Comparative Study of Microwave Assisted and Conventional Synthesis of Tp*-Complexes

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Abstract: Cobalt, copper and nickel complexes with tris(3,5-dimethyl-1H-pyrazol-1-yl)hydroborate (Tp*) were synthesized by the reaction of potassium tris(3,5-dimethyl-1H-pyrazol-1-yl)hydroborate (KTp*) with the corresponding metal(II) chloride by using conventional reflux methods and microwave methods. The two methods were compared and the microwave method was found to be less time consuming and gave higher yields.

Keywords: Pz* [3,5-dimethyl-1H-pyrazol-1-yl], KTp* [potassium tris(3,5-dimethyl-1H-pyrazol-1-yl)hydroborate], Tp*-complexes, [tris(3,5-dimethyl-1H-pyrazol-1-yl)hydroborate complexes]

1. Introduction

Pyrazole-derived ligands, known collectively as poly(pyrazolyl) ligands, are derived from two or more N-deprotonated pyrazole rings bound to a main group atom through one of the ring nitrogens [1]. The basic skeleton of the ligand involves pyrazole units bonded to a main group apex via the nitrogen atoms at the dis-placement of hydrogen [2]. Tris(pyrazolyl) borate (Tp)x ligands, known as scorpionates, have attracted considerable attention and proven to be extremely popular ligands since their introduction by Trofimenko in 1967 [3-4]. They constitute one of the most widely used group of ligands in chemistry. The reaction of KTp* ligands with metal ions is expected to give either tetrahedral or octahedral complexes depending on the reactant ratios and the nature of the metal ion.

Reactions of Tp complexes have been investigated. Studies included the synthesis of complexes containing Tp in addition to other ligands with some metals such as Ni(II), Co(II) and Mn(II).

Michiuie and Jordan have shown that reaction of the TITPMeS and TITPM* S With MC14 (M=Zr, Hf) in toluene affords [ZrTPMsCl4], [ZrTPMs*Cl4], and [HITPM*Cl4]. The complex [ZrTPMsCl4] exhibits extremely high activity for ethylene polymerization and ethylene/hexane copolymerization. Also, a series of TpxMC14 complexes (M=Ti, Zr, Tpx=TNP, TpPh, TpBu) have been synthesized [5]. The heteroleptic picolinic acid N-oxide complexes, [Ln(Tp2) (pnx)], (Ln=Y, Eu, Gd, Tb, Er, Yb or Lu), have been prepared and characterized [6]. [Tp*VCl2L] L=4-substitched pyridine N-C6H4-R (R= H, CH3, C2H5, Ph) were prepared by replacing the dimethylformamide ligand in Tp*VCl2(DMF) by various N-containing heterocycles [7]. Xing and co-workers have prepared the new oxovanadium(IV) complexes VO(HB(Pz)x)(H2B(Pz)2) and VO(B(Pz)4) [8]. Chromium(III) complexes containing Tp ligands [Cr(Tp)][CrCl3(Tp)], [CrCl3(Tp)(THF)] and [HPMe3][CrCl3(Tp)] have been synthesized [9].

The compound Tp*Mol(CO)2CH3CN has been isolated from the reaction between [Mol2(CO)4(MeCN)2] and KTp*, and has been described as a diamagnetic compound, showing well-defined 1H NMR spectroscopic properties [10]. Carrillo and co-workers have reported the synthesis of [TpMo(NNPhR)2Cl] R=Ph, Me, TpX=Tp, Tp* [11]. [Tp*W(OPh)2C6H4(OC-O2Me)2] and [Tp*W(SePh)2] have been synthesized and determined by X-ray crystallography [12]. Zn(Tp)Cl (Tp=tris(3,5-dimethyl-1-pyrazolyl)borate) was investigated [13]. (3-NH(t-butyl)-5-methyl-pyrazole)2MX2 (M = Zn, Ni, Co, Mn; n = 3, 4; X = Cl, Br) have been synthesized [14]. [Cu(NCS)2L3], [Mn(NCS)2L3],
[Mn(NCS)₂L₂] and [Zn(NCS)₂L₂][Zn(NCS)₂] complexes have been synthesized. L₁ = bis(1,3,5-dimethylpyrazolyl)methylamine, L₂ = tris(1,3,5-dimethylpyrazolyl)methylamine [15]. The V(III) complex [VTpH₂Cl] has been synthesized by the reaction of [VCl₃(THF)] (prepared in situ) and K(TpH₂), TpH₂ = hydrotris(3,5-di-tert-butylpyrazolyl)borate) [16].

