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Preparation and Reactions of the C_{3v} Ligand Tris(2-pyridyl)methane and Its Derivatives

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Tris(2-pyridyl)methanol (**1**) reacted with a 4-fold excess of $HBF_4 \cdot OEt_2$ in propionic anhydride to yield the novel intramolecular Lewis acid–base complex tris(2-pyridyl)methoxydifluoroborane. Acetyl bromide reacted with **1** to give the acetate ester. Conversion of **1** to its sodium alkoxide and reaction with SOX_2 (X = Cl, Br) gave tris(2-pyridyl)halomethane. These reacted with refluxing ethanol to yield the ethyl ether of **1**. The halides underwent lithium–halogen exchange with *n*-BuLi at −95 °C in THF to give after hydrolysis tris(2-pyridyl)methane. At higher temperatures, lithium–hydrogen exchange occurred, yielding a complex mixture of products. Mechanisms are proposed and contrasted with corresponding reactions with the triphenylmethane system. Bis[tris(2-pyridyl)methane] complexes of Co(II) and Co(III) were prepared and exhibit NMR spectra consistent with symmetrical tridentate coordination of the tris(2-pyridyl)methane ligand. The Co(II) complex shows large isotropic shifts in the NMR spectrum.

Introduction

Tris(2-pyridyl)methanol (**1**) was first reported in 1951 by Wibaut and co-workers,[1] who were primarily interested in the analogy to triphenylmethanol. They reported that, unlike the latter compound, tris(2-pyridyl)methanol did not undergo a color reaction with concentrated sulfuric acid. Since that time, tris(2-pyridyl)methanol has seldom been mentioned in the literature. Recently, however, several investigators[2-4] have noted that this compound functions as a metal ion chelate. Our own interest in this system was prompted by a need for ligands with C_{3v} symmetry and a high degree of synthetic versatility, particularly with regard to covalent attachment of the ligand to various substrates and functionalizing the ligands. The results of our investigation of the preparation, properties, and reactions of a number of tris(2-pyridyl)methane derivatives are reported herein.

Experimental Section

Bis(2-pyridyl) ketone and 2-bromopyridine were purchased from Aldrich. Thionyl bromide and *n*-butyllithium were purchased from Alfa Inorganics, Beverly, MA. THF and ether were distilled from sodium benzophenone ketyl under nitrogen immediately before use. Standard organometallic techniques were ussed for reactions involving lithium reagents. ^1H NMR spectra were obtained on a JEOL FX-900 90-MHz or a Bruker 270-MHz instrument. ^1H chemical shifts are in ppm downfield from internal Me_4Si. ^{19}F and ^{11}B spectra were obtained on a Bruker CXP 200. ^{19}F and ^{11}B chemical shifts are in ppm downfield from external CF_3COOH and $BF_3 \cdot OEt_2$, respectively. Mass spectra were obtained on a Hewlett-Packard 5985 GC-MS with a direct-inlet probe. IR spectra in Nujol mulls and KBr pellets were recorded on a Beckman IR 4250. Microanalyses were performed by Midwest Microlab, Ltd., Indianapolis, IN, or Atlantic Microlabs, Atlanta, GA. Melting points are uncorrected.

Tris(2-pyridyl)methanol (1). This compound was prepared by the method of Wibaut and co-workers[1] from bis(2-pyridyl) ketone and 2-lithiopyridine. It was obtained in 41% yield as white crystals from acetone; mp 127–128 °C (lit.[1] mp 127–128 °C).

NMR ($CDCl_3$): δ 7.21 (d^3, $J_{3,5}$ = 1.47, $J_{4,5}$ = 7.33, $J_{5,4}$ = 4.76 Hz, 3 H, py 5-H), 7.68 (t (d), $J_{4,5}$ = 7.33, $J_{4,6}$ = 1.83 Hz, 3 H, py 4-H), 7.74 (d (t), $J_{3,6}$ = 1.10, $J_{3,4}$ = 7.33 Hz, 3 H, py 3-H), 8.55 (d^3, $J_{3,6}$ = 1.10, $J_{4,6}$ = 1.83, $J_{5,6}$ = 4.76 Hz, 3 H, py 6-H), 7.27 (s, 1 H, O–H) (δ 7.09 in Me_2SO-d_6).

IR (Nujol): 3420 (7) cm^{-1}. IR (KBr): 3470 (m), 3040 (w), 2995 (w), 2995 (w), 1580 (s), 1458 (s), 1340 (s), 1232 (w), 1186 (s), 1158 (m), 1105 (m), 1041 (s), 985 (s), 920 (s), 768 (s), 730 cm^{-1} (s).

