

Electronic Supplementary Information

Zirconium arene-phosph(on)ates: chemical and structural characterization of oxy- and methyl-linked 2-naphthyl phosphonates, and mixed oxy-linked derivatives

Jay C. Amicangelo^a and Willem R. Leenstra^{*b}

^a*School of Science, Penn State Erie, The Behrend College, Erie, PA 16563*

^b*Department of Chemistry, University of Vermont, Burlington, VT 05405*

Materials and Synthetic Methodologies

Purchased chemicals were used as received. Hexamethyldisiloxane, phosphorus tribromide, 2-naphthylphosphate monosodium salt, and methylphosphonic acid were purchased from Lancaster Synthesis, Inc. Triethyl phosphite, 2-bromomethylnaphthalene, methanol, acetone, diethyl ether, and zirconyl chloride were purchased from Aldrich Chemical Co. Hydrofluoric acid was purchased from J.T. Baker, Inc. Trimethylsilylbromide, TMSBr, was synthesized according to the procedure of Gilliam and co-workers,¹ from hexamethyldisiloxane and phosphorus tribromide. Ethyl phosphate was purchased from TCI America, as a mixture of the monoethyl and diethyl forms, and monoethylphosphate was isolated from the commercial mono-di mixture according to the procedure of Stewart and Crandall.²

Diethyl 2-Naphthylmethylphosphonate, (C₂H₅O)₂P(O)CH₂C₁₀H₇ [DE2NMP].

Triethyl phosphite (1.20 mL, 7.00 mmols) was added dropwise to 2-bromomethylnaphthalene (0.916 g, 4.142 mmols) which had been heated in an oil bath to 110 °C under N₂. The mixture was heated for 1.5 hours under N₂. It was cooled to 50 °C and evacuated to remove any volatile components. The liquid was distilled under vacuum, affording DE2NMP as a colorless oil (0.964 g, 84.0%): bp 132 - 132.5 °C, 0.07 mm Hg; MS (ei) *m/z* 278 (M⁺), 141; ¹H NMR (500 MHz, CDCl₃) δ 7.77 - 7.72 (m, 4 H), 7.46 - 7.38 (m, 3 H), 4.02 - 3.95 (m, 4 H), 3.28 (d, 2 H, *J* = 21.7 Hz), 1.20 (t, 6 H, *J* = 7.1 Hz); ¹³C NMR (500 MHz, CDCl₃) δ 133.86 (d, *J* = 3.0 Hz), 132.73 (d, *J* = 2.5 Hz), 129.62 (d, *J* = 9.5 Hz), 128.85 (d, *J* = 8.4 Hz), 128.49 (d, *J* = 2.4 Hz), 128.30 (d, *J* = 5.2 Hz), 128.02 (d, *J* = 1.4 Hz), 127.96 (d, *J* = 1.2 Hz), 126.50, 126.10 (d, *J* = 1.5 Hz), 62.49 (d, *J* = 6.7 Hz), 34.36 (d, *J* = 138.0 Hz), 16.76 (d, *J* = 6.0); ³¹P NMR (500 MHz, CDCl₃) δ 26.78; IR (neat, cm⁻¹) 3055, 2928, 2931, 2907, 2870, 1633, 1601, 1508, 1443, 1392, 1367, 1250, 1163, 1053, 1027, 965, 902, 863, 824, 787, 750, 643.

2-Naphthylmethylphosphonic Acid, (HO)₂P(O)CH₂C₁₀H₇ [2NMPA].

