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Poly(1-pyrazolyl)borate Complexes of Titanium

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By virtue of their steric properties, poly(1-pyrazolyl)borates[1] stabilize unusual coordination geometries and high degrees of coordinative unsaturation.[2] The transition metal chemistry of hydrotris(1-pyrazolyl)borate ($HB(pz)_3^-$) is, to some degree, reminiscent of that of the cyclopentadienyl ion.[1] With these properties and the known instability of the lower oxidation states of the group 4A metals[3] in mind, we began an investigation of poly(1-pyrazolyl)borate complexes of titanium. A recent report of similar work[4] prompts us to present our results.

Experimental Section

All solvents were purified by distillation from sodium benzophenone ketyl except CH_2Cl_2, CH_3CN, and CH_3OH, which were distilled from P_4O_{10}, CaH_2, and $Mg(OCH_3)_2$, respectively. Potassium hydrotris(1-pyrazolyl)borate and potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate were prepared by literature methods.[5] Titanium tetra- and trichlorides were used as received (Alfa Inorganics).

Manipulations throughout were performed under an atmosphere of prepurified nitrogen. Infrared, 100-MHz ^1H NMR, and mass spectra were obtained on Perkin-Elmer 457A, Varian XL-100, and AEI MS9 instruments, respectively. Elemental analyses were by Galbraith Laboratories Inc., Knoxville, Tenn.

$HB(pz)_3TiCl_3$ (1). $K[HB(pz)_3]$ (5.18 g, 20.6 mmol) was dissolved in 100 ml of THF. To the cooled solution (0 °C) was added dropwise 2.30 ml (20.6 mmol) of $TiCl_4$ and the resulting yellow suspension was refluxed for 12 h. The yellow solid was collected by filtration, dried in vacuo, and sublimed (180 °C (2 μ)) onto a water-cooled probe, affording 3.99 g (10.9 mmol, 53%) of fine yellow-orange needles: ^1H NMR ($CDCl_3$) δ 6.28 (t, 1 H), 7.68 (d, 1 H), 8.26 (d, 1 H); ir (Nujol mull) ν_{CH} 3133 (m), ν_{BH} 2519 (s) cm^{-1}; mass spectrum *m/e* 366, $[^{12}C_9{}^1H_{10}{}^{11}B^{35}Cl_3{}^{14}N_6{}^{48}Ti]^+$, 331, $[P - Cl]^+$, 296, $[P - 2Cl]^+$.

Anal. Calcd for $C_9H_{10}BCl_3N_6Ti$: C, 29.43; H, 2.75; Cl, 28.96; N, 22.88. Found: C, 29.91; H, 2.90; Cl, 29.75; N, 23.39.

$HB(3,5\text{-}Me_2pz)_3TiCl_3$. The procedure was analogous to that for **1**. Recrystallization from hot benzene gave red-orange prisms (64%): ^1H NMR ($CDCl_3$) δ 2.32 (s, 3 H), 2.70 (s, 3 H), 5.74 (s, 1 H); ir (Nujol mull) ν_{CH} 3119 (vw), ν_{BH} 2555 (s) cm^{-1}; mass spectrum *m/e* 415, $[^{12}C_{15}{}^1H_{22}{}^{11}B^{35}Cl_3{}^{14}N_6{}^{48}Ti - Cl]^+$, 380, $[P - 2Cl]^+$.

Anal. Calcd for $C_{15}H_{22}N_6Cl_3TiB$: C, 39.91; H, 4.91; N, 18.62. Found: C, 39.92; H, 4.97; N, 18.60.

Sodium Amalgam Reduction of 1 in THF. To 450 mg (1.23 mmol) of **1** in 20 ml of THF was added a large excess Na(Hg) with vigorous stirring. The initial yellow suspension gave a green solution within several minutes, which rapidly faded to gray. The supernatant was immediately decanted, freed of suspended matter by centrifugation, and evaporated to dryness. The residue was slurried with 15 ml of THF, collected by filtration, and dried in vacuo to give 110 mg (0.27 mmol, 22%) of blue $HB(pz)_3TiCl_2(C_4H_8O)$ (**2**). An analytical sample was obtained by recrystallization from hot THF–hexane: ir (Nujol mull) ν_{CH} 3120 (w), ν_{BH} 2500 (m) cm^{-1}; mass spectrum *m/e* 331, $[^{12}C_{13}{}^1H_{18}{}^{11}B^{35}Cl_2{}^{14}N_6{}^{16}O^{48}Ti - THF]^+$, 296, $[P - Cl, THF]^+$.

