues were synthesized through the reaction of H(BPPA) with $LiN(SiMe_3)_2$ and NaH, respectively. Both were crystallized from toluene at −40 °C as colorless crystals in good yield.

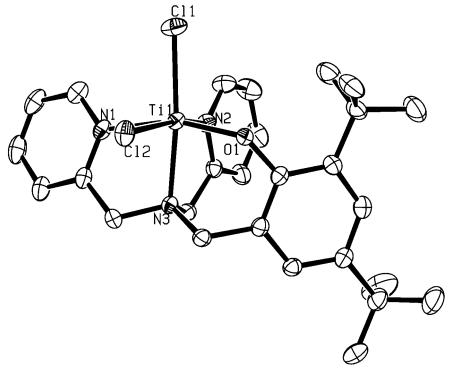
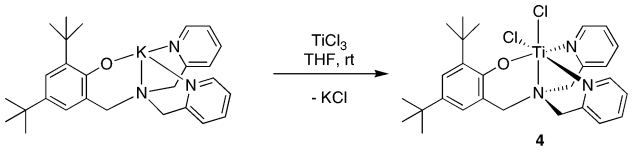


Figure 1. Thermal ellipsoid (50%) plot of **4**. Hydrogen atoms and solvent molecules have been omitted for clarity.

Scheme 1. Synthesis of **4**

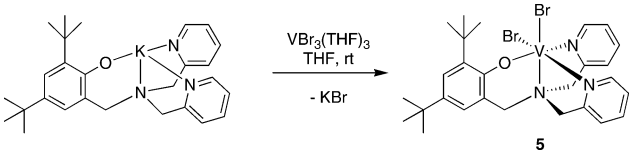


4

Table 1. Selected Bond Lengths (Å) and Angles (deg) for (BPPA)$TiCl_2$ (**4**)

Ti(1)−Cl(1)	2.385(1)	Ti(1)−Cl(2)	2.417(1)
Ti(1)−O(1)	1.862(2)	Ti(1)−N(1)	2.230(3)
Ti(1)−N(2)	2.208(3)	Ti(1)−N(3)	2.235(3)
Cl(1)−Ti(1)−Cl(2)	93.85(4)	Cl(1)−Ti(1)−O(1)	102.44(7)
Cl(1)−Ti(1)−N(1)	96.38(8)	Cl(1)−Ti(1)−N(2)	94.71(8)
Cl(1)−Ti(1)−N(3)	167.86(7)	Cl(2)−Ti(1)−O(1)	100.34(7)
Cl(2)−Ti(1)−N(1)	87.82(8)	Cl(2)−Ti(1)−N(2)	166.91(8)
Cl(2)−Ti(1)−N(3)	92.58(7)	O(1)−Ti(1)−N(1)	158.8(1)
O(1)−Ti(1)−N(2)	87.46(10)	O(1)−Ti(1)−N(3)	86.49(9)
N(1)−Ti(1)−N(2)	81.40(10)	N(1)−Ti(1)−N(3)	73.57(10)
N(2)−Ti(1)−N(3)	77.30(10)		

Scheme 2. Synthesis of **5**



5

Synthesis and Characterization of BPPA Metal−Halide Complexes. Early Metals. The reaction of K(BPPA) and $TiCl_3$ in THF proceeded cleanly giving **4**, which was isolated as dark red crystals in 55% yield (Scheme 1). X-ray quality crystals were grown from methylene chloride at −15 °C; the solid-state X-ray structure is shown in Figure 1, with selected bond lengths and angles provided in Table 1. The titanium atom in compound **4** is six-coordinate with the ligand bound in a tetradentate manner and two terminal chlorides completing the octahedron. The Ti−Cl bond lengths of 2.417(1) and 2.385(1) Å are similar to those in the related Ti(IV) compound $Ti(O_2{}^{tBu}NN')Cl_2$ (2.3929(12) and 2.2840(12) Å).[67] The Ti−O (1.862(2) Å) and Ti−N_{py} (2.230(3) and 2.208(3) Å) bond distances also correlate well with the literature values.[67] The room-temperature, solution magnetic susceptibility ($\mu_{eff} = 1.71\ \mu_B$) is close to the spin-only value of 1.73 μ_B for a d^1 complex.[68]

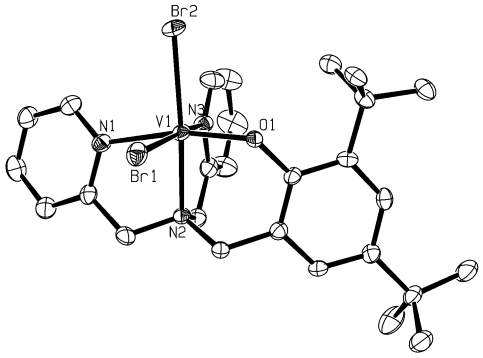


Figure 2. Thermal ellipsoid (50%) plot of **5**. Hydrogen atoms and solvent molecules have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (BPPA)VBr_2 (**5**)