Microwave-assisted synthesis is, in many ways, superior to traditional heating. The ability to elevate the temperature of a reaction well above the boiling point of the solvent increases the speed of reactions. Reactions are thus completed in minutes or even seconds. Yields are generally higher and the speed of reactions. Reactions are thus completed in

In a dedicated microwave reactor, reactions can be run in sealed vials under carefully controlled conditions at temperatures up to 200°C and pressures up to 20 bar. This provides the means to heat reactions much higher than conventional open-vessel conditions, in which the maximum temperature is limited to the boiling point of the solvent.

High-speed synthesis with microwaves has attracted considerable amount of attention in recent years [17]. More than 2000 articles have been published in the area of microwave assisted organic synthesis (MAOS) since the first reports on the use of microwave heating to accelerate organic chemical transformations by the groups of Gedye and Giguere/Majetich in 1986 [18-19]. The initial slow uptake of the technology in the late 1980s and early 1990s has been attributed to its lack of controllability and reproducibility, coupled with a general lack of understanding of the basics of microwave dielectric heating. The risks associated with the flammability of organic solvents in a microwave field and the lack of available systems for adequate temperature and pressure controls were major concerns [20].

In this work, we present a method for synthesizing complexes containing (KTP*) ligand and some transition metal atoms, (TP*-Metal), using reflux methods and microwave techniques with a comparison between the two methods.

2. Experimental

2.1. Chemicals and Materials

All solvents used (N-hexane, petroleum ether, Chloroform, Methanol, Toluene, Ether and Acetone) were obtained from different companies and they were dried by standard methods and distilled prior to use.

The chemicals used for the synthesis were reagent grade (Table 1).

| Chemicals                      | Formula        | Molecular weight | Company                             |
|--------------------------------|----------------|------------------|-------------------------------------|
| Copper chloride dihydrate      | CuCl₂.2H₂O    | 170.48           | BDH chemicals Ltd Poole England     |
| Cobalt chloride hexahydrate    | CoCl₂.6H₂O    | 237.93           | Avonchem - Khem King                |
| Nickel chloride hexahydrate    | NiCl₂.6H₂O    | 237.69           | Khem King                           |
| Potassium tetraborohydride     | KBH₃           | 170.4            | Riedel-deaen AG seehze-Hannover     |
| Hydrazine sulphate             | H₃N₂SO₄       | 130.12           | BDH chemicals Ltd Poole England     |
| 2,4-pentandione                | C₆H₇O₂        | 100.12           | Avocado Research chem. calsLtd      |
| Potassium carbonate            | K₂CO₃         | 138.21           | Alfa Aesar                         |

2.2. Instrumentations

Melting points were determined by using Electrothermal Digital Melting Point Apparatus model IA 9100.

Infrared spectra were recorded on IR spectrometer Varian 660. All the Tp*-Complexes were in KBr pellet for the measurement.

Mass spectra and Elemental analyses (C, H, N) were performed at the micro analytical center of Cairo University. 

¹³C NMR and ¹H NMR spectra were recorded on a Bruker at 400 MHz spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS).

Microwave assisted syntheses were carried out by using Milestone Microwave.

