Synthesis of New Series of Transition Metal Complexes with Poly (Pyrazolyl) Borates

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Summary: In structuring catalysis enzyme and chemistry, tridentate ligands and Scorpionate ligands are of significant worth. This study presents the synthesis of a tris(pyrazolyl)borate ligand to be utilized in transition metal complexes as possible redox shuttles. Complexes of general formula [AgTp], [MIIITp (Cl_2)] (M = Fe, Co), Tp = tri (1-pyrazolyl) borohydride and [AgTp*], [FeIIITp*(Cl_2)], Tp* = tris (3, 5-dimethyl-1-pyrazolyl) borohydride were synthesized and characterized in solid state. The Tp ligands were considered triply coordinated with the metal center with two bounded chloride atoms as per the information gathered from spectroscopic information. Entire preparations and operations were performed under argon using common Schlenk procedures. Elemental analysis was performed using (the EURO EA instrument). Thermolysis shows that the Tp ligand decomposes around 100°C and above 300°C for some complexes. The composites were simple to compose, yielded high yields, and were reasonably air sensitive. This study has examined the synthesis of a tris(pyrazolyl)borohydride ligand to develop an iron complex. Further studies conducting electrochemical tests should be carried out to demonstrate the effectiveness of this likely redox mediator.

Keywords: Scorpionate ligands; Tridentate ligands; Transition metals; Tri (1-pyrazolyl) borohydride; metal complexes.

Introduction

Bimetallic nanoparticles are significant because of the observed changes in characteristics compared to mono-metallics, considering the size effects along with the mixing of various metals, either as an alloy or as a core-shell structure [1]. These nanoparticles have significant technical potential in information storage and catalysis, putting them at the cutting edge of modern materials chemistry [1]. Synthetic approaches have synthesized bimetallic nanoparticles, producing products with various structural and physicochemical properties [2, 3]. It is promising to fabricate nanoparticles sustaining for longer period of time using environmentally benign molecules like biopolymers [4].

In structuring catalysis enzyme and chemistry, tridentate ligands and Scorpionate ligands are of significant worth. Studying the coordination chemistry of these ligands and their transition metal complexes can be very important, especially concerning steric effects and octahedral vs. tetrahedral structural preference for various transition metals. Furthermore, while creating the structures of metal binding sites of numerous metalloenzymes such as hemocyanin, blue copper proteins, and carbonic anhydrase (CA), the tris(pyrazolyl)borate and Scorpionate ligands are commonly used. Hydrotris(pyrazolyl)borates or Tp ligands are the most popular scorpionates since they initially appeared in journals in the mid-1960 Swiatoslaw Trofimenko. Tris(pyrazolyl)borates anion has the general formula $[HB(C_3N_2H_3)_3]^-$ which contains at least two pyrazolyl nitrogen donors (pz) for coordinating to a metal. A third pyrazole ring on the tetra-substituted boron atom can be curled toward the metal and may bond or screen it [5]. Another reason for the interest in studying these ligands and their complexes is their potential for use as catalysts in a wide variety of organic reactions [6]. This is especially important given that bulky Tp * ligands have proven to be suitable for separating low-coordination metal complexes.

Poly (pyrazolyl) borate has been extensively studied by organometallic, inorganic, and coordination chemists to treat compounds containing boron bound to nitrogen in the pyrazole nucleus. It resulted in a new class of boron heterocycles, transition metal compounds, and chelating ligands [7]. These monoanionic nitrogen-based ligands are mainly appealing because of the capacity to fine-tune their steric and digital properties and; thereby modify the reactivity of the bound metal center by converting the number and complexion of the substituents on the pyrazolyl moieties and the boron. These ligands are exceptionally flexible because the count of donor atoms in every ligand can differ from two to three in

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going from the bidentate ligands Bp^x to the reasonably tridentate ligands Tp^x and pz^0Tp^x. The steric features of the ligands can be improved by switching the substituents on the pyrazolyl rings. Poly (pyrazolyl) borates (Fig 1) and, in particular, the tris (pyrazolyl) borates (Tp^x) ligands are also named Trofimenko and Scorpionate [8] due to the most common tridentate coordination mode, resembling the clams and tail of a scorpion.

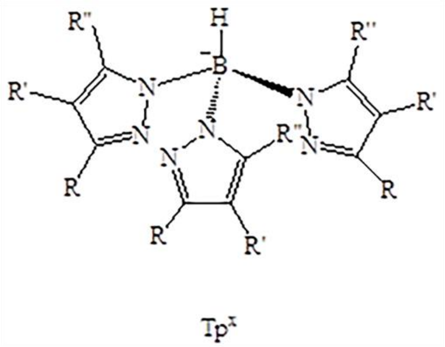


Fig. 1: General structures of Tp^x = tris (pyrazolyl) borates.