V(1)−Br(1)	2.549(1)	V(1)−Br(2)	2.543(1)
V(1)−O(1)	1.851(4)	V(1)−N(1)	2.176(4)
V(1)−N(2)	2.165(4)	V(1)−N(3)	2.131(5)
Br(1)−V(1)−Br(2)	92.18(3)	Br(1)−V(1)−O(1)	95.5(1)
Br(1)−V(1)−N(1)	87.8(1)	Br(1)−V(1)−N(2)	94.1(1)
Br(1)−V(1)−N(3)	170.3(1)	Br(2)−V(1)−O(1)	96.4(1)
Br(2)−V(1)−N(1)	96.3(1)	Br(2)−V(1)−N(2)	170.8(1)
Br(2)−V(1)−N(3)	93.0(1)	O(1)−V(1)−N(1)	166.7(2)
O(1)−V(1)−N(2)	89.7(2)	O(1)−V(1)−N(3)	92.0(2)
N(1)−V(1)−N(2)	77.2(2)	N(1)−V(1)−N(3)	83.5(2)
N(2)−V(1)−N(3)	79.8(2)		

5 was synthesized through the metathesis reaction of K(BPPA) with $VBr_3(THF)_3$ in THF and was isolated as dark red crystals in 71% yield (Scheme 2). X-ray quality crystals of **5** were grown by vapor diffusion of diethyl ether into a methylene chloride solution of **5** at room temperature. The structure is shown in Figure 2, with selected bond lengths and angles given in Table 2. As with **4**, the vanadium atom is six-coordinate with a κ^4-bound ligand in addition to two terminal bromides. The V−Br bond lengths of 2.549(1) and 2.543(1) Å are slightly longer than the bond distance found in [VBr(NS_2S_2')] (2.5029(3) Å).[69] The V−O bond length of 1.851(4) Å is slightly shorter than the V−O bond lengths in [V(salophen)$(py)_2$][$ZnCl_3$py] (1.915(9) and 1.88(1) Å);[70] however, the V−N_{py} bond lengths (2.176(4) and 2.131(5) Å) agree well with those observed in [V(salophen)$(py)_2$]-[$ZnCl_3$py]. The structure of **4** is more distorted from octahedral with N(3)−Ti(1)−Cl(1), N(2)−Ti(1)−Cl(2), and O(1)−Ti(1)−N(1) angles of 167.86(7)°, 166.91(8)°, and 158.8(1)° than **5** with N(2)−V(1)−Br(2), N(3)−V(1)−Br-(1), and O(1)−V(1)−N(1) angles of 170.8(1)°, 170.3(1)°, and 166.7(1)°. Complex **5** gives a $\mu_{eff} = 2.7\ \mu_B$, which falls in the range of expected spin-only values of 2.6−2.8 μ_B for a V^{3+} d^2 complex.[68]

The redox properties of compounds **4** and **5** were investigated using cyclic voltammetry, and the results are

(67) Boyd, C. L.; Toupance, T.; Tyrrell, B. R.; Ward, B. D.; Wilson, C. R.; Cowley, A. R.; Mountford, P. *Organometallics* **2005**, *24*, 309−330.

(68) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1980; pp 627−628.

(69) Nekola, H.; Wang, D.; Gruning, C.; Gatjens, J.; Behrens, A.; Rehder, D. *Inorg. Chem.* **2002**, *41*, 2379−2384.

(70) Mazzanti, M.; Gambarotta, S.; Floriani, C.; Chiesivilla, A.; Guastini, C. *Inorg. Chem.* **1986**, *25*, 2308−2314.

Table 3. Electrochemical Data for **4** and **5**[a]

	oxidation	reduction
(BPPA)$TiCl_2$	−0.588 V[b]	−2.55 V
(BPPA)VBr_2	+0.100 V[b]	−1.84 V

[a] Potentials are referenced to Fc/Fc^+. Cyclic voltammograms recorded at a scan rate of 25 mV/s in CH_2Cl_2 with [nBu$_4$N][PF_6] (0.3 M) as the supporting electrolyte. [b] Reversible process.

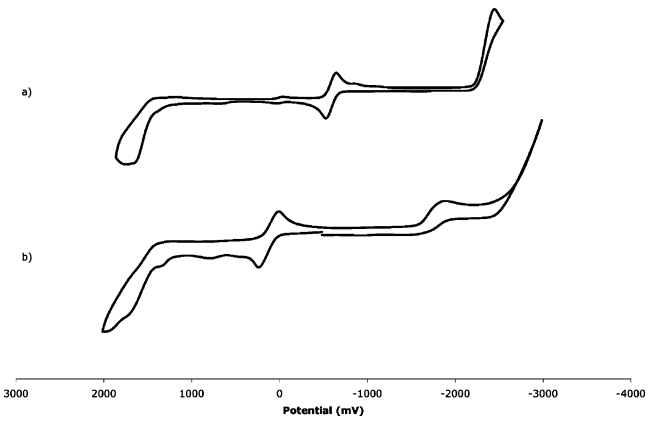
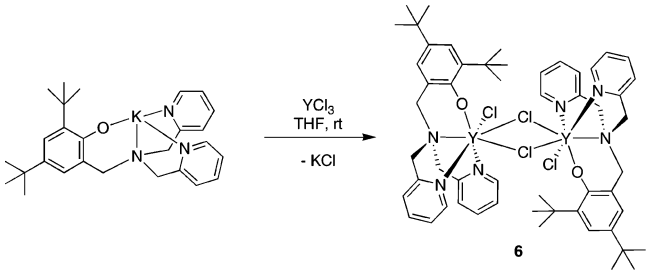


Figure 3. Cyclic voltammograms of **4** (a) and **5** (b).