Tris(2-pyridyl)bromomethane (9). Tris(2-pyridyl)methanol, 1.00 g (3.8 mol), was dissolved in 10 mL of THF and treated with 0.1 g (4.2 mol) of NaH (as 50% dispersion in mineral oil). The resulting solution was cooled to −70 °C and treated dropwise with a solution of 0.87 g (4.2 mol) of $SOBr_2$ in 5 mL of THF. The cooling bath was removed from the reaction mixture, and it was allowed to warm to room temperature. It then was hydrolyzed, and the organic layer plus methylene chloride extracts of the aqueous layer were combined, washed with 1 N $NaHCO_3$ and water, dried over sodium sulfate, and concentrated on a rotary flash evaporator. Two recrystallizations of the residue from acetone gave 0.44 g (35%) of white crystals, mp 135–135.5 °C.

NMR ($CDCl_3$, 270 MHz, 298 K): δ 7.19 (d^3, $J_{3,5}$ = 1.19, $J_{4,5}$ = 7.45, $J_{5,6}$ = 4.77 Hz, 3 H, py 5-H), 7.49 (d (t), J = 1.04, $J_{3,4}$ = 8.04 Hz, 3 H, py 3-H), 7.6m (approximate d^3, $J_{3,4}$ = 8.04, $J_{4,5}$ = 7.45, $J_{4,6}$ = 1.79 Hz, 3 H, py 4-H), 8.60 (d^3, $J_{3,6}$ = 0.89, $J_{4,6}$ = 1.7., $J_{5,6}$ = 4.77 Hz, 3 H, py 6-H).

IR (KBr): 3080 (w), 3045 (w), 3000 (w), 1580 (s), 1455 (s), 1422 (s), 1285 (w), 1147 (w), 1090 (w), 1045 (w), 983 (m), 955 (w), 925 (w), 917 (w), 892 (w), 841 (w), 770 (s), 758 (s), 739 (s), 681 (m), 650 (m), 608 (m), and 401 cm^{-1} (m).

Anal. Calcd for $C_{16}H_{12}N_3Br$: C, 58.91; H, 3.75; N, 12.88; Br, 24.50. Found: C, 58.88; H, 3.74; N, 12.87; Br, 24.45.

Tris(2-pyridyl)chloromethane (10). This compound was synthesized by employing thionyl chloride in the above procedure. It was obtained in 58.2% yield as white crystals from acetone; mp 166–167 °C.

NMR ($CDCl_3$ 270 MHz, 298 K): δ 7.20 (d^3, $J_{3,5}$ = 1.03, $J_{4,5}$ = 7.39, $J_{4,6}$ = 4.72 Hz, 3 H, py 5-H), 7.52 (approximate d (t), $J_{3,5}$ = 1.03 Hz, $J_{3,4}$ = 8.00 Hz, 3 H, py 3-H), 7.68 (approximate t (d), $J_{3,4}$ = 8.00, $J_{4,5}$ = 7.39, $J_{4,6}$ = 1.03 Hz, 3 H, py 4-H), 8.5. (d^3, $J_{3,6}$ = 1.03, $J_{4,6}$ = 1.85, $J_{5,6}$ = 4.72 Hz, 3 H, py 6-H).

IR (KBr): 3045 (w), 3000 (w), 1582 (s), 1459 (s), 1430 (sh), 1425 (s), 1288 (m), 1160 (sh), 1150 (m), 1095 (m), 1052 (m), 990 (s), 918 (w), 870 (w), 778 (s), 768 (s), 747 (s), 698 (s), 655 (s), 615 (m), 410 cm^{-1} (m).

Anal. Calcd for $C_{16}H_{12}N_3Cl$: C, 68.20; H, 4.29; N, 14.92; Cl, 12.58. Found: C, 68.18; H, 4.30; N, 14.92; Cl, 12.57.

Tris(2-pyridyl)ethoxymethane (12). Tris(2-pyridyl)bromomethane, 0.30 g (0.92 mmol), was dissolved in 10 mL of absolute ethanol, and this solution was refluxed for 2 h. The reaction mixture then was cooled, and most of the ethanol was removed on a rotary flash evaporator. The residue was treated with 5 mL of 1 N Na_2CO_3 solution and 10 mL of methylene chloride. The organic extract was dried over Na_2SO_4, and the residue obtained after removal of solvent was recrystallized from 50:50 pentane–ether. The product was obtained in 81% yield as white crystals, mp 110–111 °C.