Considering the inherent instability of complexes containing a strongly oxidizing Ag(I) ion and a reducing (borohydride) ligand, the chemistry of tris(pyrazolyl)borate complexes (generically, Tp) with a silver(I) is rather underdeveloped as compared to rich coordination chemistry of the identical ligands with many other metals [9]. Recently, crystal structures of complexes of the kind [Ag(Tp)L] (where L is a monodentate co-ligand such as phosphine) have been reported, whose simple pseudo-tetrahedral structures are favored by tris(pyrazolyl)borates' general inclination to coordinate as face-capping terdentate chelates [9].

Since the discovery of binary silver(I) complexes with tris(pyrazolyl)borate ligands in 1979, the complexes containing solely tris(pyrazolyl)borate ligands have been a mystery. It was suggested that the complexes could be oligomeric via a bridging coordination mode of the ligand-based on mass spectroscopic and osmometric results, and indeed dimeric Cu(I) complexes of the form [Cu (Tp)] are known, in which both Tp ligands bridge both metal ions to yield centrosymmetric compounds.

According to Keane and Harman [10], a new origination of –bases has been augmented that contain the standard form TpM (L) (-acid) (where Tp = hydrotis (pyrazolyl) borate, M = rhenium, molybdenum, tungsten, L = variable ligand, and –acid CO, NO^+). The fusion of numerous pentaphenyl, cyclopentadienyl, hydrotris (pyrazolyl) borate ligands and the unusual responsiveness of such hindered ligands in their coordination to ruthenium (II) center were also explained [11]. Based on the significant synthetic techniques, coordination characteristics, spectroscopic, and constructional attributes of this substantial category of ligands, Santini et al. [7] reported the synthesis and features of poly (pyrazolyl) borate and associated boron-centered scorpionate ligands.

Previously, synthetic, spectroscopic, and structural characterization of different silver{poly(pyrazol-l-yl)}borates(triorganophosphine) complexes have been reported, which depict relevant spectroscopic and molecular features [12]. For instance, there are different behaviors of $[Ag(PR_3)(HB(pz)_3]$ in solution as compared to the solid state. The Tolman cone angle and pK_a of PR_3 determine the solution's stability; whereas there is similarity in the binding of $HB(pz)_3$ and $Ag(PR)_3$ in the solid state, despite electronic and steric characteristics of N- and P-donor ligand. Therefore, there is high desire for development of a new synthetic protocol mediated by a recyclable catalyst as stated by a previous study [13]. Considering this, the present study aims to present the synthesis of a tris(pyrazolyl)borate ligand to be utilized in transition metal complexes as possible redox shuttles to understand coordination chemistry between poly(pyrazolyl)borates towards silver(I) acceptors.

Experimental

Materials

Entire preparations and operations were performed under argon using common Schlenk procedures. All metal halide starting materials and silver nitrate were acquired from ACROS and consumed without additional purification. Potassium trispyrazolylborate and potassium tris (3, 5-dimethyl-1-pyrazolyl) borate were purchased from Sigma Aldrich. Commercially available solvents such as acetonitrile, ethanol (absolute 99.7%), methanol (HPLC grade), diethyl ether, and chloroform were purchased from M-TEDIA.

Elemental analysis was performed using (the EURO EA instrument). ^1H NMR (Nuclear Magnetic Resonance) spectra were recorded on a Bruker spectrometer operating at 400.13 MHz, using CD_3CN as the solvent and TMS as the internal standard. The ^{13}C NMR spectrum was obtained with a Bruker spectrometer running at 100.61 MHz. The ATR-FTIR spectrum was recorded using a Bruker Vertex 70 FT-IR spectrometer in combination with the Vertex Pt-ATR-FTIR accessory at room temperature. The melting point was measured with Stuart Scientific Melter (uncorrected ± 0.1 ° C). Thermo gravimetric analysis (TGA) was performed on a netzsch STA 409 pc instrument at a heating rate of 10ºC min^{-1} under argon.

Synthesis and modification of the ligands

Synthesis of silver tri (1-pyrazolyl) borohydride ligand (AgTp)

A solution of silver nitrate (0.6737 g, 3.96 mmol) in acetonitrile (10.0 mL) is poured drop by drop into a solution of potassium boron hydride (1.0 g, 3.96 mmol) in given acetonitrile (10.0 ml). The mixture was stirred in the dark overnight at room temperature when a precipitate formed. The product was filtered, washed with distilled water (25 ml), and the solid was filtered again and dried in a vacuum to remove solvents.