Scheme 3. Synthesis of **6**



summarized in Table 3. Representative cyclic voltammograms (CV) are shown in Figure 3. The CV of **4** shows a reversible oxidation at −0.588 V for the Ti(III)/Ti(IV) couple and an irreversible reduction at −2.55 V. Similarly, the CV of **5** also shows a reversible oxidation at +0.100 V and an irreversible reduction at −1.35 V.

The reaction of K(BPPA) with YCl_3 in THF led cleanly to the formation of **6** (Scheme 3). Large colorless blocks suitable for X-ray crystallography were grown from a solution of methylene chloride layered with pentane at room temperature and isolated in 61% yield. The solid-state X-ray structure of **6** is shown in Figure 4, with selected bond lengths and angles given in Table 4. Dimeric **6** is seven-coordinate in the solid state with each yttrium atom bound to the BPPA ligand in addition to one terminal and two bridging chlorides. The two halves of the dimer are related by a center of inversion between the two yttrium atoms, with the asymmetric unit being the (BPPA)YCl_2 fragment. The $Y-N_{py}$ bond distances of 2.572(4) and 2.501(3) Å are similar to the value found in the related compound $Y_2(O_2{}^{tBu}NN')_2(-Cl)_2(py)_2$ (2.520(7) Å),[67] as is the Y−O bond distance of 2.127(3) Å (2.155(6) and 2.139(5) Å). The bridging Y−Cl bond lengths of 2.671(1) and 2.794(1) Å are also comparable to those found in $Y_2(O_2{}^{tBu}NN')_2(\mu\text{-}Cl)_2(py)_2$ (2.744(2) and

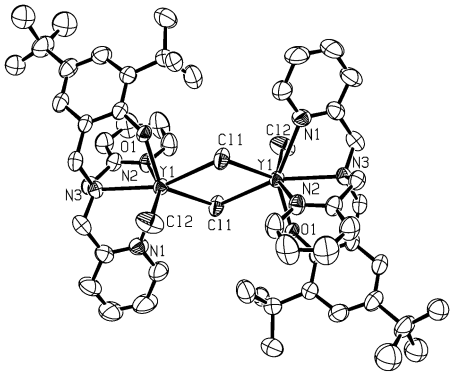
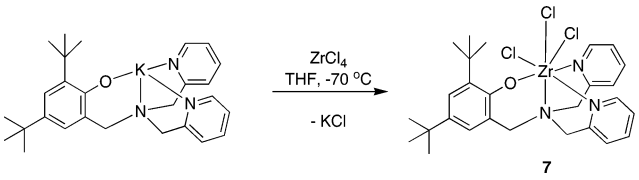


Figure 4. Thermal ellipsoid (50%) plot of **6**. Hydrogen atoms, modeled disorder in *tert*-butyl groups, and solvent molecules have been omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [(BPPA)YCl_2]$_2$ (**6**)

Y(1)−Cl(1)	2.671(1)	Y(1)-Cl(1*)	2.794(1)
Y(1)−Cl(2)	2.586(1)	Y(1)−O(1)	2.127(3)
Y(1)−N(1)	2.572(4)	Y(1)−N(2)	2.501(3)
Y(1)−N(3)	2.521(3)		
Cl(1)−Y(1)−Cl(1*)	73.62(4)	Cl(1)−Y(1)−Cl(2)	116.06(4)
Cl(1)−Y(1)−O(1)	128.77(8)	Cl(1)−Y(1)−N(1)	80.62(9)
Cl(1)−Y(1)−N(2)	78.37(8)	Cl(1)−Y(1)−N(3)	131.91(8)
Cl(2)−Y(1)−O(1)	100.95(8)	Cl(2)−Y(1)−N(1)	79.07(9)
Cl(2)−Y(1)−N(2)	157.07(9)	Cl(2)−Y(1)−N(3)	89.83(8)
O(1)−Y(1)−N(1)	143.3(1)	O(1)−Y(1)−N(2)	80.3(1)
O(1)−Y(1)−N(3)	78.8(1)	N(1)−Y(1)−N(2)	86.4(1)
N(1)−Y(1)−N(3)	64.6(1)	N(2)−Y(1)−N(3)	67.8(1)
Y(1)−Cl(1)−Y(1*)	106.38(4)		

Scheme 4. Synthesis of **7**



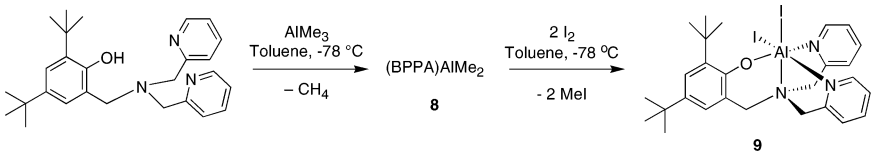
2.789(2) Å).[71] In solution, the ^{1}H NMR spectrum of **6** indicates the presence of equivalent pyridyl groups. Also of note are the two equivalent diastereotopic methylene resonances corresponding to the two 2-picolyl fragments, indicating the ligand remains fully coordinated in solution.