Anal. Calcd for $C_{13}H_{18}BCl_2N_6OTi$: C, 38.66; H, 4.49; B, 2.68; Cl, 17.56; N, 20.80. Found: C, 38.24; H, 4.65; B, 2.93; Cl, 17.75; N, 20.54.

Reaction of Methanolic $TiCl_3$ with $K[HB(pz)_3]$. To a solution of 2.30 g (14.9 mmol) of $TiCl_3$ in 100 ml of CH_3OH was added 5.5 g (21.8 mmol) of $K[HB(pz)_3]$ and the mixture was stirred for 3 h. The solvent was evaporated to give a dark gum which solidified on trituration with ether. The solid was treated with THF repeatedly until the washings were colorless, leaving a pale blue solid. Extraction with boiling CH_3CN (20 ml), filtration, and removal of solvent in vacuo afforded 1.81 g (5.51 mmol, 37%) of $[HB(pz)_3TiCl(OCH_3)]_2$ (**3**); an analytical sample was recrystallized twice from CH_3CN: ir (Nujol mull) ν_{CH} 3122 (m), ν_{BH} 2512 (m) cm^{-1}; mass spectrum *m/e* 619, $[^{12}C_{20}{}^1H_{28}{}^{11}B_2{}^{35}Cl_2{}^{14}N_{12}{}^{16}O_2{}^{48}Ti_2 - Cl]^+$, 327, $[P/2]^+$.

Anal. Calcd for $C_{20}H_{26}B_2Cl_2N_{12}O_2Ti_2$: C, 36.57; H, 4.30; B, 3.29; Cl, 10.80; N, 25.58; O, 4.87; Ti, 14.59. Found: C, 36.71; H, 4.10; B, 3.30; Cl, 10.68; N, 25.48; O (by difference), 5.31; Ti, 14.42.

Extraction of the dark gum above with ether gave a deep purple solution. A purple solid was obtained by slow evaporation. Recrystallization from hot CH_2Cl_2–hexane gave fine purple needles, $HB(pz)_3TiCl_2(C_3H_3N_2H)$ (7%) (**4**): ir (Nujol mull) ν_{NH} 3360 (s), ν_{CH} 3200 (m), 3170 (m), ν_{BH} 2535 (m) cm^{-1}.

Anal. Calcd for $C_{12}H_{14}BCl_2N_8Ti$: C, 36.04; H, 3.53; B, 2.70; Cl, 17.73; N, 28.01; Ti, 11.98. Found: C, 35.48; H, 3.45; B, 2.62; Cl, 19.38; N, 27.83; Ti, 11.69.

Results and Discussion

Titanium tetrachloride reacts with $K[HB(pz)_3]$ and potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate ($K[HB(3,5\text{-}Me_2pz)_3]$) to give $HB(pz)_3TiCl_3$ (**1**) and $HB(3,5\text{-}Me_2pz)_3TiCl_3$ without contamination by more substituted products (eq 1). Attempts to prepare bis[hydrotris(1-pyrazolyl)borate] Ti(IV) complexes were unsuccessful even under forcing conditions, e.g. treating **1** with a large excess of $HB(pz)_3^-$ at elevated temperatures for prolonged periods (in fact, **1** is inert to molten $Tl[HB(pz)_3]$[6]). The inability of **1** to undergo further substitution by $HB(pz)_3^-$ is not surprising in light of the highly crowded geometry required for disubstituted products. The sterically hindered nature of **1** is reflected by its resistance to hydrolysis. The compound is unaffected by treatment with water, in contrast to the isoelectronic $(\eta\text{-}C_5H_5)TiCl_3$ and amine adducts of $TiCl_4$ which are hydrolyzed by moist air.[3d,7]

$$K[HB(pz)_3] + TiCl_4 \xrightarrow[THF]{} HB(pz)_3TiCl_3 \xrightarrow[\text{excess } HB(pz)_3]{\quad\times\quad} \tag{1}$$