The elemental analysis for $C_9H_{10}BAgN_6$; calculated: C, 33.69; H, 3.14; N, 26.19, found: C, 32.49; H, 3.29; N, 25.85. The color: beige. The yield: 0.9831g (77.24%), m.p: 164-166 ˚C.^{1}H NMR (δ ppm) (CD_3CN, 400.13 MHz): δ= 6.09 (tri, 3H), 7.46 (s, 3H), 7.57 (d, 3H). ^{13}C NMR (CD_3CN, 100.61 MHz): δ= 102.88, 134.09, 139.13. IR: (υ B-H) 2435.8 cm^{-1}, (υ C=N) 1502.7 cm^{-1}, (υ C=C) 1401.2 cm^{-1}.

Synthesis of silver tris (3, 5-dimethyl-1-pyrazolyl) borohydride (AgTp)*

A solution of silver nitrate (0.5051g, 2.97 mmol) in acetonitrile (10.0 ml) was added dropwise to a solution of potassium tris (3, 5-dimethyl-1-pyrazolyl) borohydride (1.0g, 2.97 mmol) in acetonitrile (10.0 ml). The mixture was stirred in the dark overnight at room temperature when a precipitate formed. The solid was filtered, rinsed with distilled water (25 ml), and dried in a vacuum to remove solvents. The elemental analysis for $C_{15}H_{22}BAgN_6$; calculated C, 44.48; H, 5.47; N, 20.75, found: C, 44.02; H, 5.25; N, 20.55. The color: beige. The yield: 0.9615g (79.85%), m.p: 251-253 ˚C. ^{1}H NMR (δ ppm) (CD_3CN, 400.13 MHz): δ= 2.12 (s, 9H), 2.21 (s, 9H), 5.64 (s, 3H). ^{13}C-NMR (CD_3CN, 100.61 MHz): δ= 12.03, 12.83, 103.33, 143.18, 146.04. IR: (υ B-H) 2436.2 cm^{-1}, (υ C=N) 1537 cm^{-1}, (υ C=C) 1413 cm^{-1}.

Synthesis of the complexes

Dichloro {tri (1-pyrazolyl) borohydride} Iron (III) $Fe(C_9H_{10}BN_6)Cl_2$

To a one necked schlenk flask connected to a reflux condenser was charged with AgTp salt (0.1g, 0.311 mmol) in acetonitrile (10.0 ml), a solution of $FeCl_3.6H_2O$ (0.0842g, 0.311mmol) in acetonitrile (15 ml) was added. The mixture was refluxed at 82 ° C. with stirring for 4 hours. Then the mixture was stirred at room temperature overnight, and a precipitate was formed. The product was filtered, then the solvent was removed by a rotary evaporator, and the solid was further dried in a vacuum to constant weight to afford Fe $(C_9H_{10}BN_6)Cl_2$ complex with red color.

The elemental analysis for $Fe(C_9H_{10}BN_6)Cl_2$; calculated C, 31.81; H, 2.97; N, 24.73, found: C, 31.59; H, 2.78; N, 24.44. The color: red. The yield: 0.0905g (85.5%), m.p: 225-227 ºC. IR: (υ B-H) 2525.5 cm^{-1}, (υ C=N) 1503.8 cm^{-1}, (υ C=C) 1403.8 cm^{-1}, (υ M-Cl) 758.5 cm^{-1}, (υ M-N) 457.1 cm^{-1}.

Dichloro {tris (3, 5-dimethyl-1-pyrazolyl) borohydride} Iron (III) $Fe(C_{15}H_{22}BN_6)C_{l2}$

To a one necked schlenk flask connected to a reflux condenser was charged with AgTp* salt (0.1g, 0.246 mmol) in acetonitrile (10.0 ml), a solution of $FeCl_3.6H_2O$ (0.0667g, 0.246 mmol) in acetonitrile (15 ml) was added. The mixture was refluxed by stirring at 82°C for four hours, then stirred overnight at room temperature, resulting in the formation of a precipitate. The result was filtered, the solvent was evaporated using a rotary evaporator, and the solid was then vacuum dried to a constant weight to get $Fe(C_{15}H_{22}BN_6)Cl_2$ complex with an orange color.

The elemental analysis for $Fe(C_{15}H_{22}BN_6)Cl_2$; calculated C, 42.50; H, 5.23; N, 19.82, found: C, 41.97; H, 5.51; N, 19.76. The color: orange. The yield: 0.0788 g (75.33%), m.p: 265-267 ˚C. IR: (υ B-H) 2552.9 cm^{-1}, (υ C=N) 1538.9 cm^{-1}, (υ C=C) 1442.8 cm^{-1}, (υ M-Cl) 803.5 cm^{-1}, (υ M-N) 496.49 cm^{-1}.