Trimethylsilylbromide (4.50 mL, 34.8 mmol) was added dropwise to the phosphonate ester DE2NMP (3.474 g, 12.48 mmol) and the mixture stirred overnight at room temperature under N₂. The excess bromotrimethylsilane was evacuated off and the resulting solid refluxed in 35.0 mL of methanol overnight under N₂. The methanol was removed under reduced pressure, the solid residue treated with cold acetone and filtered to afford 2NMPA as a white solid (2.774 g, 93.0%): mp = 233 - 234 °C; MS (ei) *m/z* 222 (M⁺), 141; ¹H NMR (500 MHz, DMSO-d₆) δ 7.97 - 7.91 (m, 3 H), 7.84 (s, 1 H), 7.60 - 7.53 (m, 3 H), 3.24 (d, 2 H, *J* = 21.5 Hz); ¹³C NMR (500 MHz, DMSO-d₆) δ 132.94 (d, *J* = 2.9 Hz), 131.94 (d, *J* = 9.0 Hz), 131.56 (d, *J* = 2.3 Hz), 128.48 (d, *J* = 4.9 Hz), 127.74 (d, *J* = 8.1 Hz), 127.38, 127.24, 127.22, 125.91, 125.28, 35.52 (d, *J* = 131.9 Hz); ³¹P NMR (500 MHz, DMSO-d₆) δ 22.60; IR (KBr, cm⁻¹) 3050, 3018, 2927, 2860, 1598, 1506, 1407, 1283, 1250, 1058, 1001, 951, 946, 892, 861, 827, 744, 720, 643; UV (MeOH, nm, M⁻¹cm⁻¹) λ_{max} (ε) 227 (104,000), 252 (2620), 261 (3940), 268 (5020), 277 (5310), 287 (3490), 305 (326), 314 (183), 319 (174).

Zirconium Bis(2-naphthyl phosphate), Zr(O₃POC₁₀H₇)₂ [Zr(ONap)₂]. A solution of zirconyl chloride (0.166 g, 0.514 mmol) in 2.5 mL of water was added dropwise to a solution of 2-naphthyl phosphate monosodium salt (0.252 g, 1.026 mmol) in 5.0 mL of water with stirring. Subsequently, 1.0 mL of 2.038 M HF (2.04 mmol) and 30.0 mL of water were added to the mixture and it was refluxed under nitrogen for six days. The solution was cooled to room temperature and the solid was filtered, washed with water, acetone, diethyl ether and air dried to yield Zr(ONap)₂ as a faint pink colored solid (0.236 g, 86.0%): ³¹P NMR (500 MHz, solid state) δ -29.5; XRD d₀₀₁ (Å) 19.6; IR (KBr, cm⁻¹) 3086, 3062, 3053, 3033, 1634, 1600, 1579, 1510,

1466, 1441, 1355, 1251, 1220, 1172, 1118, 1075, 1063, 1000, 958, 879, 854, 804, 771, 761, 740, 702, 618, 607, 534, 514, 484; TGA (150 °C to 1000 °C, $\text{Zr}(\text{ONap})_2 \rightarrow \text{ZrP}_2\text{O}_7$) % Wt Loss: Exptl (Calcd)³ 43.5 (50.5); UV (glycerol mull, nm) λ_{max} 237, 282, 286, 294, 309, 316, 325.

Zirconium 2-Naphthyl phosphate Methylphosphonate, $\text{Zr}(\text{O}_3\text{POC}_{10}\text{H}_7)_1(\text{O}_3\text{PCH}_3)_1$ [$\text{Zr}(\text{ONap})_1(\text{Me})_1$]. A solution of zirconyl chloride (0.183 g, 0.567 mmol) in 5.0 mL of water was added dropwise to a solution of 2-naphthyl phosphate monosodium salt (0.140 g, 0.568 mmol) and methylphosphonic acid (0.054 g, 0.564 mmol) in 5.0 mL of water with stirring, 10.0 mL of water was used to rinse the zirconyl chloride flask and added to the mixture. This was followed by 0.30 mL of 2.0 M HF (0.60 mmol) and the entire mixture was refluxed under flowing nitrogen for six days. After cooling to room temperature, the solid was collected by centrifugation, washed successively with water, acetone, diethyl ether, and air dried, yielding $\text{Zr}(\text{ONap})_1(\text{Me})_1$ as a white solid (0.217 g, 94.0%): ³¹P NMR (500 MHz, solid state) δ 7.0, -28.1; XRD d_{001} (Å) 15.3; IR (KBr, cm^{-1}) 3058, 3028, 2992, 2927, 2854, 1632, 1600, 1580, 1512, 1467, 1441, 1384, 1356, 1312, 1253, 1220, 1169, 1100, 1044, 985, 941, 880, 852, 811, 790, 747, 702, 647, 606, 538, 512, 476; TGA (150 °C to 1000 °C, $\text{Zr}(\text{ONap})_1(\text{Me})_1 \rightarrow \text{ZrP}_2\text{O}_7$) % Wt Loss: Exptl (Calcd)³ 33.6 (34.9); UV (glycerol mull, nm) λ_{max} 236, 280, 291, 307, 324.