Reduction of **1** with Na(Hg) in THF gives a deep green solution which fades to blue within minutes. The blue color is attributable to the previously reported[4] $HB(pz)_3TiCl_2(THF)$ (**2**), which can be isolated in good yields from the solution. Analytical, mass spectral, and infrared data are consistent with this formulation. In our hands, attempts at isolation of the green intermediate were not successful. Decantation of the green solution from excess reductant still resulted in formation of the blue species, **2**. The green intermediate is, therefore, a Ti(III) complex undergoing substitution or isomerization to give the observed product, as suggested in eq 2. Surprisingly, the reaction is unaffected by the presence of triethylphosphine. Reportedly, **2** is unchanged by crystallization from hot CH_3CN.[4] Further reduction of **2** with Na(Hg) resulted in a deep purple solution from which only intractable materials could be obtained.

$$1 \xrightarrow[Na(Hg)]{} [HB(pz)_3TiCl_2]_n \xrightarrow[THF]{} \underset{2}{HB(pz)_3TiCl_2(THF)} \tag{2}$$

Treatment of methanolic $TiCl_3$ with $K[HB(pz)_3]$ (after passing through a green intermediate) affords a pale blue solid which is formulated as $[HB(pz)_3TiCl(OCH_3)]_2$ (**3**) on the basis of analytical data. The mass spectrum supports the proposed dimeric nature of **3**, since an isotope cluster corresponding nearly exactly to that calculated for a $[P - Cl]^+$ unit is observed as a dominant feature. Further, the envelope corresponding to the monomer is observed with approximately equal amounts of isotope clusters corresponding to $HB(pz)_3TiCl_2^+$ and $HB(pz)_3Ti(OCH_3)_2^+$, suggesting cleavage of a dimer, accompanied by statistical scrambling of ligands. Accordingly, we propose the structure indicated in eq 3 and note that **3** may arise from solvolysis of an intermediate such as that suggested in eq 2. The presence of a similar intermediate is suggested by the similarity of color changes.

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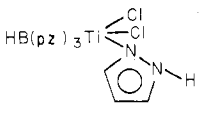
(3)

A deep purple component, isolated in minor amounts, corresponds to $HB(pz)_3TiCl_2(C_3H_3N_2H)$ (**4**) on the basis of



4

analytical data. The presence of an N–H stretch implies an N-coordinated pyrazole unit.

The addition of a large excess of $K[HB(pz)_3]$ did not give disubstitution products, consistent with the chemistry found for Ti(IV).

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Synthesis and Characterization of New Isomeric Water-Soluble Porphyrins. Tetra(2-*N*-methylpyridyl)porphine and Tetra(3-*N*-methylpyridyl)porphine

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Numerous studies on the kinetics and mechanisms of porphyrin[1,2] and metalloporphyrin[3,4] reactions have been done using the monomeric and fully water-soluble tetra(4-*N*-methylpyridyl)porphine (TMpyP(4)).[5] Since an isomeric series of water-soluble porphyrins would yield valuable structure–reactivity information similar to that obtained with 2,4-disubstituted deuteroporphyrin dimethyl esters in nonaqueous media,[6] we report the synthesis and characterization of the ortho (2) and meta (3) *N*-methylated derivatives tetra(2-*N*-methylpyridyl)porphine (TMpyP(2)) and TMpyP(3). Although the Mössbauer parameters of the solid oxy-bridged iron dimers of the parent tetrapyridylporphines (TpyP) were similar,[7] the parent isomers were electrochemically reduced by different mechanisms in 1.0 M HCl.[8] We demonstrate that certain TMpyP and TpyP types behave differently with respect to both acid solvolysis of the zinc chelates and protonation.