Dichloro {tri (1-pyrazolyl) borohydride} Cobalt (III) $Co(C_9H_{10}BN_6)Cl_2$

To a one necked schlenk flask connected to a reflux condenser was charged with AgTp salt (0.1g, 0.311 mmol) in acetonitrile (10.0 ml), a solution of $CoCl_2.6H_2O$ (0.0741g, 0.311mmol) in acetonitrile (15 ml) was added. The mixture was refluxed at 82 ° C. with stirring for 4 hours; then, the mixture was stirred at room temperature for the full night, and a precipitate was formed. The result was filtered, the solvent was evaporated using a rotary evaporator, and the solid was vacuum dried to a constant weight to get the yellow Co ($C_9H_{10}BN_6$) Cl_2 complex. During this reaction, Co^{+2} changed to Co^{+3}.

The elemental analysis for $Co(C_9H_{10}BN_6)Cl_2$; calculated C, 31.53; H, 2.94; N, 24.51, found: C,31.21; H, 3.03; N, 24.40. The color is yellow. The yield: 0.0751g (70.31%), m.p: 282-284 ˚C. ^1H NMR (δ ppm) (CD_3CN, 400.13 MHz): δ= 6.39 (s, 3H), 6.747 (s, 3H), 8.181 (s, 3H). ^{13}C NMR (CD3CN, 100.61 MHz): δ= 108.88, 138.96, 144.76. IR: (ʋ B-H) 2517.6 cm^{-1}, (ʋ C=N) 1504.7 cm^{-1}, (ʋ C=C) 1408.4 cm^{-1}, (ʋ M-Cl) 753.8 cm^{-1}, (ʋ M-N) 460.2 cm^{-1}.

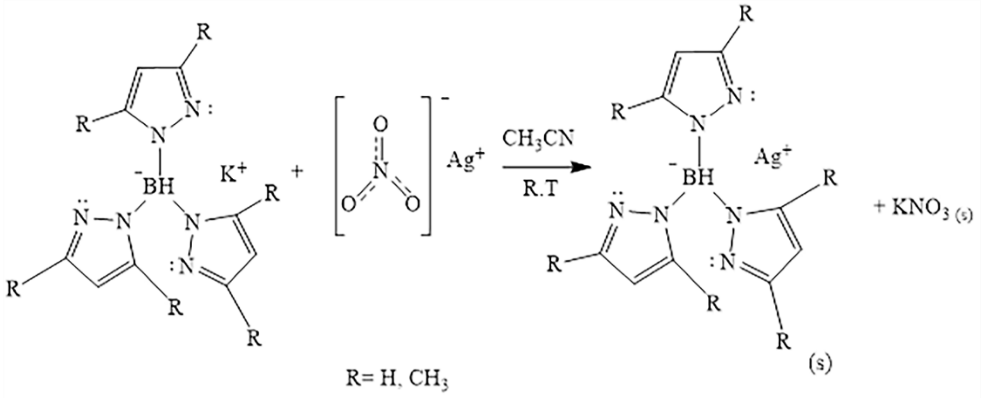
Results and Discussion

Synthesis and Characterization

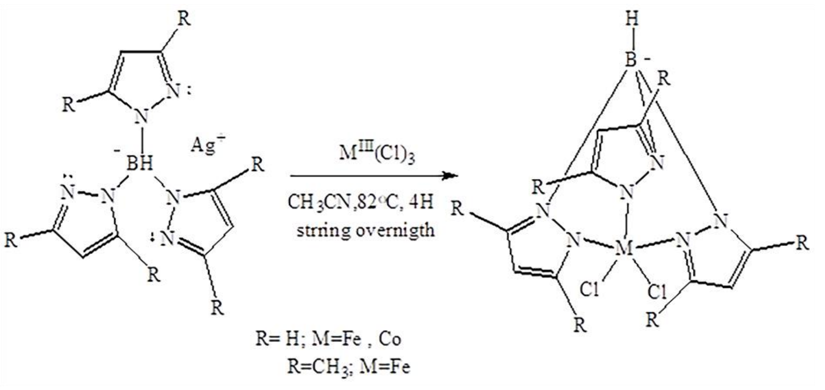
Silver salt of tri(1-pyrazolyl)borohydride (AgTp) and tris(3, 5-dimethyl-1-pyrazolyl)borohydride (AgTp*) were prepared by reacting the potassium salt as received with silver nitrate in acetonitrile solvent as shown in the scheme below.

The compound (3–5) was synthesized by reacting a metal halide (III) with a silver salt of the corresponding anion in acetonitrile (anion exchange) (scheme number). The problems are considerably air-stable and can be handled in a laboratory atmosphere for a brief period.

All synthesized compounds are distinguished by IR spectroscopy, thermogravimetry, ^1H-NMR and ^{13}C-NMR spectroscopy, and elemental analysis (EA). The ligands are distinguished by their physical properties, elemental analysis, IR, ^1H-NMR, and ^{13}C-NMR spectroscopy. Their infrared spectrum has a B-H peak between 2450-2550 cm^{-1}, the imine peak (C=N) of the pyrazole ring between 1500-1550 cm^{-1}, and the C=C peak between 1400-1450 cm^{-1}.



