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POLYPYRAZOLYLBORATE COMPLEXES OF TITANIUM AND VANADIUM

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Summary

A series of polypyrazolylborate complexes of the type $Cp_2Ti(Pz_{4-x}BH_x)$ (where x is 0, 1, or 2; Pz is pyrazole or substituted pyrazole) have been prepared. Electron spin resonance and electronic spectroscopy indicate that the cyclopentadienyl groups are *pentahapto* and the pyrazolylborate ligand is bidentate. The reaction between Cp_2VCl and $KHBPz_3$ gave a mixture of compounds from which the vanadium(II) compound, $CpV(HBPz_3)$, was isolated. $KHBPz_3$ reacts with $MCl_3(THF)_3$ (where M = Ti, V) to give $MCl_2(THF)(HBPz_3)$ as paramagnetic air sensitive crystalline solids. Cyclopentadienyltitanium trichloride reacts with $KHBPz_3$ to give $Cp(HBPz_3)TiCl_2$ as a deep red crystalline solid. Reduction of this compound with zinc gave $Cp(HBPz_3)TiCl$ which can also be prepared from $[CpTiCl_2]_x$ and $KHBPz_3$.

Introduction

Since the discovery of the pyrazolylborate ligands by Trofimenko [1] many papers have appeared in the literature describing their transition metal derivatives. Most studies have been directed towards metals in Groups VIB, VIIB and VIII. In this paper is described the preparation and characterization of the first polypyrazolylborate** complexes of titanium and vanadium. Emphasis has been placed on preparing polypyrazolylborate compounds where the analogous cyclopentadienyl compounds are known.

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* Contribution No. 2242.

** For brevity Pz = $N_2C_3H_3$.

Results and discussion

A. Titanium(IV) complexes

Cyclopentadienyltitanium trichloride reacts immediately with $KHBPz_3$ in dichloromethane to give a deep red crystalline precipitate along with KCl. Removal of the solvent by rotary evaporation, followed by washing with H_2O gives pure $Cp(HBPz_3)TiCl_2$. The compound is completely insoluble in most common organic solvents and decomposes when dissolved in hot dimethylformamide or nitromethane. The compound is moderately air stable; however it does decompose on standing after several months.

Cp_2TiCl_2 with aluminum alkyls is known to be a good hydrogenation catalyst for olefins [2]. However, $Cp(HBPz_3)TiCl_2$, neither by itself nor with six equivalents of Et_2AlCl, was active in the hydrogenation or isomerization of 1-butene in benzene to 90°C and 42 psi pressure.

B. Titanium(III) complexes

The reduction of $Cp(HBPz_3)TiCl_2$ with zinc dust in tetrahydrofuran gave $Cp(HBPz_3)TiCl$ as a greeen solid. A more convenient preparation involves the reaction of $[CpTiCl_2]_x$ with one equivalent of $KHBPz_3$ in THF. Potassium chloride rapidly precipitates and, after filtration, $Cp(HBPz_3)TiCl$ can be isolated in good yield.

The reaction of $TiCl_3$ with one equivalent of $KHBPz_3$ in THF gave a purple precipitate. After stirring for two hours the solution was filtered and the compound was extracted from KCl with boiling acetonitrile. Cooling to -40°C overnight gave bright blue crystals of $TiCl_2(THF)(HBPz_3)$. It is interesting that the coordinated THF was not displaced by acetonitrile during the recrystallization. The cyclopentadienyl analogue, $TiCl_2(THF)Cp$ [3], readily loses the coordinated THF to form the polymeric $[TiCpCl_2]_x$. An attempt to remove the coordinated THF in the pyrazolylborate complex by heating in vacuum only resulted in decomposition.