Zirconium Bis(ethylphosphate), $\text{Zr}(\text{O}_3\text{POC}_2\text{H}_5)_2$ [$\text{Zr}(\text{OEt})_2$]. To a solution of zirconyl chloride (0.616 g, 1.911 mmol) in 11.0 mL of water was added 3.86 mL of 1.98 M HF (7.64 mmol). This was then added to a solution of monoethylphosphate (0.482 g, 3.824 mmol) in 15.0 mL of water with stirring and the solution was refluxed for six days under nitrogen. The mixture was cooled to room temperature, and the solid was filtered, washed with water, acetone, diethyl ether and air dried to afford $\text{Zr}(\text{OEt})_2$ as a white solid (0.644 g, 99.4%): ³¹P NMR (500 MHz, solid state) δ -19.82, -20.82, -21.80; XRD d_{001} (Å) 11.6 (lit⁴ d_{001} = 11.7 Å); IR (KBr, cm^{-1}) 2982, 2932, 2911, 2872, 1632, 1480, 1454, 1445, 1396, 1386, 1371, 1295, 1166, 1122, 1073, 1048, 979, 810, 784, 602, 538, 478; TGA (150 °C to 1000 °C, $\text{Zr}(\text{OEt})_2 \rightarrow \text{ZrP}_2\text{O}_7$) % Wt Loss: Exptl (Calcd)³ 17.4 (21.8).

References

- 1 W. F. Gilliam, R. N. Meals, and R. O. Saver, *J. Am. Chem. Soc.*, 1946, **68**, 1161-1163.
- 2 D. C. Stewart and H. W. Crandall, *J. Am. Chem. Soc.*, 1951, **73**, 1377-1378.
- 3 See TGA Results and Discussion section for a definition of the calculated % weight losses.
- 4 G. Alberti, U. Costantino, S. Allulli, and N. Tomassini, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1113-1117.