Scheme-1: Synthesis of ligands (AgTp) and (AgTp*)



Scheme-2: Synthesis and suggested structure of transition metal complexes with AgTp and AgTp* ligands.

^{1}H-NMR spectra (CD_3CN, δ ppm) of the silver tri(1-pyrazolyl)borohydride ligand ($C_9H_{10}BAgN_6$) show three types of hydrogen peaks, the first type of hydrogen at δ= 6.09 ppm for Hb (C=C-H), and the second type is for Ha (HC=N) at δ= 7.46 ppm, and the last one is at δ= 7.57 for Hc (HC-N). Meanwhile, the peak of B-H generally appears below 0 ppm (Fig. 2a).

The ^{13}C-NMR (CD_3CN) spectra of silver tri(1-pyrazolyl)borohydride ligand show three types of carbon that appear at 139.13, 134.09, 102.88 ppm, which was related to C=N, C-N, C=C, respectively (Fig 2b). Fig 3 shows the ^{1}H-NMR spectra (CD_3CN, δ ppm) for the silver tris(3,5-dimethyl-1-pyrazolyl)borohydride ligand ($C_{15}H_{22}BAgN_6$), which shows three types of singlet hydrogen peaks, the first peak for Hb* (C=C-H) at δ= 5.64 ppm, and the peaks for the electron-donating group ($-CH_3$) are 2.21 and 2.12 ppm. (Ha* and Hc*) respectively.

The ^{13}C-NMR (CD_3CN) spectra of silver tris(3,5-dimethyl-1-pyrazolyl) borohydride ligand show peaks at 146.04, 143.18, 103.33, 12.83, 12.03 ppm, which were related to C=N, C-N, C=C, CH_3 respectively. In addition $-CH_3$ had the lowest chemical shift due to its electron-donating group, as shown in Fig 3.

Iron (III) complexes

Complexation of the AgTp and AgTp* ligands with $FeCl_3.6H_2O$ in acetonitrile results in $Fe(Tp)Cl_2$ and $Fe(Tp^*)Cl_2$ complexes, keeping two Cl as a ligand. The complexes are powder-like and stable under environmental conditions. The iron (III) complexes produced were distinguished by their physical features, IR spectroscopy, elemental analysis, and magnetic susceptibility. The IR spectra showed a slight shift in the main peaks for $Fe(Tp)Cl_2$ compared to the IR spectra for Ag(Tp) salt. The peak of B-H, C=N, and C=C shift from 2435.8, 1502.7, and 1401.2 cm^{-1}, to 2525.5, 1503.8, and 1403.8 cm$^{-1,}$ respectively, and the appearance of the new bands υ(M-N) at 457.1cm^{-1} and υ(M-Cl) at 758.5 cm^{-1} which indicate the complexation Fe(III) with the ligand, and Fe(III) with the Cl.

For $Fe(Tp^*)Cl_2$ compared to the IR spectra for Ag(Tp*) salt, the IR spectra showed slight shifts in the peaks of B-H, C=N, and C=C shift from 2436.2, 1537, and 1413cm^{-1} to 2552.9, 1538.9 and 1442.8cm^{-1} respectively, and the appearance of the new bands υ(M-N) at 496.4cm^{-1} and υ(M-Cl) at 803.5cm^{-1} which indicate the complexation Fe(III) with the ligand, and Fe(III) with the Cl.

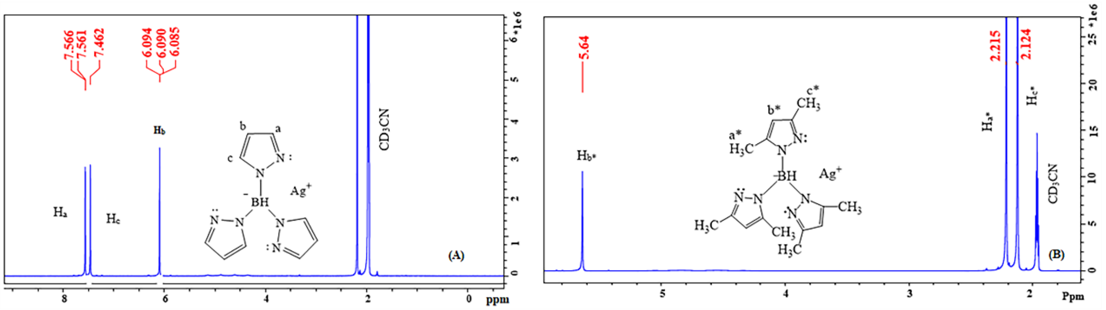


Fig. 2: (a) ^{1}H-NMR spectra for the silver tri (1-pyrazolyl) borohydride ligand (AgTp); (b) ^{1}H-NMR spectrum for the silver tris(3,5-dimethyl-1-pyrazolyl)borohydride ligand (AgTp*).