The electronic spectrum of $TiCl_2(THF)(HBPz_3)$ consisted of a broad peak at 17620 cm^{-1} with a shoulder at 14730 cm^{-1}. For a d^1 ion in an octahedral environment two electronic transitions are expected in the visible region due to a splitting of the $^2E_{2g}$ levels [4]. This splitting is calculated to be 2890 cm^{-1} for $TiCl_2(THF)(HBPz_3)$. The magnetic moment in CH_2Cl_2 was 1.7 BM and is entirely consistent with a d^1 system.

The reaction of Cp_2TiCl with one equivalent of $KHBPz_3$ in tetrahydrofuran gave an air sensitive, bright blue crystalline compound $Cp_2Ti(HBPz_3)$. The compound is paramagnetic (μ_{eff} 1.69 BM) and exhibits a very sharp signal in the electron spin resonance spectrum at $g = 1.983 \pm 0.001$ which also shows hyperfine coupling to $^{47,49}Ti$, $\langle a_{Ti} \rangle = 11.2$ Gauss. Two broad absorptions are observed in the electronic spectrum at 635 and 740 nm. The mass spectrum shows a parent ion at m/e 391.129 (calcd. m/e 391.132). The structure of $Cp_2Ti(HBPz_3)$ is interesting since it is isoelectronic with $(C_5H_5)_3Ti$[*]. In order to achieve a 17-electron configuration, two bonding schemes are possible: (a) a bidentate $HBPz_3$ ligand and two *pentahapto*-C_5H_5 groups or (b) a tridentate $HBPz_3$ ligand with

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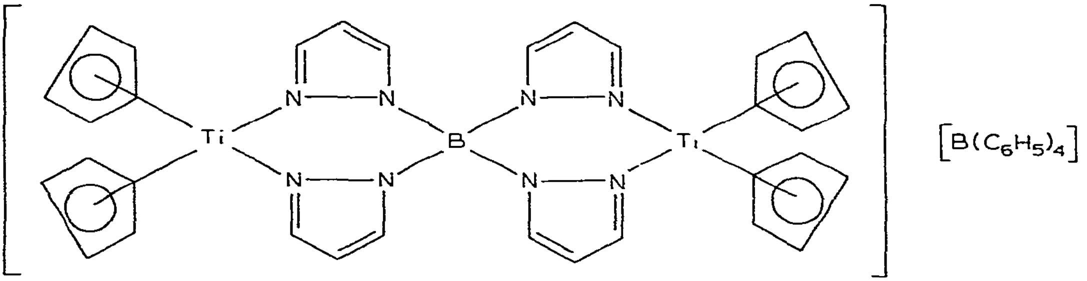
[*] An X-ray crystal structure of $(C_5H_5)_3Ti$ shows that the molecule contains two normal *pentahapto*-C_5H_5 units and an unusual *dihapto*-C_5H_5, giving the titanium atom a 17-electron configuration [5].

one *trihapto*- and one *pentahapto*-C_5H_5 group. Due to the paramagnetism of the compound, no NMR spectrum could be obtained so several other polypyrazolylborate complexes were synthesized for comparison.

The reactions of Cp_2TiCl with $KHB[3,5\text{-}(CH_3)_2Pz]_3$, $KBPz_4$, and KH_2BPz_2 gave air sensitive crystalline products. The ESR and electronic spectra are very similar to the hydrotris(1-pyrazolyl)borate complex (Table 1). Since the dihydrobis(1-pyrazolyl)borate ligand can only bond as a bidentate ligand*, two *pentahapto*-C_5H_5 groups are expected in $Cp_2Ti(Pz_2BH_2)$. The tetrapyrazolylborate complex reacts with a further equivalent of Cp_2TiCl in the presence of sodium tetraphenylborate to give the spiro compound I. There can be little doubt that the tetrapyrazolylborate ligand is bridging between two titanium atoms. The visible spectrum shows two absorptions at 634 and 717 nm (Fig. 1). If we assume the local symmetry to be roughly C_{2v} two *d—d* transitions are expected and in fact two are observed; the separation between these two bands being 1820 cm^{-1}. The electronic spectra of the other complexes (Table 1) are very similar except in a few cases the doublet was not resolved and only a single broad absorption was observed. The frequency of the high energy band is some-