NMR ($CDCl_3$): δ 1.25 (t, J = 7.0 Hz, 3 H, CH_3), 3.38 (q, J = 7.0 Hz, 2 H, CH_2), 7.13 (d^3, $J_{3,5}$ = 1.37, $J_{4,5}$ = 7.32, $J_{5,6}$ = 4.73 Hz, 3 H, py 5-H), 7.67 (approximate d (t), $J_{4,6}$ = 1.83, $J_{4,5}$ = 7.32, $J_{3,4}$ = 8.09 Hz, 3 H, py 4-H), 7.74 (approximate d^3, $J_{3,6}$ = 0.92, $J_{3,5}$ = 1.37, $J_{3,4}$ = 8.09 Hz, 3 H, py 3-H), 8.58 (d^3, $J_{3,6}$ = 0.92, $J_{4,6}$ = 1.83, $J_{5,6}$ = 4.73 Hz, 3 H, py 6-H).

IR (KBr): 3045 (w), 2955 (m), 2880 (m), 1555 (s), 1451 (s), 1412 (s), 1282 (w), 1190 (w), 1143 (w), 1090 (sh), 1061 (s), 1041 (s), 1023 (sh), 985 (s), 930 (m), 880 (m), 758 (m), 652 (m), 605 cm^{-1} (w).

Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.19; H, 5.89; N, 14.42. Found: C, 74.18; H, 5.92; N, 14.40.

Tris(2-pyridyl)methane (17). A solution of 0.155 g (0.475 mmol) of tris(2-pyridyl)bromomethane in 5 mL of THF was cooled to −100 °C, and the resulting suspension then was treated dropwise at −90 to −100 °C with 0.33 mL of 1.6 M *n*-BuLi in hexane. As the addition

(1) Wilbaut, J. P.; de Jonge, A. P.; Van der Voort, H. G. P.; Otto, H. L. *Recl. Trav. Chim. Pays-Bas.* **1951**, *70*, 1054–1060.
(2) Boggess, R. K.; Baberg, S. J. *J. Inorg. Nucl. Chem.* **1980**, *42*, 21–26.
(3) Brown, R. S.; Huguet, J. *Can. J. Chem.* **1980**, *58*, 889–901.
(4) Faller, J. W.; White, D. L., manuscript in preparation.

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progressed, the suspension was converted to a pale yellow solution. After being stirred at −100 °C for 10 min, the reaction mixture was treated with 1 mL of water in 5 mL of THF and then allowed to warm to room temperature. Extraction with CH_2Cl_2 and recrystallization from ether gave 0.065 g (55%) of product, mp 99–100 °C.

NMR ($CDCl_3$): δ 5.99 (s, 1 H, C–H), 7.15 (d^3, $J_{3,5}$ = 1.70, $J_{4,5}$ = 7.78, $J_{5,6}$ = 4.79 Hz, 3 H, py 5-H), 7.33 (approximate d (t), $J_{3,4}$ = 7.93, $J_{3,5}$ = 1.70, $J_{3,6}$ = 0.90 Hz, 3 H, py 3-H), 7.63 (t (d), $J_{4,5}$ = 7.78, J = 1.95 Hz, 3 H, py 4-H), 8.59 (d^3, $J_{3,6}$ = 0.90, $J_{4,6}$ = 1.80, $J_{5,6}$ = 4.79 Hz, 3 H, py 6-H).

IR (KBr): 3062 (w), 3040 (w), 3002 (m), 2820 (w), 1580 (vs), 1563 (s), 1459 (s), 1425 (s), 1295 (m), 1185 (w), 1148 (m), 1100 (w), 1088 (w), 1048 (w), 990 (m), 780 (sh), 760 s), 741 (s), 685 (m), 658 (s), 635 (m), 498 (w), 400 cm^{-1} (w).

Anal. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 17.00. Found: C, 77.64; H, 5.34; N, 16.98.

Tris(2-pyridyl)methyl Acetate (3). A solution of 2.63 g (1.0 mmol) of tris(2-pyridyl)methanol in 20 mL of DMF was treated with 1 mL (1.7 g, 14 mmol) of acetyl bromide. An exothermic reaction raised the temperature of the dark red reaction mixture to 40 °C; it was then heated to 105 °C and held at that temperature for 3 h. The mixture then was cooled to 25 °C, and volatiles were removed in vacuo. The residue was dissolved in 30 mL of water, and this solution was made alkaline with 1 N $NaCO_3$. Extraction with CH_2Cl_2, workup, and recrystallization from acetone–ether gave 1.47 g (48%) of product, mp 125–127 °C. An analytically pure sample, mp 126.5–127 °C, was obtained by two additional recrystallizations and displayed the following properties.

IR (KBr): 3045 (m), 3000 (m), 1730 (s), 1573 (s), 1458 (s), 1422 (s), 1360 (m), 1290 (w), 1232 (s), 1210 (sh), 114k (m), 1095 (m), 1035 (s), 990 (m), 965 (w), 938 (w), 885 (w), 789 (m), 765 (s), 740 (s), 690 (m), 662 (m), 638 (m), 612 (m), 555 (7), 406 (m) cm^{-1}.