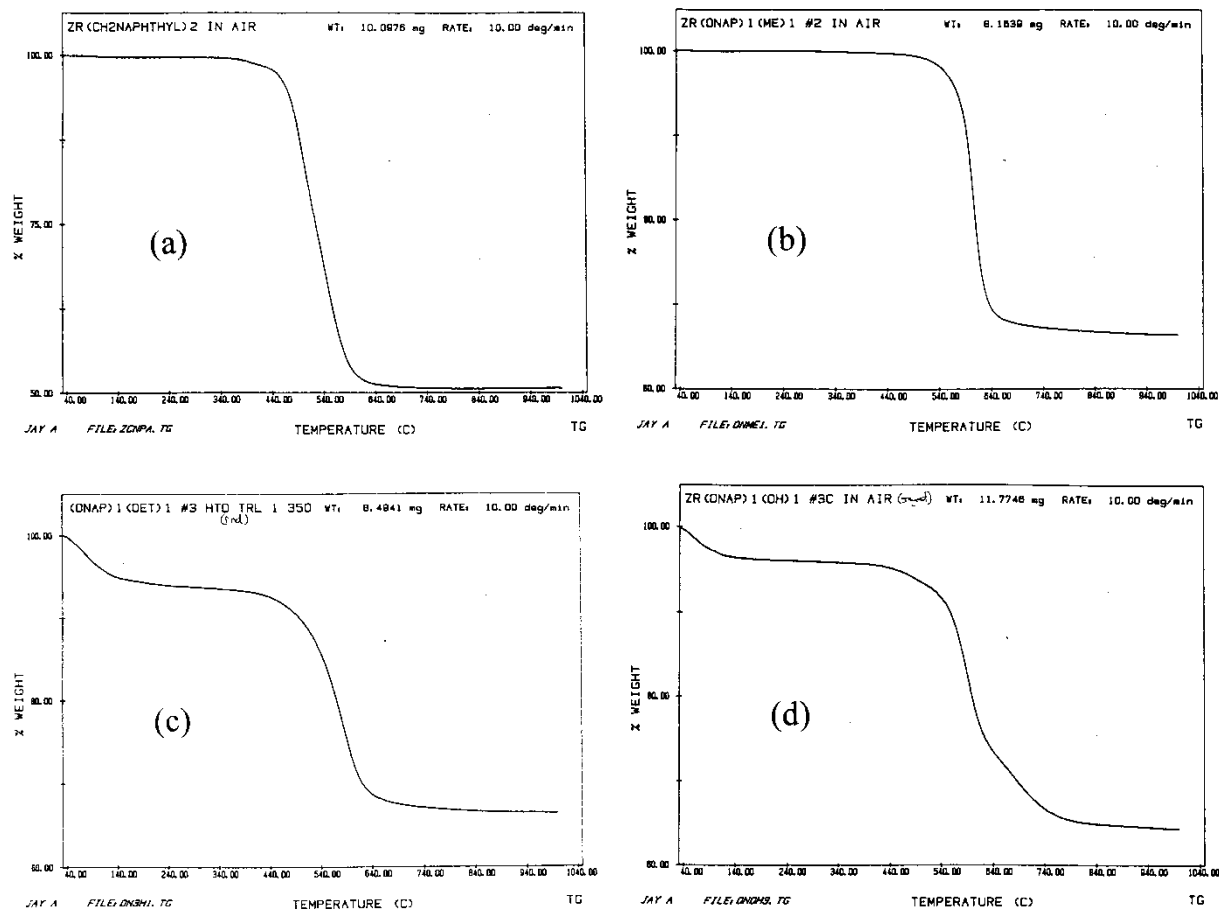


Fig. 1S Thermal gravimetric analysis curves of (a) $\text{Zr}(\text{CH}_2\text{Nap})_2$, (b) $\text{Zr}(\text{ONap})_1(\text{Me})_1$, (c) $\text{Zr}(\text{ONap})_1(\text{OH})_1$, and (d) *stg* $\text{Zr}(\text{ONap})_1(\text{OH})_1$.