The metathesis reaction between K(BPPA) and $ZrCl_4$ in THF led to the formation of **7** in 64% yield (Scheme 4). Compound **7** is sparingly soluble in THF and methylene chloride but can be crystallized from pyridine at −15 °C. Though numerous attempts were made, crystals suitable for X-ray crystallography were not obtained. The ^{1}H NMR spectrum of **7** in pyridine-d_5 is nearly identical to that of **6** in the same solvent. This similarity suggests the zirconium atom may be seven-coordinate with three bound chlorides and a κ^4-bound ligand, as was observed in the case of **6**.

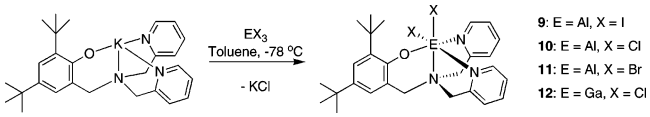
Group 13 Metals. The synthesis of Group 13 metal−BPPA complexes can be achieved via two routes: protonolysis and metathesis. Compound **8** was prepared by reaction of $AlMe_3$ with H(BPPA) in toluene at −78 °C. Following removal of solvent under vacuum, **8** was obtained as an off-white solid and was characterized by ^{1}H and ^{13}C-

(71) Long, D. P.; Chandrasekaran, A.; Day, R. O.; Bianconi, P. A.; Rheingold, A. L. *Inorg. Chem.* **2000**, *39*, 4476−4487.

Scheme 5. Synthesis of **8** and **9**



Scheme 6. Synthesis of Group 13 BPPA Halide Complexes (E = Al, X = Cl, Br, I; E = Ga, X = Cl)



{^{1}H} NMR spectroscopy. Attempts to crystallize **8** from a variety of solvent systems were unsuccessful. Compound **8** is stable below 0 °C and can be stored cold as the solid or in solution for several months without visible decomposition. Upon warming to room temperature, solutions and solid samples of **8** decomposed, as evidenced by a color change from colorless to magenta. Upon mild heating of a sealed NMR tube of **8** in C_6D_6, decomposition was observed with concomitant release of CH_4 (see below).

Halogenation of **8** with 2 equiv of I_2 in toluene at −78 °C afforded **9** as orange plates following crystallization from methylene chloride (Scheme 5). The ^{1}H NMR spectrum of **9** shows two sharp diastereotopic methylene resonances, assigned to the 2-picolyl groups, as well as equivalent pyridyl groups suggesting full coordination of the ligand in solution. No ^{27}Al NMR shift was observed, presumably as a result of the large quadrupole moment for aluminum. Crystals of **9** were of twinned and were not suitable for X-ray structural analysis.

The aluminum dichloride (**10**) and dibromide (**11**) complexes of BPPA were prepared *via* reaction of K(BPPA) with $AlCl_3$ and $AlBr_3$, respectively (Scheme 6). Both **10** and **11** were crystallized from methylene chloride, yielding fine colorless needles. X-ray quality crystals of **10** were obtained by vapor diffusion of pentane into a methylene chloride solution. The structure of **10** is shown in Figure 5, with selected bonds and angles provided in Table 5. The aluminum atom is six-coordinate with a κ^4-bound BPPA ligand and two terminal chlorides. The octahedral coordination geometry around the aluminum center is distorted as a result of the chelating ligand, with N(1)−Al(1)−Cl(1), N(2)−Al(1)−Cl(1), and N(3)−Al(1)−O(1) angles all ∼170°. The Al(1)−Cl(1) bond length is slightly longer than that of Al(1)−Cl(2) due to the greater trans influence of pyridine than amine. The bond lengths about the aluminum atom are slightly shorter when compared with the related compound $L_2Al_2Cl_2$(py) (L = MeC(O)CHC{NCH2CH(Me)O}Me) (Al−Cl = 2.3936(5) Å, Al−O = 1.8823(10) Å, Al−N_{py} = 2.1373(12) Å) but remain consistent with those of other crystallographically characterized six-coordinate Al(III) compounds.[72]

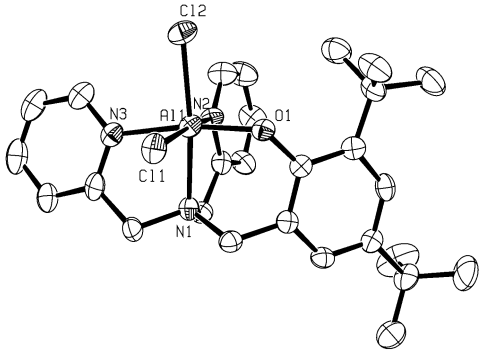


Figure 5. Thermal ellipsoid (50%) plot of **10**. Hydrogen atoms and solvent molecules have been omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for (BPPA)$AlCl_2$ (**10**)