(I)

TABLE 1

ELECTRONIC AND ESR SPECTRAL DATA FOR SOME POLYPYRAZOLYLBORATE COMPLEXES OF TITANIUM(III)

Complex [a]	Absorption spectra [b]		ESR spectra [c]	
	Wavelength (nm)	Molar extinction (coefficient)	g_{iso}	$\langle a_{Ti} \rangle$ (G)
Cp_2TiPz_3BH	635	45	1.983	11.2
	740	48		
Cp_2TiPz_4B	622	63	1.983	11.0
	707	65		
$Cp_2TiPz_2BH_2$	~750 (broad)	~63		
$Cp_2Ti[3,5\text{-}(CH_3)_2Pz]_3BH$	~770 (broad)	~100	1.980	~13
$(Cp_2TiPz_2BPz_2TiCp_2)[BPh_4]$	634	76	1.982	~5
	717	80		

[a] Pz = $N_2C_3H_3$. [b] Spectra were recorded in 1 cm cells using THF as solvent. [c] *g* values are accurate to ±0.001.

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[*] The presence of several broad bands in the infrared spectrum in the region 2300-2500 cm^{-1} negates the possibility of B—H—Ti interactions.

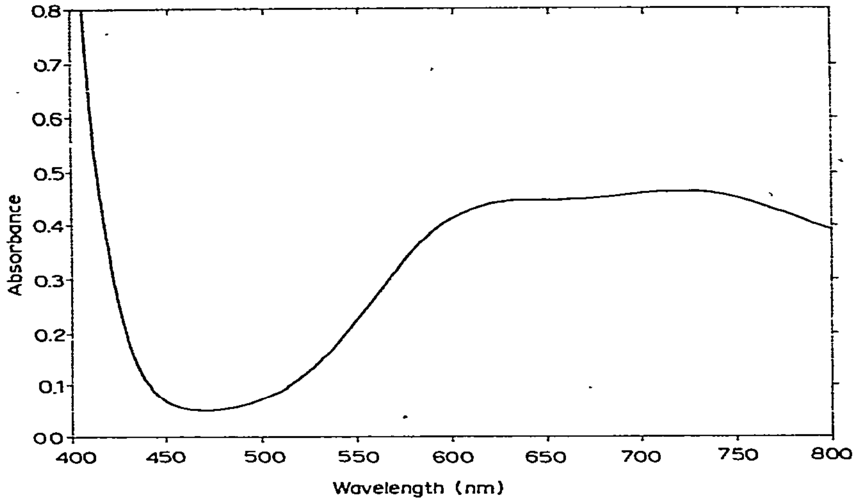


Fig. 1. Electronic spectrum of $(Cp_2TiPz_2BPz_2TiCp_2)BPh_4$ in tetrahydrofuran.

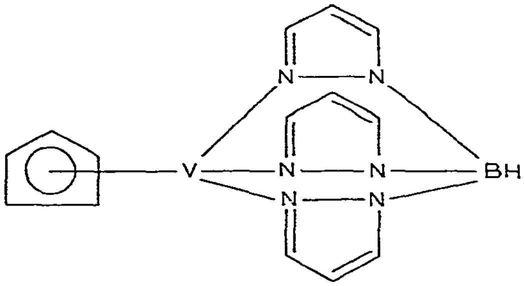
what higher than that observed for Cp_2TiCl (13300 cm^{-1}) which is consistent with the pyrazolylborate ligands having a ligand field strength higher than that of chloride. The electron spin resonance spectra also show very sharp signals at room temperature flanked by $^{47,49}Ti$ satellites. The resonances are all very similar at $g = 1.981 \pm 0.001$. If the structures of the various compounds were not similar, different visible and ESR spectra would be expected. Therefore it seems likely that in all the complexes the pyrazolylborate ligand is bidentate with the third and fourth rings (where applicable) either free or coordinated to another metal atom.