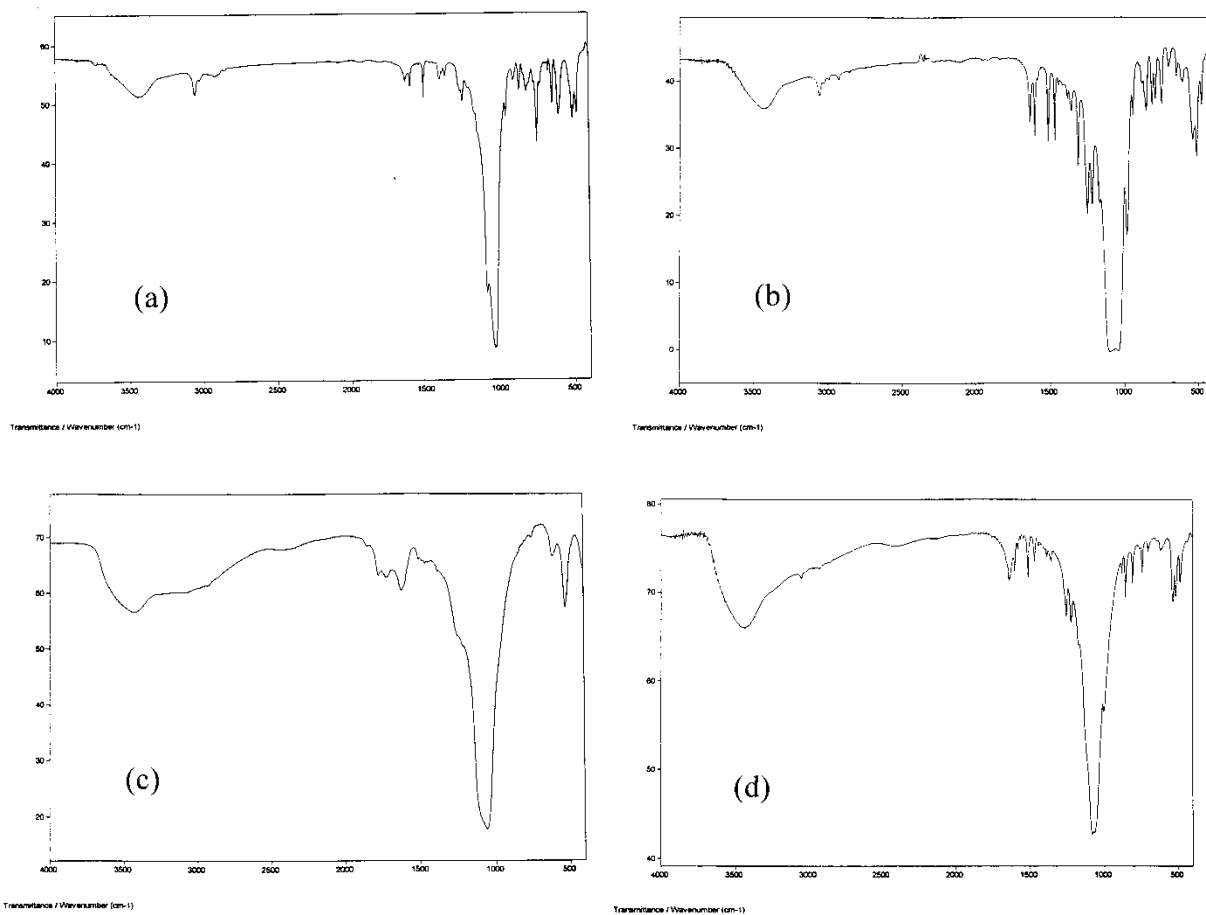


Fig. 2S Infrared spectra of (a) $\text{Zr}(\text{CH}_2\text{Nap})_2$, (b) $\text{Zr}(\text{ONap})_1(\text{Me})_1$, (c) $\text{Zr}(\text{ONap})_1(\text{OH})_1$, and (d) *stg* $\text{Zr}(\text{ONap})_1(\text{OH})_1$.