NMR ($CDCl_3$): δ 2.32 (s, 3 H, CH_3), 7.15 nd^3, $J_{5,6}$ = 4.85, $J_{4,5}$ = 7.50, $J_{3,5}$ = 1.18 Hz, 3 H, py 5-H), 7.68 (t (d), $J_{4,5}$ = 7.50, $J_{3,4}$ = 8.80, $J_{4,6}$ = 1.91 Hz, 3 H, py 4-H), 7.82 (d (t), $J_{3,4}$ = 8.80, $J_{3,5}$ = 1.18, $J_{3,6}$ = 1 Hz, 3 H, py 3-H), 8.55 (d^3, $J_{5,6}$ = 4.85, $J_{4,6}$ = 1.91, $J_{3,6}$ = 1 Hz, 3 H, py 6-H).

Anal. Calcd for $C_{18}H_{15}N_3O_2$: C, 70.80; H, 4.95; N, 13.77. Found: C, 70.62; H, 5.16; N, 13.62.

[Tris(2-pyridyl)methoxy-κ*N*,κ*O*]difluoroborane (7). A solution of 0.26 g (1.0 mmol) of tris(2-pyridyl)methanol in 5 mL of propionic anhydride was treated with 1.3 g (8.0 mmol) of HBF_4·OEt_2. A white solid precipitated almost immediately. The suspension was stirred at 25 °C for 4 h before being diluted with 10 mL of anhydrous ether. The solid was isolated by centrifugation and washed with two 10-mL portions of ether. It then was dissolved in CH_2Cl_2, and this solution was treated with aqueous 1 N $NaHCO_3$ until alkaline and then was washed neutral with water. Removal of solvent in vacuo and recrystallization of the residue from acetone–ether gave 0.19 g (61%) of white crystalline solid, mp 213–214 °C. When 40% aqueous HBF_4 was substituted for HBF_4·OEt_2 in the above procedure, a yield of 45% was obtained.

IR (KBr): 3118 (w), 3050 nw), 1615 (m), 1580 (sh), 1570 s), 1472 (s), 144l (s), 1430 (s), 1305 (w), 1255 (w), 1205 (sh), 1155 (sh), 1129 (s), 1100 (s), 1070 (s), 1042 (sh), 987 (s), 970 (sh), 940 (w), 898 (s), 883 (sh), 792 (s), 769 (s), 753 (s), 740 (s), 705 (w), 670 (m), 660 (m), 640 (m), 610 (m), 570 (w), 548 (w), 512 (w), 490 (w), 472 (w) cm^{-1}.

^1H NMR ($CDCl_3$, 270 MHz, 298 K): δ 7.21 (d^3, $J_{5,6}$ = 4.85, $J_{4,5}$ = 7.47, $J_{3,5}$ = 1.17 Hz, 2 H, py 5′,5′-H's), 7.67 (t (d), $J_{3,4}$ = 5.72, $J_{4,6}$ = 1.17 Hz, 1 H, py 4-H), 7.70 (t (d), $J_{4,5}$ = 7.47, $J_{3,4}$ = 8.06, $J_{4,6}$ = 1.91 Hz, 2 H, py 4′,4′-H's), 7.88 (d (t), $J_{3,4}$ = 8.06, $J_{3,5}$ = 1.17, $J_{3,6}$ = 1 Hz, 2 H, py 5′,5′-H's), 8.1. (d^3, $J_{4,5}$ = 7.62, $J_{5,6}$ = 8.2, $J_{3,5}$ = 1.47 Hz, 1 H, py 5-H), 8.47 (br, d (t), $J_{3,4}$ = 5.72, $J_{3,5}$ = 1.2 Hz, 1 H, py 3-H), 8.5 (d^3, $J_{5,6}$ = 4.85, $J_{4,6}$ = 1.91, $J_{3,6}$ = 1 Hz, 2 H, py 6"pm,6‴-H's), 8.76 (br d, $J_{5,6}$ = 8.81 Hz, 1 H, pyr 6-H).

^{19}F NMR ($CDCl_3$): ^{19}F–^{11}B singlet at +69.8 with a shoulder at +69.9 ppm tentatively assigned to ^{19}F–^{10}B.

^{11}B NMR ($CDCl_3$): broad singlet at −6.77 ppm.

Mass spectrum (*m*/*z*): 312 (6.2), $(M + 1)^+$; 311 (27.6), M^+; 292 (10.2), $(M - F)^+$; 246 (42.0), $(M - BF_2)^+$; 233 (100), $M - C_5H_4N)^+$; 168 (12.1), $(M - BF_2C_5H_4N)^+$.