The infrared spectrum of $Cp_2Ti(Pz_2BH_2)$ shows a number of vibrations in the 2300-2800 cm^{-1} region characteristic of terminal (B—H) stretching vibrations. The reaction of this compound with a further molar equivalent of Cp_2TiCl in the presence of $NaBPh_4$ led to the preparation of a new complex with no terminal B—H vibrations and what was hoped to be $(Cp_2TiPz_2BH_2TiCp_2)[BPh_4]$. However the analytical data shows that this is not obtained and attempts to obtain electronic and ESR spectra were unsuccessful due to decomposition of the sample.

C. Vanadium complexes

A reaction between Cp_2VCl and $KHBPz_3$ in tetrahydrofuran gave a mixture of products from which a bright green crystalline complex could be isolated by sublimation. The analytical and mass spectral data (parent ion at *m/e* 329.0886; calcd. *m/e* 329.0891) are consistent with structure II. The compound is paramagnetic (μ_{eff} 3.59 BM) and a cryoscopic molecular weight measurement in benzene indicated that II is monomeric. The electronic spectrum shows only a single absorption at 688 nm (ϵ 102). Although II is formally analogous to vanadocene, $V(C_5H_5)_2$, it is much less reactive and only slowly air oxidized.

$VCl_3(THF)_3$ reacts with one equivalent of $KHBPz_3$ in THF to give a sparingly soluble green solid $VCl_2(THF)[HBPz_3]$. Unlike the titanium(III) system, there



(II)

appears to be no cyclopentadienyl analogue of the vanadium(III) compound. The magnetic moment (μ_{eff} 2.7 BM) and electronic spectrum suggest an octahedral d^2 configuration.

Experimental

All reactions were performed under an atmosphere of nitrogen either in a Vacuum Atmospheres Drybox or on the bench using standard techniques for the manipulation of air sensitive compounds. All solvents were dried by passage through columns containing molecular sieves (Linde 4A) and sparged with nitrogen prior to use.

Anhydrous metal halides were purchased from Research Organic/Inorganic Chemicals Incorporated. $CpTiCl_3$ was obtained commercially from Alfa/Ventron.

Microanalyses were performed by the Physical and Analytical Division of this department.

Preparation of $TiCp_2Pz_3BH$

To a dark green-brown suspension of $TiCp_2Cl$ (2.61 g, 12.21 mmol) in 200 ml of THF was added dropwise a solution of $KHBPz_3$ (3.08 g, 12.21 mmol) in 50 ml of THF. The solution immediately turned dark blue with a precipitate of KCl. After magnetically stirring the solution for one hour, it was filtered, the KCl was washed with THF until colorless and the filtrate was reduced in volume to give a dark blue oil. The addition of ether results in the formation of large blue crystals. The flask was cooled at —40°C for one hour, the crystals were filtered off and washed with pentane. The yield was quantitative m.p. 137-138°C.

The analytical sample was recrystallized from THF and ether, then dried in vacuo. Anal.: Found: C, 60.96; H, 5.41; N, 21.46; Ti, 12.19. $C_{19}H_{21}BN_6Ti$ calcd.: C, 58.19; H, 5.40; N, 21.44; Ti, 12.22%. Magnetic moment in CH_2Cl_2: $\chi_M = 992 \times 10^{-6}$ emu/mol; μ_{eff} 1.7 BM.

Preparation of $Cp_2TiPz_2BPz_2$

To a suspension of Cp_2TiCl (2.0 g, 9.36 mmol) in THF was added $KBPz_4$ (2.98 g, 9.36 mmol). The solution turned green and eventually dark blue. After stirring for 12 hours the solution was filtered and the solvent removed by rotary evaporation to give a dark blue solid. The crystals were washed from the flask with ether and dried. Yield 3.66 g (86%) m.p. 231-232°C. Anal.: Found: C, 58.95; H, 5.21; N, 23.56; Ti, 9.74. $C_{22}H_{22}BN_8T$ calcd.: C, 57.79; H, 4.85; N, 24.52; Ti 10.48%. Magnetic moment in CH_2Cl_2: $\chi_M = 1265.07 \times 10^{-6}$ emu/mol; μ_{eff} 2.0 BM.