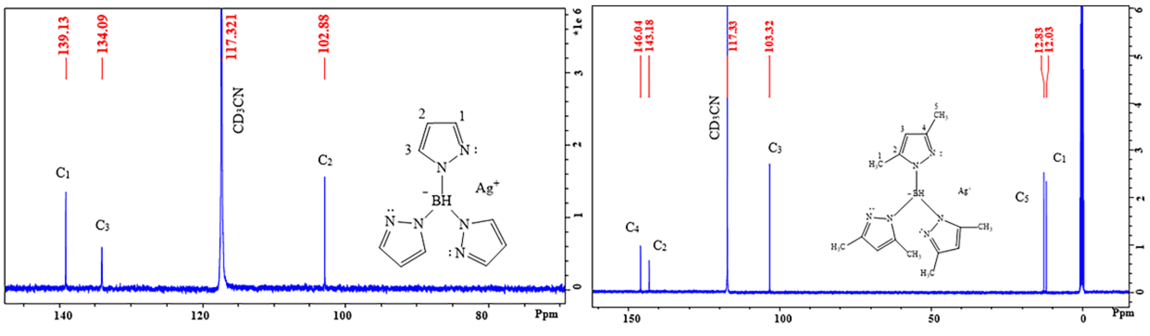


Fig. 3: (a) ^{13}C-NMR spectra for the silver tri (1-pyrazolyl) borohydride ligand (AgTp); (b) ^{13}C-NMR spectra for the silver tris(3,5-dimethyl-1-pyrazolyl)borohydride ligand (AgTp*).

Cobalt (III) complex

A complication of the AgTp ligand with $CoCl_2.6H_2O$ in acetonitrile results in $Co^{III}(Tp)Cl_2$, keeping two Cl as a ligand. The complexes are powder-like and stable under environmental conditions. The Co(III) complex was characterized by its physical properties, IR spectroscopy, elemental analysis, magnetic susceptibility, and NMR spectroscopy (Table-1).

The IR spectra showed a slight shift in the central peaks for $Co(Tp)Cl_2$ compared to the IR spectra for Ag(Tp) salt. The peak of B-H, C=N, and C=C shift from 2435.8, 1502.7, and 1401.2 cm^{-1}, to 2517.6, 1504.7, and 1408.4 cm^{-1}, respectively, and the appearance of the new bands indicate the complexation Co(III) with the ligand, and Co(III) with the Cl, where υ(M-N) at 460.2 cm^{-1} and υ(M-Cl) at 753.8 cm^{-1}.

^{1}H-NMR spectra (CD_3CN, δ ppm) of $Co(Tp)Cl_2$ show shifts in the main peaks of C=CH, HC=N, and HC-N from δ= 6.09, 7.46, and 7.57 ppm, to 6.39, 6.75 and 8.18 ppm, respectively. The ^{13}C-NMR spectra (CD_3CN) of $Co(Tp)Cl_2$ show shifts in the main peaks of C=N, C-N, and C=C from 139.13, 134.09, 102.88 ppm, to 144.76, 138.96, and 108.88 ppm, respectively.

Thermogravimetric analysis (TGA) was executed for the complexes. The CoTpCl2 complex begins to degrade at approximately 231.2 ° C. This is related to a mass loss of 11.30% by weight. This mass loss corresponds to one loss of chloride that probably contributes 10.4 wt% of the total connection mass. Similar behavior is observed with the $FeTpCl_2$ complex associated with a loss of 10.78 wt%. at 310.9 °C. Both complexes $CoTpCl_2$ and $FeTpCl_2$ also show a second loss at above 350 °C (19.03 wt.% (one pyrazole ring [19.6 wt.%])) and (22.33 wt.% (one pyrazole ring [19.7 wt.%])) respectively.

Table-1: Infrared spectral data for the AgTp and AgTp* ligands and their transition metal complexes (υ: the wavenumber in cm^{-1})

		Infrared spectral				
No.	**Name**	**υ(B-H)**	**υ(C=N)**	**υ(C=C)**	**υ(M-Cl)**	**υ(M-N)**
1	**AgTp**	**2435.8**	**1502.7**	**1401.2**	**-**	**-**
2	**AgTp***	**2436.2**	**1537**	**1413**	**-**	**-**
3	**$Fe(Tp)Cl_2$**	**2525.5**	**1053.8**	**1403.8**	**758.5**	**457.1**
4	**$Fe(Tp^*)Cl_2$**	**2552.9**	**1538.9**	**1442.8**	**803.5**	**496.4**
5	**$Co(Tp)Cl_2$**	**2517.6**	**1504.7**	**1408.4**	**753.8**	**460.2**

The $FeTp^*Cl_2$ complex shows its first decomposition onset at ca. 100 °C, with a mass loss of 17.16 wt.%. This mass loss matches with the loss of the tow of chloride atoms {contributing 16.29 wt.% of the total mass of the compound}. The second loss at above 400 °C (24.49 wt. % (one dimethyl pyrazole ring [22.71 wt.%])).