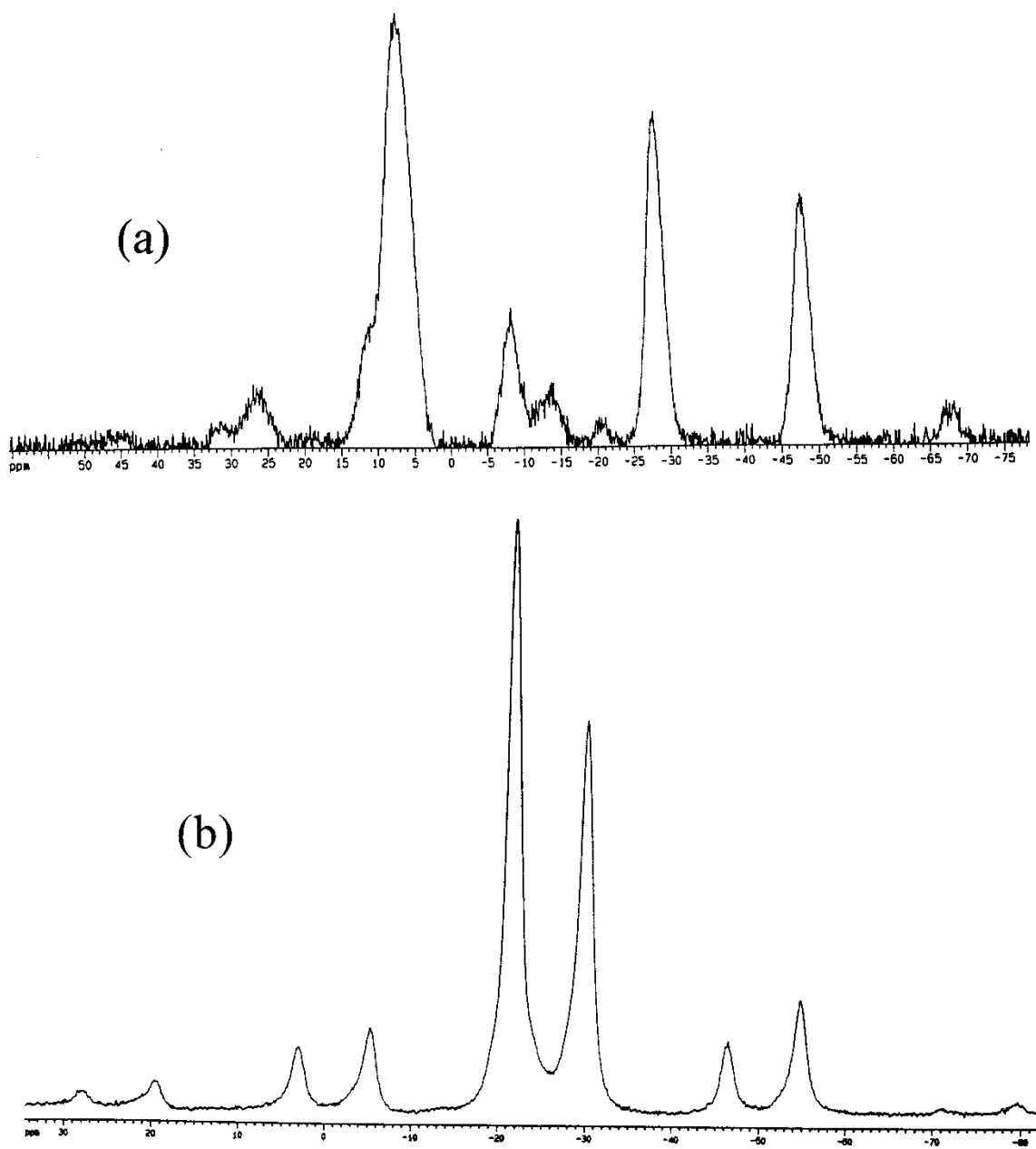


Fig. 3S Solid-state ^{31}P NMR spectrum of (a) $\text{Zr}(\text{ONap})_1(\text{Me})_1$ and (b) *stg* $\text{Zr}(\text{ONap})_1(\text{OH})_1$.