Preparation of $(Cp_2TiPz_2BPz_2TiCp_2)[BPh_4]$

To a solution of Cp_2TiCl (2.0 g, 9.36 mmol) in 80 ml of THF was added $KBPz_4$ (1.49 g, 4.68 mmol). The solution was stirred for one hour to give a deep green color. The addition of $NaBPh_4$ (1.60 g, 4.68 mmol) caused an immediate color change to blue. The solution was stirred for one hour, filtered and the THF volume was reduced. Ether was slowly added to give bright blue crystals which were filtered off and washed with ether. Yield was 4.0 g (95%), m.p. 284-285°C. Anal.: Found: C, 70.73, 69.96, 70.22; H, 5.45, 5.44, 5.37; N, 11.81, 11.51, 11.58. $C_{56}H_{52}B_2N_8Ti_2$ calcd.: C, 74.19; H, 5.78; N, 12.36%.

Preparation of $Cp_2Ti(3,5\text{-}Me_2Pz)_3BH$

To a solution of Cp_2TiCl (2.13 g, 10 mmol) in THF was added $KHB[3,5\text{-}(CH_3)_2Pz]_3$ (3.36 g, 10 mmol). The solution was stirred for 12 hours and filtered. The KCl was washed with THF until colorless, then the solvent was removed by rotary evaporation to give a blue solid that was washed from the flask with ether and pentane. Yield was 3.53 g (74%) m.p. 231-232°C. Anal.: Found: C, 63.46; H, 6.63; N, 17.49. $C_{25}H_{32}BN_6Ti$ calcd.: C, 63.18; H, 6.79; N, 17.69%. Magnetic moment in C_6H_6: $\chi_M = 942.0 \times 10^{-6}$ emu/mol; μ_{eff} 1.7 BM.

Preparation of $Cp_2TiPz_2BH_2$

To a suspension of Cp_2TiCl (3.0 g, 14.0 mmol) in ether was added NaH_2BPz_2 (2.39 g, 14.0 mmol). The solution was stirred for one hour, filtered and the volume of ether was reduced. Pentane was added and the flask was cooled to —40°C to give blue-green crystals. Yield 2.3 g (45%) m.p. 115-125°C. Anal.: Found: C, 58.85; H, 5.50; N, 16.08. $C_{16}H_{18}BN_4Ti$ calcd.: C, 59.12; H, 5.58; N, 17.24%.

Preparation of $Cp(HBPz_3)V$

Cp_2VCl (1.50 g, 6.93 mmol) was dissolved in THF and a solution of $KHBPz_3$ (1.73 g, 6.93 mmol) in THF was slowly added. The solution became dark green and after stirring for one hour was filtered. The THF was removed by rotary evaporation and ether was added to give a red brown solid and green solution. After filtration, pentane was added to the green solution. The solution was cooled to —40°C for several days to give green crystals. Yield 1.08 g (47%); m.p. 212-213°C. The compound was purified by sublimation at 150°C/10^{-4} mmHg. Anal.: Found: C, 50.38; H, 4.61; N, 25.84; V, 14.96. $C_{14}H_{15}BN_6V$ calcd.: C, 51.09; H, 4.59; N, 25.54; V, 15.48%. Visible spectrum in THF: 688 (14530); ϵ, 102. No ESR spectrum was observed to 144K. Magnetic moment in C_6H_6: $\chi_M = 5149.87 \times 10^{-6}$ emu/mol; μ_{eff} 3.6 BM.