Anal. Calcd for $C_{16}H_{12}BF_2N_3O$: C, 61.77; H, 3.89; N, 13.51. Found: C, 62.09, 62.12; H, 3.84, 3.87; N, 13.70, 13.97.

***N*-[Tris(2-pyridyl)methyl]aniline (14).** Tris(2-pyridyl)bromomethane, 0.100 g (0.307 mmol), was dissolved in 0.3 mL of aniline, and the resulting solution was heated to 100 °C and held at that temperature for about 1 h. The reaction mixture then was cooled to room temperature and treated with 2 mL of ether to yield a white precipitate. This was isolated by centrifugation, washed with ether, and then dissolved in 2 mL of water. This solution was made alkaline with 1 N NaOH, and the resulting white precipitate was in turn isolated by centrifugation and washed with water. The product was dissolved in CH_2Cl_2, and the resulting solution was dried over Na_2SO_4. The residue obtained by evaporation of solvent was recrystallized from acetone to yield 0.045 g (44%); mp 217–219 °C.

NMR ($CDCl_3$, 270 MHz, 298 K): δ 6.54 (d, J = 8.07 Hz, 2 H, aniline 2,6-H's), 6.5l (approximate d^2, J = 7.04, 8.07 Hz, 1 H, aniline 6–H), 6.95 (d^2, J = 7.04, 8.07 Hz, 2 H, aniline 3,5-H's), 7.12 (d^3, $J_{3,5}$ = 1.17, $J_{4,5}$ = 7.34, $J_{5,6}$ = 4.84 Hz, 3 H, py 5-H), 7.58 (approximate t (d), $J_{4,6}$ = 1.91, $J_{4,5}$ = 7.34 Hz, $J_{3,4}$ = 8.07 Hz, 3 H, py 4-H), 7.71 (approximate d (t), $J_{3,4}$ = 8.07 Hz, J = 1.17 Hz, 3 H, py 3-H), 8.59 (d^3, $J_{3,6}$ = 0.88, $J_{4,6}$ = 1.91, $J_{5,6}$ = 4.84 Hz, 3 H, py 6-H).

IR (Nujol): 3335 cm^{-1} ns). IR (KBr): 3340 (s), 3055 (w), 3055 (w), 3005 (w), 1593 (s), 1500 (s), 1460 (m), 1425 (s), 1322 (m), 1150 (w), 1123 (w), 1086 (w), 1071 (w), 1050 (w), 992 (m), 941 (w), 863 (w), 798 (w), 769 (m), 745 (s), 690 (m), 678 (m), 659 (m), 615 (m), 575 (w), 543 (w), 520 (w), 495 (w), 458 (w), 410 cm^{-1} (w).

Mass spectrum (*m*/*z*): 340 (0.8), 33 (4.8), 338 (20.6), M^+; 262 (1.8), 261 (18.7), 260 (100), $(py)_3CN^+$; 247 (7.8), 246 (44.9), 245 (2.1), 244 (2.1), $(py)_3C^+$.

Bis[tris(2-pyridyl)methane]cobalt(II) Hexafluorophosphate (19). To 90 mg (0.36 mmol) of $(2\text{-py})_3CH$ in 2 mL of MeOH was added 26 mg (0.20 mmol) of anhydrous $CoCl_2$ dissolved in 2 mL of H_2O. This solution was heated gently and allowed to stir for 15 min. A solution of 99 mg (0.59 mmol) of $NaPF_6$ in 3 mL of H_2O (neutralized with 0.1 N NaOH) was then added to the above orange solution, during which time a fine tan precipitate appeared. The precipitate was isolated by centrifugation, washed with water, and dried in vacuo at 25 °C for 24 h. Recrystallization was achieved by slow evaporation of an acetonitrile–toluene solution and yielded 108 mg (68%) of orange crystals of $[[(2\text{-py})_3CH]_2Co](PF_6)_2$, mp >350 °C.

Anal. Calcd for $C_{32}H_{26}N_6P_2F_{12}Co$: C, 45.56; H, 3.11; N, 9.96. Found: C, 45.45; H, 3.10; N, 9.78.

^1H NMR (CD_3CN, 298 K): δ 109.76 (br s, 1 H), 94.91 (br s, 3 H), 24.20 (s, 3 H), 14.29 (s, 3 H), −41.11 (br s, 3 H).