Al(1)−Cl(1)	2.306(2)	Al(1)−Cl(2)	2.259(2)
Al(1)−O(1)	1.802(3)	Al(1)−N(1)	2.098(4)
Al(1)−N(2)	2.081(4)	Al(1)−N(3)	2.084(4)
Cl(1)−Al(1)−Cl(2)	92.7(1)	Cl(1)−Al(1)−O(1)	95.9(1)
Cl(1)−Al(1)−N(1)	91.4(1)	Cl(1)−Al(1)−N(2)	170.1(1)
Cl(1)−Al(1)−N(3)	88.5(1)	Cl(2)−Al(1)−O(1)	95.3(1)
Cl(2)−Al(1)−N(1)	171.1(1)	Cl(2)−Al(1)−N(2)	94.1(1)
Cl(2)−Al(1)−N(3)	94.4(1)	O(1)−Al(1)−N(1)	92.2(2)
O(1)−Al(1)−N(2)	89.8(2)	O(1)−Al(1)−N(3)	169.2(2)
N(1)−Al(1)−N(2)	81.1(2)	N(1)−Al(1)−N(3)	77.8(2)
N(2)−Al(1)−N(3)	84.6(2)		

In contrast to **9**, the solution ^{1}H NMR spectrum of **10** reveals two broad diastereotopic 2-picolyl methylene resonances, indicating that the complex may exhibit some fluxional behavior in solution; however, the ^{27}Al NMR shift of 31.5 ppm is within the range commonly encountered for six-coordinate aluminum complexes.[73] No crystallographic data were obtained for **11**, but the ^{1}H NMR spectrum has similar resonances to the spectrum of **9**. Furthermore, the ^{27}Al NMR shift of 29.2 ppm also suggests a six-coordinate environment.[73]

The reaction of K(BPPA) and $GaCl_3$ afforded **12** in modest yield (Scheme 6). Large colorless needles of **12** suitable for X-ray diffraction were grown by vapor diffusion of pentane into a methylene chloride solution of **12** at 5 °C. The solid-state structure of **12** is isostructural with that of **10**, as shown in Figure 6 with selected bond lengths and angles provided in Table 6. The bond lengths about the gallium atom are slightly shorter when compared with the related compound $GaCl(1,2\text{-}O_2C_6Cl_4)$(py)(phen) (py = C_5H_5N, phen = 1,10-phenanthroline) (Ga−O = 1.952(4) Å, Ga−N_{py} = 2.155(4) Å, Ga−Cl = 2.329(2) Å) but remain consistent with those of other crystallographically characterized six-coordinate Ga(III) compounds.[74]

Uranium. Reaction of $UI_3(THF)_4$ with K(BPPA) led to the subsequent isolation of the product **13** in relatively low yield, presumably *via* disproportionation of the metal.

(72) Doherty, S.; Errington, R. J.; Housley, N.; Clegg, W. *Organometallics* **2004**, *23*, 2382−2388.
(73) Atwood, D. A.; Harvey, M. J. *Chem. Rev.* **2001**, *101*, 37−52.
(74) Lawson, Y. G.; Norman, N. C.; Orpen, A. G.; Quayle, M. J. *Acta Crystallogr., Sect. C* **1997**, *53*, 1805−1809.

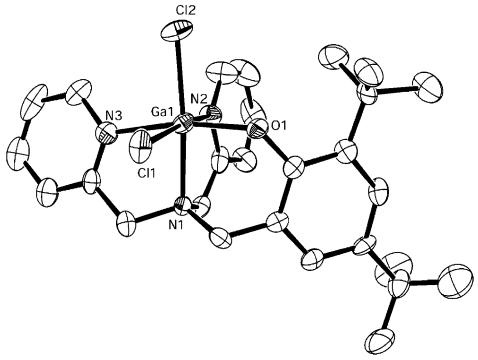


Figure 6. Thermal ellipsoid (50%) plot of **12**. Hydrogen atoms and solvent molecules have been omitted for clarity.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for (BPPA)$GaCl_2$ (**12**)

Ga(1)−Cl(1)	2.332(2)	Ga(1)−Cl(2)	2.278(2)
Ga(1)−O(1)	1.891(5)	Ga(1)−N(1)	2.144(7)
Ga(1)−N(2)	2.138(7)	Ga(1)−N(3)	2.150(7)
Cl(1)−Ga(1)−Cl(2)	94.0(1)	Cl(1)−Ga(1)−O(1)	96.1(2)
Cl(1)−Ga(1)−N(1)	90.8(2)	Cl(1)−Ga(1)−N(2)	169.9(2)
Cl(1)−Ga(1)−N(3)	87.9(2)	Cl(2)−Ga(1)−O(1)	94.9(2)
Cl(2)−Ga(1)−N(1)	171.2(2)	Cl(2)−Ga(1)−N(2)	93.7(2)
Cl(2)−Ga(1)−N(3)	96.5(2)	O(1)−Ga(1)−N(1)	91.9(2)
O(1)−Ga(1)−N(2)	89.8(2)	O(1)−Ga(1)−N(3)	167.6(3)
N(1)−Ga(1)−N(2)	80.8(3)	N(1)−Ga(1)−N(3)	76.3(3)
N(2)−Ga(1)−N(3)	84.6(3)		