Preparation of $TiClCp(HBPz_3)$

To a susepension of $(TiCp_2Cl)_x$ (2.0 g, 10.88 mmol) in THF was added a solution of $KHBPz_3$ (2.74 g, 10.88 mmol) in THF. The color rapidly turned green and after stirring overnight the solution was filtered and the filtrate was reduced in volume. Ether was added and the flask was cooled to —40°C for 24 hours to give a green powder that was filtered and washed with ether. Yield 3.0 g (79%) m.p. >150°C (dec.). Anal.: Found: C, 46.78; H, 5.16; Cl, 9.90; N, 19.26; Ti, 13.15. $C_{14}H_{15}BClN_6Ti$ calcd.: C, 46.52; H, 4.18; Cl, 9.81; N, 23.25; Ti, 13.25%.

ESR (toluene), broad resonance at $g = 1.978$, $\langle a_{Ti} \rangle = 13$ Gauss.

Preparation of $TiCi_2Cp(HBPz_3)$

$TiCl_3Cp$ (10.0 g, 45.6 mmol) was dissolved in 250 ml of CH_2Cl_2 and with stirring $KHBPz_3$ (11.5 g, 45.6 mmol) was added. A deep red crystalline precipitate separated. After stirring for two hours the solvent was evaporated by rotary evaporation and the solids were washed from the flask with water (in the air), methanol and petroleum ether to give 14.97 (83%) of deep red crystals. m.p. >300°C. Anal.: Found: C, 42.13; H, 3.78; Cl, 17.91; N, 21.02; Ti, 12.13. $TiC_{14}H_{15}BCl_2N_6Ti$ calcd.: C, 42.36; H, 3.81; Cl, 17.65; N, 21.17; Ti, 12.07%.

Preparation of $TiCl_2(THF)(HBPz_3)$

To a magnetically stirred suspension of $TiCl_3$ (8.0 g, 52.0 mmol) in THF was slowly added a solution of $KHBPz_3$ (13.1 g, 52.0 mmol). The solution gradually turned purple and deposited a purple precipitate. After stirring for two hours the solution was filtered. The solids were boiled in acetonitrile, filtered from the KCl cooled and the volume was reduced. Ether was added, followed by hexane and the solution was filtered to give a purple solid. Yield was 15.2 g (79%). The analytical sample was recrystallized from hot acetonitrile, m.p. 184-185°C. Anal.: Found: C, 38.22; H, 4.41; Cl, 18.51; N, 20.71; Ti, 12.39. $C_{13}H_{18}BCl_2N_6OTi$ calcd.: C, 38.64; H, 4.49; Cl, 17.55; N, 20.81; Ti, 11.86%.

No ESR spectrum at room temp; complex spectrum in frozen toluene. Visible spectrum in THF: 567 (17620); ϵ, 46 (br); 679 (14730); ϵ, 32 (sh). Magnetic moment in CH_3CN, $\chi_M = 982.31 \times 10^{-6}$ emu/mol $\mu_{eff} = 1.7$ BM.

Preparation of $VCl_2(THF)(HBPz_3)$

$VCl_3(THF)_3$ (4.0 g, 10.7 mmol) was suspended in THF and a solution of $KHBPz_3$ (2.70 g, 10.7 mmol) was slowly added. The color gradually changed from red to purple and deposited a green solid. The solution was filtered and the solids were washed with THF. The compound was dissolved in dichloromethane, filtered from the KCl and stripped to dryness to give light green crystals. Yield was 4.01 g (92%) m.p. 238°C. Anal.: Found: C, 36.84; H, 4.28; N, 21.24. $C_{13}H_{18}BCl_2N_6OV$ calcd.: C, 38.36; H, 4.46; N, 20.65%.

Visible spectrum (THF): 437 (22860); ϵ, 19; 627 (15940); ϵ, 10. No ESR spectrum was observed at –60°C. Magnetic moment in CH_3CN: $\chi_M = 2832.15 \times 10^{-6}$ emu/mol; $\mu_{eff} = 2.7$ BM.

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