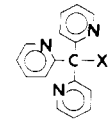
Bis[tris(2-pyridyl)methane]cobalt(III)] Hexafluorophosphate (20). To 49 mg (0.058 mmol) of $[(2\text{-py})_3CH]_2Co^{II}[PF_6]_2$ in 3 mL of CH_3CN was added 16.5 mg (0.065 mmol) of $AgPF_6$ with stirring. Over the course of 15 min, the solution changed from orange to yellow with the appearance of a fine gray precipitate. The solution was filtered and the filtrate reduced in volume by about 50%. Two milliliters of toluene was added, and 29 mg (51%) of yellow crystals, mp 350 °C, was obtained by slow evaporation of this solution.

Anal. Calcd for $C_{32}H_{26}N_6P_3F_{18}Co$: C, 38.89; H, 2.65; N, 8.50. Found: C, 38.80; H, 2.69; N, 8.31.

^1H NMR (CD_3CN, 298 K): δ 7.24 (d^2, $J_{6,5}$ = 6.1, $J_{6,4}$ = 1.2 Hz, 3 H, py 6-H), 7.33 (s, 1 H, C–H), 7.34 (overlapping d^3, $J_{5,4}$ = 7.1, $J_{5,6}$ = 6.1, $J_{5,3}$ = 1.6 Hz, 3 H, py 5-H), 8.30 (overlapping d^3, appears as a 1:2:1 t (d), $J_{4,3}$ = 7.8, $J_{4,5}$ = 7.1, $J_{4,6}$ = 1.2 Hz, 3 H, py-4H), 8.3m (d^2, $J_{3,4}$ = 7.8, $J_{3,5}$ = 1.6, 3 H, py 3-H).

Results and Discussion

One of the original reasons for the preparation and study of tris(2-pyridyl)methanol was the comparison to triphenylmethanol. Although there are major differences (vide infra), the triphenylmethyl system is still a useful analogue for choosing reagents and reaction conditions and for hypothesizing mechanisms in the tris(2-pyridyl)methyl system. A priori, one would expect the tris(2-pyridyl)carbonium ion (**2**)



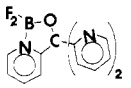
1 X = OH
2 X = +
3 X = $OCOCH_3$,

to be destabilized relative to the triphenylcarbonium ion due to the electronegativity of the pyridine nitrogens. However, greater resonance stabilization may be possible in **2** since there is less steric hindrance to a planar configuration from ortho hydrogens.[5,6] Both of these factors would tend to stabilize

tris(2-pyridyl)carbanion relative to triphenylcarbanion. The basicity of the pyridine nitrogens and the acidity of the pyridine ring hydrogens were complicating factors of unknown magnitude, and in actual reactions these predominated over the simple resonance and electronegativity analogies. Certain features appeared worthy of investigation relative to potential donor properties of the C–OH moiety and the chemistry of the carbinol when acting as a ligand.

The failure of Wibaut and co-workers[1] to obtain a colored, stabilized carbonium ion from tris(2-pyridyl)methanol discouraged further investigation of the chemistry of this system at that time. We repeated the reaction of tris(2-pyridyl)-methanol with concentrated sulfuric acid and also tried HPF_6 and HBF_4 under a variety of conditions. In no case was a colored reaction product or other indication of a stabilized carbonium ion observed. Instead, one (or more) of the pyridine nitrogens was protonated, and the resulting cation did not undergo O-protonation and C–O cleavage to yield a carbonium ion. The greater basicity of the pyridine nitrogen vis-ā-vis the oxygen and intramolecular H bonding prevented the latter reaction.

A novel reaction was observed, however, when **1** was treated with 4 equiv of $HBF_4{\cdot}OEt_2$ or 40% aqueous HBF_4 in propionic anhydride. A nonionic, base-stable product was isolated, the properties of which were consistent with structure **7**. The ^1H

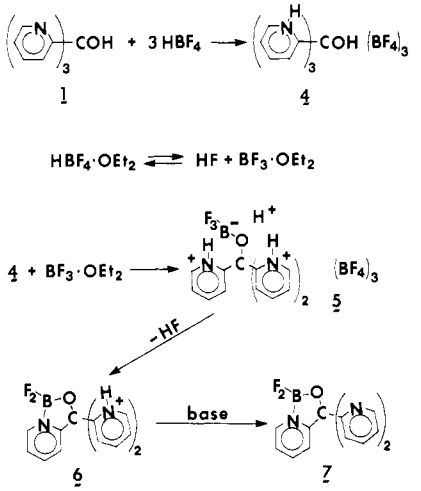


7

assignments were based on spin-decoupling experiments. The apparent absence of ^{19}F–^{11}B spin–spin coupling in the ^{19}F and ^{11}B spectra was attributed to quadrupole broadening.[7] The shoulder appearing 0.1 ppm upfield from the ^{19}F maximum has been tentatively assigned to the ^{19}F–^{11}B resonance.[8] Last, the mass spectrum of the product clearly shows the parent ion and ions resulting from loss of F and BF_2.