Although this was unexpected, the isolation of **13** was reproducible, albeit in low crystalline yield. Attempts to isolate the U(IV) chloride analogue directly from interaction of UCl_4 and K(BPPA) failed to yield any isolable crystalline material. X-ray quality crystals of **13** were grown from a concentrated solution of methylene chloride at −40 °C. The X-ray structure is shown in Figure 7, with selected bond lengths and angles provided in Table 7. The solid-state structure shows a monomeric U(IV) coordinated κ^4 by the BPPA ligand and to three terminal iodides. The seven-coordinate uranium is best described as distorted pentagonal bipyrimidal. The two U−N_{py} bond lengths (2.616(2) and 2.627(2) Å) are comparable to those in [U(tpa)(OMe)I_3] (tpa = tris[(2-pyridyl)methyl]amine) (U−$N_{pyridyl}$ = 2.61(3) Å av).[75] The basal U−N bond length (2.591(2) Å) is significantly shorter than in [U(tpa)(OMe)I_3] (2.6672(18) Å),[75] though comparable with the shortest U−N_{py} bond in [UI_4(py)$_3$] (2.586(4) Å).[76] The U−O bond length (2.050(4) Å) is shorter than those in [U(OPh)$_4$(dmpe)$_2$] (U−O = 2.158(3)−2.182(4) Å),[77] [U(O(2,6-^{t}Bu(C_6H_3))$_3$(NEt_2)] (U−O = 2.140(3)−2.146(5) Å)[78] and in [U(O(2,6-^{t}Bu(C_6H_3))$_4$] (U−O = 2.136(5) Å).[79,80] The three U−I bonds are within error (3.067(3), 3.057(6), and 3.057(4) Å) and are slightly shorter than the U−I bond lengths in [U(tpa)(OMe)I_3] (tpa = tris-[(2-pyridyl)methyl]amine) (3.1776(2), 3.1678(2), and 3.1931(2) Å).[75]

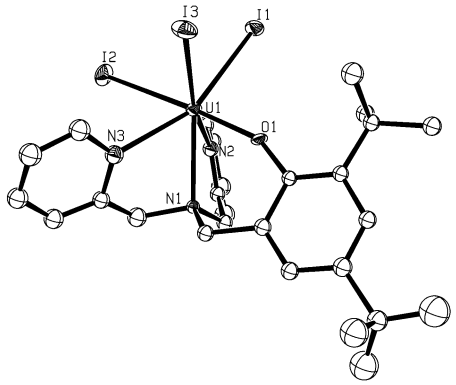


Figure 7. Thermal ellipsoid (30%) plot of **13**. Hydrogen atoms and solvent molecules have been omitted for clarity.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for (BPPA)UI_3 (**13**)

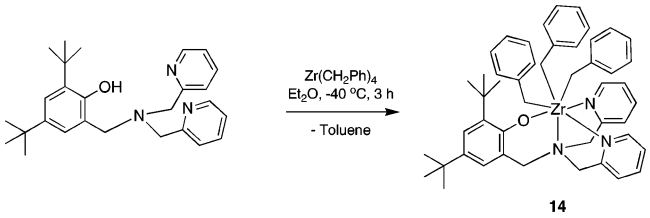
U(1)−I(1)	3.067(3)	U(1)−N(2)	2.627(3)
U(1)−I(2)	3.057(6)	U(1)−N(3)	2.591(2)
U(1)−I(3)	3.057(4)	U(1)−O(1)	2.050(4)
U(1)−N(1)	2.616(2)		
I(1)−U(1)−I(2)	90.26(2)	I(3)−U(1)−N(1)	82.76(3)
I(1)−U(1)−I(3)	84.25(6)	I(3)−U(1)−N(2)	164.34(5)
I(2)−U(1)−I(3)	41.58(5)	I(3)−U(1)−N(3)	130.98(4)
I(1)−U(1)−O(1)	90.32(3)	I(3)−U(1)−O(1)	89.13(3)
I(1)−U(1)−N(1)	158.03(4)	N(1)−U(1)−N(2)	110.75(2)
I(1)−U(1)−N(2)	80.42(3)	N(1)−U(1)−N(3)	64.33(5)
I(1)−U(1)−N(3)	136.42(4)	N(1)−U(1)−O(1)	107.10(4)
I(2)−U(1)−N(1)	73.84(4)	N(2)−U(1)−N(3)	64.11(3)
I(2)−U(1)−N(2)	80.12(5)	N(2)−U(1)−O(1)	94.09(4)
I(2)−U(1)−N(3)	106.66(4)	N(3)−U(1)−O(1)	69.07(3)
I(2)−U(1)−O(1)	174.01(2)		

BPPA Metal−Alkyl Complexes. Numerous reactions with **6** and alkylating reagents such as LiR, MgR_2, RMgCl, and ZnR_2 were attempted. In a typical reaction, for example, the metal complex was suspended in THF at −70 °C before the slow addition of a THF solution of alkylating reagent, and then the reaction mixture was warmed to room temperature. The colorless starting materials changed color to dark red upon warming under all conditions examined. The solution ^{1}H NMR spectrum of the crude intractable material displayed a multitude of resonances between 1.5 and 2.0 ppm.

The protonolysis of Y−C bonds has been shown to be effective for preparing ligated metal complexes,[30,31,81] and with this in mind, the protonolysis reaction of H(BPPA) and $Y(CH_2SiMe_3)_3(THF)_2$ was explored in pentane. As the reaction proceeded at −70 °C, a white solid precipitated from the colorless reaction mixture. Upon removal of the cold bath, the solution quickly changed color to forest green and finally to dark red before reaching room temperature.[53] No isolable product could be obtained from the intractable mixture that was formed.