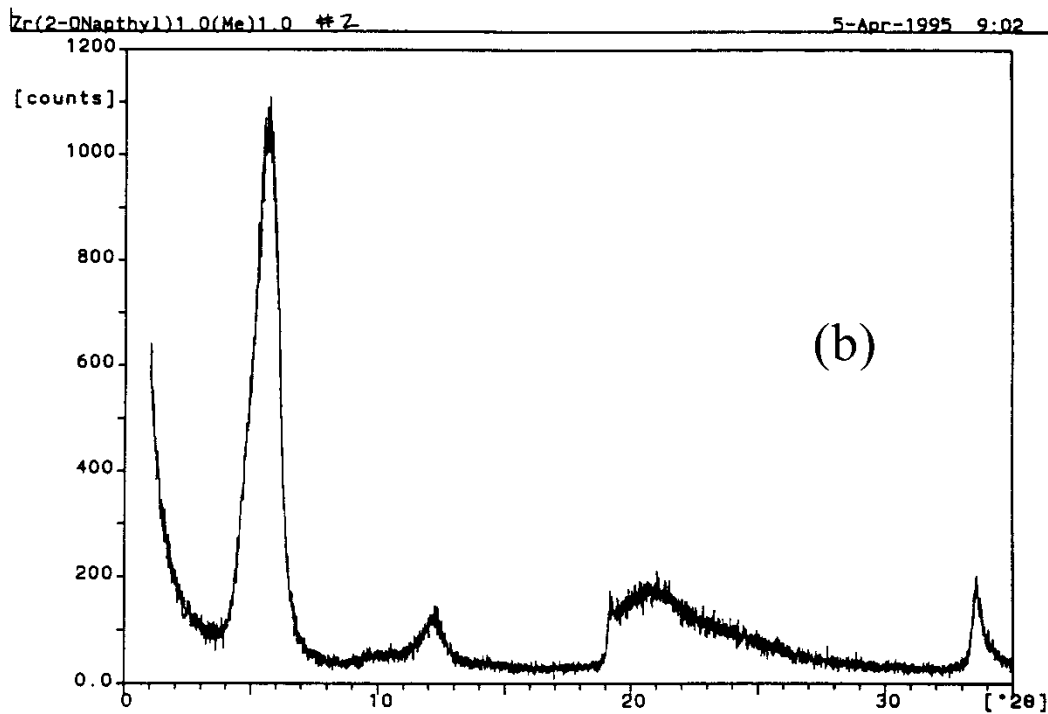
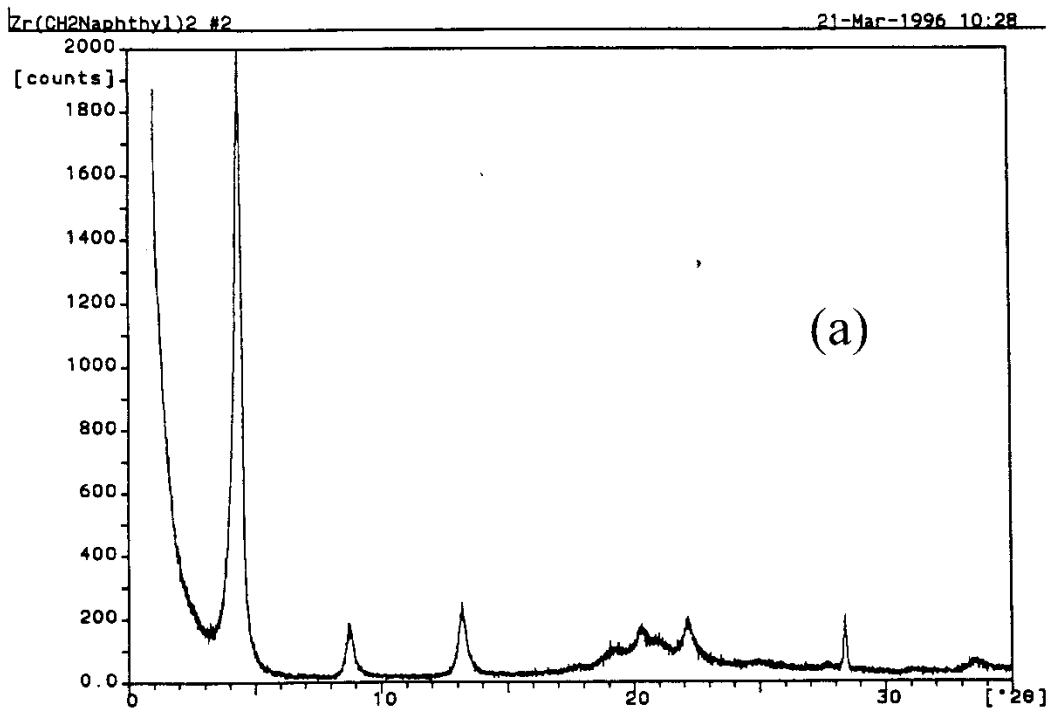


Fig. 4S X-ray diffraction patterns of (a) Zr(CH₂Nap)₂ and (b) Zr(ONap)₁(Me)₁. The sharp peak at 28.4° in panel (a) is due to silicon added as an internal standard.