Gerrard and co-workers[11] characterized 1:1 pyridine complexes of simple alkoxydifluoroboranes and also isolated an insoluble 2:1 complex. The ^1H NMR spectrum of **7** indicates that it is a 1:1 complex. The corresponding protons of the two noncomplexed pyridine rings have identical chemical shifts and are comparable to those of the starting material **1**; the protons of the complexed ring are shifted downfield, indicating a decreased electron density.

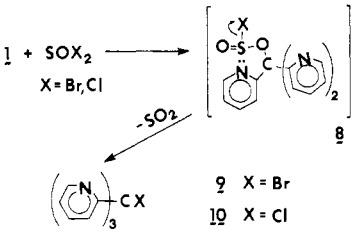
The reactions of HBF_4, BF_4^-, and BF_3 with Lewis bases[12-14] suggest a number of possible reaction mechanisms. The one illustrated here accounts for the experimental observations. The initial equivalents of acid react to form pyridinium salts. The resulting tris(2-pyridiniumyl)methanol tris(tetrafluoroborate) (**4**) reacts with BF_3OEt_2 (or other Lewis base complexes of BF_3) present in the reaction mixture to yield **5**. This intermediate eliminates HF to form the intermolecular Lewis acid–base complex **6**. Cook[15] reported an analogous reaction



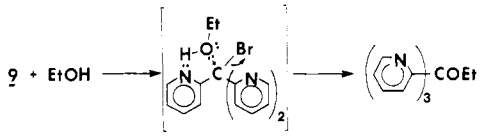
between pyridine 1-oxide and aqueous HBF_4 that involved elimination of HF and formation of the BF_3 complex. The product **6** is stabilized by an intramolecular complex formation with one of the pyridine nitrogens. This is the same phenomenon that accounts for the enhanced hydrolytic stability of diethanolamine esters of boronic acids.

The difficulty of C–O cleavage in tris(2-pyridyl)methanol is further illustrated by its reaction with acetyl bromide. In contrast again to triphenylmethanol, it gave the acetyl ester (**3**) rather than the halomethane.

The chloro- and bromomethanes were available through reaction of the methoxide with the appropriate thionyl halide. The reaction may proceed via an S_N2 mechanism involving an intimate ion pair derived from **8**, although an S_N1 mechanism cannot be excluded.[16]



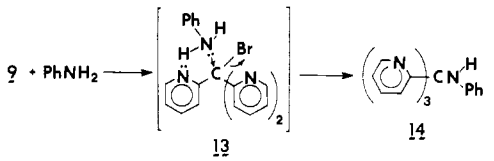
The halomethanes could be converted to alkyl ethers (e.g., **12**) by refluxing in the appropriate alcohol. Again, an S_N2 mechanism appears likely and possibly involves hydrogen bonding as in **11**.



The reaction of **9** with aniline yielded the N-substituted aniline, probably, by a mechanism analogous to that above. In contrast, triphenylhalomethanes react via an electrophilic attack of trityl ion on aniline to give (4-aminophenyl)triphenylmethane (**15**).[17]

Tris(2-pyridyl)bromomethane underwent lithium–halogen exchange cleanly at −95 °C, and hydrolysis of the pale yellow reaction mixture gave the parent member of the series, tris(2-pyridyl)methane (**17**) in 55% yield. When the reaction

(5) Schuster, I. I.; Colter, A. K.; Kurland, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 4679–4687.
(6) Hoffmann, R.; Bissell, R.; Farnum, D. G. *J. Phys. Chem.* **1969**, *73*, 1789–1800.
(7) Harris, R. K.; Mann, B. E. "NMR and the Periodic Table"; Academic Press: London, 1978; Chapter 4.
(8) The isotope effect observed for $^{10}BF_4^-$ was 0.05 ppm downfield.[9] An anomalous (i.e., downfield) shift has been observed in C_6HD_5.[10]
(9) Kuhlman, K.; Grant, D. M. *J. Phys. Chem.* **1964**, *68*, 3708.
(10) Yonemitsu, T.; Kubo, K. *J. Chem. Soc., Chem. Commun.* **1981**, 309.
(11) Gerrard, W.; Mooney, E. F.; Peterson, E. G. *J. Inorg. Nucl. Chem.* **1967**, *29*, 943–49.
(12) (a) Wamser, C. A. *J. Am. Chem. Soc.* **1948**, *70*, 1209–1215. (b) Wamser, C. A. *Ibid.* **1951**, *73*, 405–416.
(13) Meeswein, H. *Ber. Dtsch. Chem. Ges. B* **1933**, 66B, 411.
(14) (a) Diehl, P.; Granacher, *J. Helv. Phys. Acta* **1958**, *31*, 43–44. (b) Diehl, P.; Ogg, R. A., Jr. *Nature (London)* **1957**, *180*, 114.
(15) Cook, D. *Chem. Ind. (London)* **1964**, 1259.
(16) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; pp 302–303 and references therein.
(17) MacKenzie, C. A.; Chuchani, G. *J. Org. Chem.* **1955**, *20*, 336–345.