(75) Karmazin, L.; Mazzanti, M.; Pecaut, J. *Inorg. Chem.* **2003**, *42*, 5900−5908.
(76) Berthet, J. C.; Thuery, P.; Ephritikhine, M. *Inorg. Chem.* **2005**, *44*, 1142−1146.
(77) Edwards, P. G.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1981**, *103*, 7792−7794.
(78) Hitchcock, P. B.; Lappert, M. F.; Singh, A.; Taylor, R. G.; Brown, D. *J. Chem. Soc., Chem. Commun.* **1983**, 561−3.
(79) Berg, J. M.; Clark, D. L.; Huffman, J. C.; Morris, D. E.; Sattelberger, A. P.; Streib, W. E.; Van der Sluys, W. G.; Watkin, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 10811−21.
(80) Vandersluys, W. G.; Sattelberger, A. P. *Polyhedron* **1989**, *8*, 1247−1249.
(81) Bambirra, S.; Boot, S. J.; van Leusen, D.; Meetsma, A.; Hessen, B. *Organometallics* **2004**, *23*, 1891−1898.

Scheme 7. Synthesis of **14**



14

All attempts to alkylate **7** with standard alkylating reagents were thwarted by decomposition. As with yttrium, the colorless reaction mixtures turned dark red upon warming to room temperature, and intractable material was obtained. It was found, nonetheless, that the reaction of H(BPPA) and $Zr(CH_2Ph)_4$ in diethyl ether at −40 °C led cleanly to the formation of **14** (Scheme 7). Isolation of **14** was accomplished by removal of solvent under vacuum at 0 °C, leaving a bright orange powder. The desired product was extracted with DME, quickly filtered, and concentrated. Cooling to −40 °C led to the isolation of thermally unstable, orange parallelograms of **14** in 36% yield. X-ray quality crystals grown from DME at −40 °C provided the solid-state X-ray structure shown in Figure 8 (selected bond lengths and angles in Table 8). The zirconium atom is seven-coordinate with a κ^4-bound BPPA ligand and three coordinated benzyl groups. The Zr−O bond distance of 2.044(3) Å is similar to those found in a related bis(phenolate) zirconium complex with Zr−O distances of 2.000(4) and 2.008(4) Å.[82] The $Zr-N_{py}$ bond lengths of 2.372(4) and 2.506(4) Å and the Zr−C bond distances of 2.349(5), 2.358(4), and 2.394(4) Å are also similar to those found in the literature.[82] The ^{1}H NMR spectrum of **14** in C_6D_6 shows equivalent pyridyl groups, as well as a pair of equivalent diastereotopic 2-picolyl protons. The three sets of benzyl protons appear to be in rapid exchange on the NMR time scale at room temperature, as evidenced by the presence of one broad peak integrating to six protons centered at 2.60 ppm. As an NMR sample of **14** in toluene-d_8 is cooled to −20 °C, the broad resonance corresponding to the benzyl protons separates to three sets of peaks. Two sets of benzyl protons remain in the region between 2 and 3 ppm, and one set shifts downfield to 4.98 ppm, suggestive of a μ^2-benzyl group.[83] Although not observed in the crystal structure, in solution this interaction may provide additional electron density, as well as steric protection to the zirconium center.

Reactivity of 14. It was observed that a solution of **14** underwent a color change from bright orange to dark red upon standing at room temperature overnight. To determine the identity of the decomposition product, the thermal decomposition of **14** was monitored by ^{1}H NMR spectroscopy. A NMR tube sample of **14** in either THF-d_8 or C_6D_6 was heated to 35 °C for 2 h, leading to full conversion to a new species. The ^{1}H NMR spectrum of the product displays an asymmetric molecule as indicated by the presence of two different pyridyl donor groups. Of note is the upfield shift

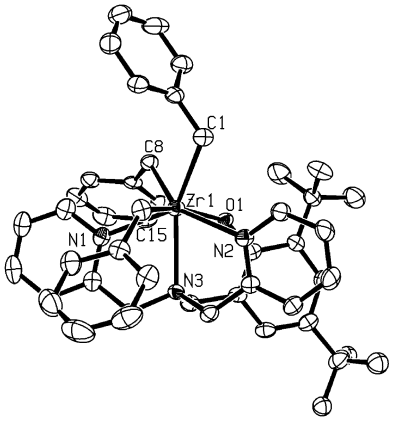
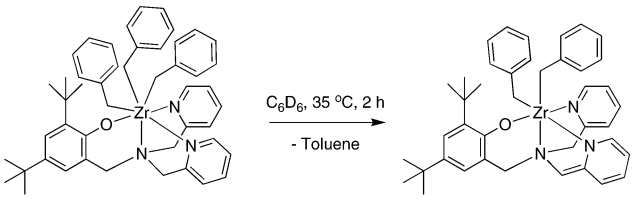


Figure 8. Thermal ellipsoid (50%) plot of **14**. Hydrogen atoms, modeled disorder of *tert*-butyl group, and solvent molecules have been omitted for clarity.