Table-2: Thermogravimetric analyses of the complexes between room temperature and 550 °C with a heating rate of 10 °C/min.

complex	**Tonset °C**	**Wt. loss%**	**Tonset °C**	**Wt. loss%**	**Tonset °C**	**Wt. loss%**	**Tonset °C**	**Wt. loss%**	**Total loss%**
$CoTpCl_2$	**231.2**	**11.30**	**365**	**19.03**	**-**	**-**	**-**	**-**	**30.38**
$FeTpCl_2$	**310.9**	**10.87**	**403.2**	**11.33**	**478.5**	**11.11**	**-**	**-**	**33.31**
$FeTp^*Cl_2$	**242.7**	**17.16**	**456.2**	**24.49**	**-**	**-**	**-**	**-**	**41.65**

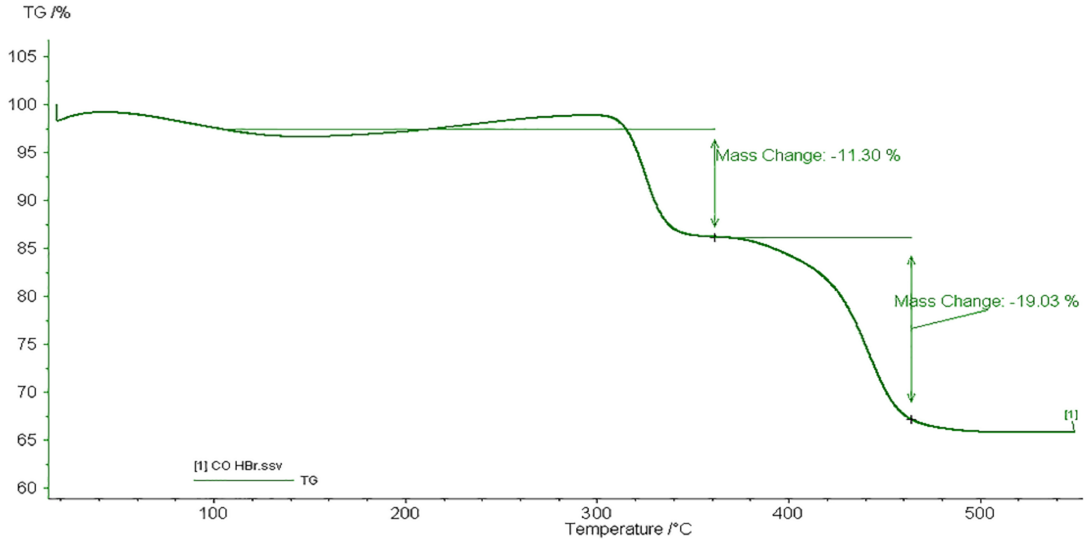


Fig 4: Graph of $CoTpCl_2$.