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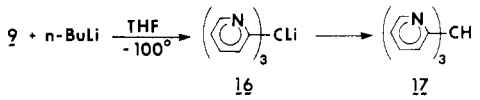
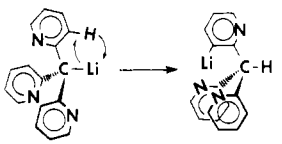


16 17

temperature was allowed to reach −70 to −60 °C, however, side reactions took place that resulted in lower yields of **17** contaminated with byproducts that were very difficult to remove. The reddish orange color of the reaction mixture under these conditions indicated that lithium–hydrogen exchange was taking place to produce lithiopyridines. Examination of molecular models suggested that an intramolecularly directed metalation[18] could be involved.



16 18

Attempted coupling reactions of **9** with PhLi or PhLi TMEDA gave after hydrolysis low yields of **17** and no detectable coupling product. Lithium–hydrogen exchange, perhaps preceded by lithium–halogen exchange, occurred instead of the desired coupling and elimination of LiBr.

Conclusions

The tris(2-pyridyl)methanes constitute a metal ion–ligand system with C_{3v} symmetry and considerable synthetic versatility. Tris(2-pyridyl)methanol, the synthetic precursor, can be obtained in moderate yield in one step from commercially available starting materials. This compound can easily be converted into esters and halides. The latter can be converted into ethers by refluxing with the appropriate alcohols. Tris(2-pyridyl)halomethanes can be converted to the lithium reagent at −95 °C, but this compound is highly reactive and undergoes side reactions as the temperature is increased. Hydrolysis of the lithium reagent provides the parent member of the series, tris(2-pyridyl)methane.

In contrast to the triphenylmethane system, the reactions of tris(2-pyridyl)methane derivatives do not involve stabilized carbonium ions. Instead, they are characterized by S_N2-type reaction mechanisms.

These syntheses provide a wide range of functionalized tridentate ligands.[19] This allows facile control of solubility, complex charge, and potential modes of covalent attachment of the ligands to substrates or supports. The ligands tend to bind in a tridentate manner in most of their complexes, as suggested by the equivalence of all of corresponding resonances in the three pyridyl rings in the diamagnetic cobalt complex ion $[(2\text{-py})_3CH]_2Co^{III}$ (**20**). The effective 3-fold symmetry is also implied by the equivalence of the isotropically shifted resonances in the cobalt(II) analogue, **19**. Whereas N,N′,O binding may occur in the binding of tripyridylcarbinol,[20] the mode of attachment in tripyridylmethane is limited to N,N′,N″ binding. This is particularly important in model enzyme studies where comparisons between pyrazolylborates, tripyridylmethanes, and tripyridylcarbinols can be made.[3,21]

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Registry No. **1**, 73569-80-9; **3**, 81940-16-1; **7**, 81956-59-4; **9**, 81940-17-2; **10**, 81940-18-3; **12**, 81940-19-4; **14**, 81940-20-7; **17**, 77429-58-4; **19**, 81956-61-8; **20**, 81970-27-6; ethanol, 64-17-5; acetyl bromide, 506-96-7; $HBF_4 \cdot OEt_2$, 67969-82-8; aniline, 62-53-3.

(18) Slocum, D. W.; Sugarman, D. I. In "Polyamine-Chelated Alkali Metal Compounds"; Langer, A. W., Ed.; American Chemical Society: Washington, D.C., 1974; Adv. Chem. Ser. No. 130, Chapter 12.

(19) Treatment of the halides with Grignards or dialkylmagnesium reagents provide a general method for the preparation of alkyl and aryl analogues (Faller, J. M.; Maheu, L., unpublished work).

(20) An X-ray crystal structure of the cobalt(III) derivative formed with tripyridylcarbinol contains one $(py)_3COH$-*N,N′,N″* and one $(py)_3CO^-$-*N,N′,O* ligand (Faller, J. W.; White, D. L., unpublished work).

(21) Tang, C. C.; Davalian, D.; Huang, P.; Breslow, R. *J. Am. Chem. Soc.* **1978**, *100*, 3918–3922.