Table I. ZnP Solvolysis Half-Lives (seconds) in 1.0 M Acid Solutions (25 °C)

	HCl	HNO_3
Zn-TMpyP(3)[a,b]	17	89
Zn-TpyP(3)	13	57
Zn-TMpyP(4)	28	165
Zn-TpyP(4)	24	131
Zn-TMpyP(2)	5.0×10^3	6.9×10^4
Zn-TpyP(2)	1.3×10^3	

[a] In 1.0 M $HClO_4$ for Zn-TMpyP(3), $t_{1/2} = 59$ s, and for Zn-TpyP(3), $t_{1/2} = 45$ s. [b] Data are an average of four determinations, ±10%.

Experimental Section

TpyP(2) and Tpy(3) were purchased from ManWin Coordination Chemicals, Washington, D.C. 20059. The tosylate salts were made by refluxing either chloroform or DMF solutions of the porphyrin with excess methyl *p*-toluenesulfonate. Both of the alkylated porphyrins spontaneously precipitated from hot chloroform solutions and were washed with ether and air-dried. The crystalline tosylate of TMpyP(3) could be filtered from the hot DMF solution, while the ortho derivative required the addition of ether to the cold DMF reaction mixture to precipitate the porphyrin salt. The tosylate (Ts) or iodide of TMpyP(3) (from CH_3I) also forms at room temperature by stirring the porphyrin and methylating agent overnight in chloroform.[5] Anal. Calcd for H_2–TMpyP·4Ts·$3H_2O$, $C_{76}H_{66}N_8S_4O_{12}\cdot 3H_2O$: C, 61.0; H, 5.11; N, 7.90. Found for TMpyP(2): C, 60.9; H, 5.4; N, 7.8. Found for TMpyP(3): C, 61.3; H, 5.2; N, 8.1.

The absorption spectra of the porphyrins in 1.0 M HCl (25 °C) are as follows (λ, nm (log ε)): for TMpyP(3), 632 (4.39), 582 (3.57), 432 (5.60); for TMpyP(2), 634 (3.13), 582 (3.86), 545 (3.57), 512 (4.2), 413 (5.5); for TpyP(2), 633 (3.93), 585 (4.08), 437 (5.33). The TpyP(2) spectra agree with literature data.[8] The tosylate-free bases at pH 7 followed Beer's law over a 260-fold dilution (4.5×10^{-4}–1.7×10^{-6} M).

Results and Discussion

TMpyP(4) precipitates immediately from 2.0 M $HClO_4$, and TMpyP(3) requires 24 h at 0 °C, while TMpyP(2) remains in solution. The solubilities in $CHCl_3$ at 25 °C for TpyP(4), -(3), and -(2) are (3, 226, and 12) $\times 10^{-3}$ mol dm^{-3}, respectively. The same relative order was found in the monofluoro (4, 3, and 2) phenyl-substituted tetraphenylporphine series.[9]

All reported porphyrins, TMpyP(3), TMpyP(4), and their parent TpyP's are in the diacid (H_4P) forms in 1.0 M HCl. TMpyP(2), however, has essentially the same free base (H_2P) spectra at pH 7 as in 1.0 M HCl, making it the least basic porphyrin toward proton addition known. This is presumably a consequence of the repulsive and inductive effects of the four positive *N*-methyl groups in close proximity to the central nitrogen atoms. TpyP(2) in 1.0 M HCl is a mixture of the diacid and the monocation (H_3P) forms. Both the steric effects of the bulky *N*-alkyl groups and the permanent positive charges in the ortho positions could make TpyP(2) more basic than TMpyP(2). This positive charge effect on basicity decreases with the distance of the *N*-alkyl groups from the porphyrin center, as evidenced by the similar apparent basicities of the substituted and unsubstituted meta and para derivatives.

The acid solvolysis behavior of the zinc porphyrin isomers was studied in 1.0 M acid solutions at 25 °C. Under pseudo-first-order conditions, the reactions were first order in ZnP, and the observed half-lives are given in Table I. The rate differences between HCl and HNO_3 for TpyP(4)) were shown to arise from different rate laws.[5,10] In a series of zinc 2,4-disubstituted deuteroporphyrins,[6] the rates of solvolysis were faster the higher the basicity of the free base porphyrin toward protons (pK_3). The same trend is apparent here; the parent meta and para Zn–TpyP derivatives are slightly more reactive than their Zn–TMpyP adducts, while Zn–TpyP(2) reacts 4