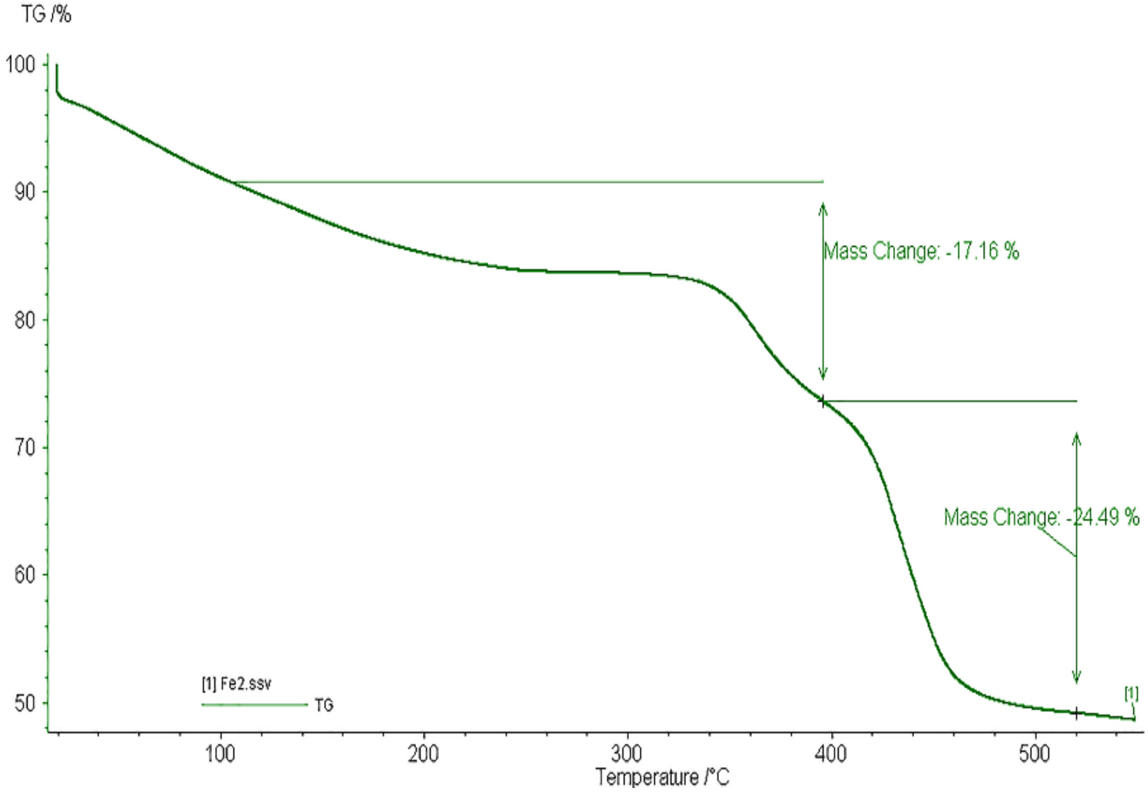


Fig. 5: Graph of FeTp*Cl_2.

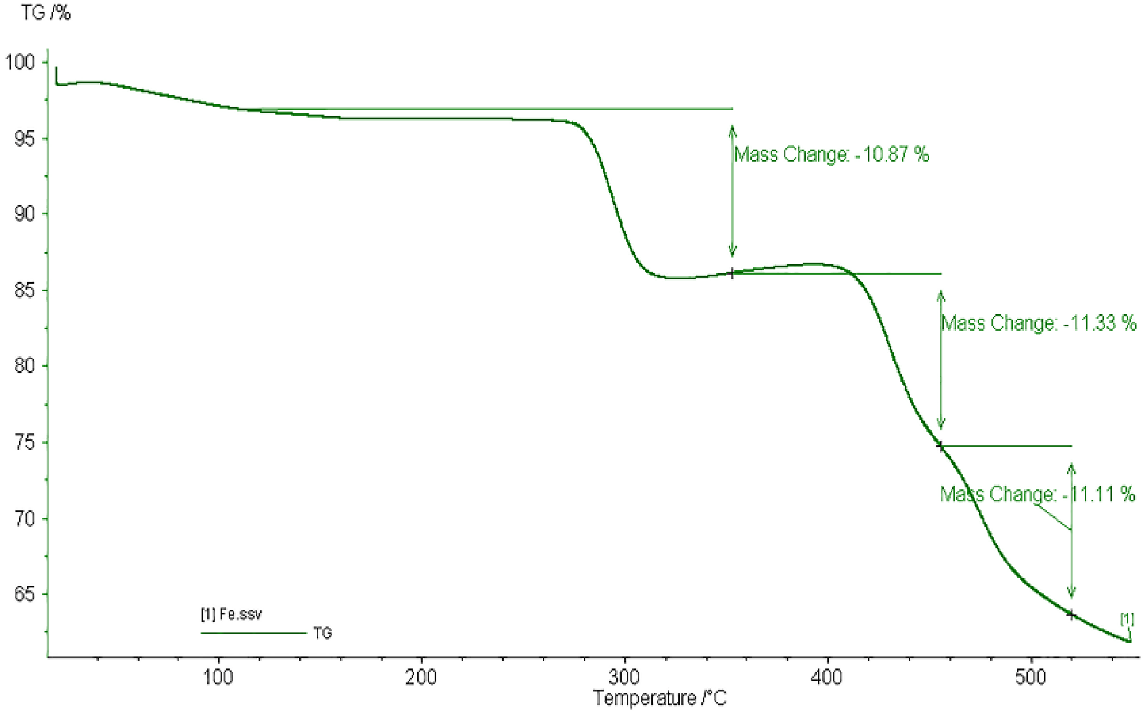


Fig. 6: Graph of FeTpCl_2.

Conclusion

This study presents the synthesis of a tris(pyrazolyl)borate ligand to be utilized in transition metal complexes as possible redox shuttles. The synthesis of the metalation and Tp ligand was achieved effectively. The effective electrochemical reversibility is proven through electrochemical studies, while the solubility did not yield adequate solubilities for DSSC solution with three tunable positions. This study has examined the synthesis of a tris (pyrazolyl)borohydride ligand to develop an iron complex. Further electrochemical tests should be carried out to demonstrate the effectiveness of this likely redox mediator. In addition, linking this complex to a specific dye and testing should be accomplished to determine the maximum efficiency.

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