Table 8. Selected Bond Lengths (Å) and Angles (deg) for $(BPPA)Zr(CH_2Ph)_3$ (**14**)

Zr(1)−O(1)	2.044(3)	Zr(1)−N(1)	2.372(4)
Zr(1)−N(2)	2.506(4)	Zr(1)−N(3)	2.467(4)
Zr(1)−C(1)	2.349(5)	Zr(1)−C(8)	2.358(4)
Zr(1)−C(15)	2.394(4)		
O(1)−Zr(1)−N(1)	121.7(1)	O(1)−Zr(1)−N(2)	74.1(1)
O(1)−Zr(1)−N(3)	80.0(1)	O(1)−Zr(1)−C(1)	98.7(1)
O(1)−Zr(1)−C(8)	82.1(1)	O(1)−Zr(1)−C(15)	154.2(1)
N(1)−Zr(1)−N(2)	131.6(1)	N(1)−Zr(1)−N(3)	69.3(1)
N(1)−Zr(1)−C(1)	131.5(1)	N(1)−Zr(1)−C(8)	78.9(1)
N(1)−Zr(1)−C(15)	74.0(1)	N(2)−Zr(1)−N(3)	69.7(1)
N(2)−Zr(1)−C(1)	81.5(1)	N(2)−Zr(1)−C(8)	148.2(1)
N(2)−Zr(1)−C(15)	80.3(1)	N(3)−Zr(1)−C(1)	150.4(1)
N(3)−Zr(1)−C(8)	126.7(1)	N(3)−Zr(1)−C(15)	88.4(1)

Scheme 8. Decomposition of **14**



15

of one set of pyridyl protons with the ortho proton resonance appearing in the vinyl region at 5.14 ppm (see below). In addition to the loss of symmetry, 1 equiv of toluene is observed to be present at 2.31 ppm, as well as a new singlet resonance integrating to one proton at 3.9 ppm in THF-d_8. With the aid of a ^{1}H−^{1}H COSY experiment, all eight pyridyl protons were assigned, and the presence of five of the six sets of diastereotopic methylene protons corresponding to the six bridging and six benzyl protons were also identified. The $^1J_{CH}$ of the carbon adjacent to the singlet proton at 3.9 ppm is 175 Hz, indicative of an sp^2-hybridized carbon. To provide further evidence for the structure of the thermolysis product, a ^{1}H−^{15}N HMBC experiment was carried out. The proton resonance at 3.9 ppm is split into a doublet with a $^2J_{NH}$ of 4.1 Hz. These data are consistent with the assigned thermolysis product **15** (Scheme 8) with BPPA transformed to a new tetradentate dianionic ligand with the loss of aromaticity in one of the pyridyl groups. A related decomposition reaction was reported recently by Bercaw et al.[53] The loss of aromaticity of a pyridyl group as a result of

(82) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Organometallics* **2001**, *20*, 3017−3028.
(83) Giesbrecht, G. R.; Whitener, G. D.; Arnold, J. *Organometallics* **2000**, *19*, 2809−2812.

deprotonation of a 2-picolyl proton has been observed previously by ^{1}H NMR spectroscopy and by X-ray crystallography.[53,84] Attempts to obtain crystalline material of **15** were unsuccessful.

Reaction of **14** and H[B(C_5F_5)$_4$·2Et_2O] in C_6D_5Cl resulted in an immediate color change from bright orange to yellow-orange and formation of the cationic species **16**. The ^{1}H and ^{19}F NMR spectra show a clean conversion to a new compound with concomitant loss of 1 equiv of toluene. According to ^{1}H NMR, the pyridyl groups remain equivalent, as do the diastereotopic 2-picolyl and benzyl protons. In contrast to the parent complex, **16** appears to be thermally robust with no decomposition observed in solution after sitting for several days at room temperature in a sealed NMR tube. Attempts to crystallize **16** were unsuccessful.

Summary

A broad examination of the usefulness of the TDMA ligand BPPA has been undertaken. Complexes **4**−**7** and **9**−**13** were synthesized and isolated in good yields and were characterized by NMR, IR, EA, magnetic susceptibility, and when possible, X-ray crystallography. In all structurally characterized cases, the BPPA ligand coordinates to the metal center in a tetradentate fashion. Additionally, the ligand shows a mild degree of flexibility, as demonstrated by the ability of the pyridine groups to be either cis or trans to one another in the solid state.

We believe these BPPA derivatives may function as useful starting materials for the preparation of a range of coordination complexes, although the preliminary signs are that their organometallic chemistry may be somewhat limited. Despite numerous attempts to synthesize a (BPPA)YR_2 complex through metathesis and protonolysis reactions, only intractable mixtures were obtained. Aluminum (**8**) and zirconium (**14**) alkyl complexes were successfully prepared and isolated, but both are prone to thermal decomposition via deprotonation of the BPPA ligand. In the case of **14**, the transformation of the BPPA ligand from a monoanionic to a dianionic ligand was monitored by NMR spectroscopy. A more stable alkyl complex was obtained following the protonation of **14** by H[B(C_5F_5)$_4$·2Et_2O]. The cationic species **16** was observed by ^{1}H and ^{19}F NMR spectroscopy.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this work and Dr. Fred Hollander and Dr. Allen Oliver for crystallographic assistance. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Supporting Information Available: Crystallographic information files (CIF) and a detailed summary of the X-ray diffraction data for compounds **4**−**6**, **10**, and **12**−**14**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC700775K

(84) Ben-Ari, E.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2006**, *128*, 15390−15391.