2.3. Syntheses

2.3.1. The Ligand; Potassium Tris(3,5dimethyl pyrazolyl) Hydroborate (KTP*)

Potassium tris(3,5dimethyl pyrazolyl) hydroborate (KTP*) was synthesized with the use of microwave according to the method described in a previous publication [21]. (Yield: 90 %); m.p: >380°C. IR (cm⁻¹): ν(BH) 2436, ν(CH) 2862, 2925, 2960; ¹H NMR (DMSO): δ 2.05 (9H, CH₃), δ 3.17 (9H, CH₂), δ 5.53 (3H, CH), δ 8.53 (1H, BH); ¹³C NMR (DMSO): δ 12.4 (C₄), 13.7(C₅), 103.2 (C₆), 141.9 (C₁), 144.6 (C₃).

2.3.2. Synthesis of Metal-Tp* Complexes

(i) Complex of Tp* with Cobalt (II) Chloride (H1)

Two methods were adopted in the synthesis of complex (H1):

Method A (reflux):
A solution of 0.6022g of KTP* (1.79mmole, 10ml MeOH) was added drop wise to a stirred solution of 0.4822g of cobalt (II) chloride (2.02mmole, 10ml MeOH) in a 50 mL round bottom flask. The flask was fitted with a condenser and the mixture was stirred at room temperature for 5h. A blue precipitate was obtained. Recrystallization of the product was carried out in chloroform. Blue crystalline solid was obtained, 83% yield. (m.p: 170°C); IR (cm⁻¹): ν (BH) 2511.58, ν (CH) 2923.18. MS: m/z: 391[M⁺], 95[C₃H₇N₅]²⁻, 107[BH(C₆H₁₃N₅)⁺], 356[BJH(C₆H₁₃N₅)Co]⁺.

Method B (microwave):
A powder mixture of cobalt (II) chloride (0.3215g, 1100°C) and KTP* (0.3215g, 1100°C) was obtained. 83% yield. (m.p: 170°C); IR (cm⁻¹): ν(BH) 2511.58, ν(CH) 2923.18. MS: m/z: 391[M⁺], 95[C₃H₇N₅]²⁻, 107[BH(C₆H₁₃N₅)⁺], 356[BJH(C₆H₁₃N₅)Co]⁺.
1.35mmole) and KTp* (0.4015g, 1.19mmole) was heated in a
glass tube in TFM vessel on the rotating balance plate inside
the microwave at 750 watt and 80°C for 17min. The rotor
was cooled to room temperature. Chloroform was added to
the reaction mixture and the product was washed several
times with chloroform and filtered. The product was isolated
as a blue powder. (Yield: 92%); m.p: 170°C; IR (cm⁻¹): ν
(BH) 2511, ν (CH) 2923.

(ii) Synthesis of Nickel-Tp* Complex (H2)
Two methods were adopted in the synthesis of complex
(H2):
Method A (reflux):
A solution of 0.4099g of KTp* (1.21mmole, 10ml MeOH)
was added drop wise to a stirred solution of 0.3279g of nickel
(II) chloride (1.37mmole, 10ml MeOH) in a 50 mL round
bottom flask. The flask was fitted with a condenser and the
mixture was stirred at room temperature for 5h. A purple
precipitate was obtained. Recrystallization of the product was
carried out in chloroform. Purple crystalline solid was
obtained, 78% yield. (m.p: >380°C); IR (cm⁻¹): ν (BH) 2512.62, ν (CH) 2923.14. MS: m/z: 391[M]⁺, 95[C₅H₇N₂]⁻, 107[BH(C₅H₇N₂)]⁻, 355[BH(C₅H₇N₂)₃Ni]⁻.
Method B (microwave):
A powder mixture of nickel (II) chloride (0.3279g,
1.37mmole) and KTp* (0.4099g, 1.21mmole) was heated in a
glass tube in TFM vessel on the rotating balance plate inside
the microwave at 750 watt and 80°C for 17min. The rotor
was cooled to room temperature. Chloroform was added to
the reaction mixture and the product was washed several
times with chloroform and filtered. The product was isolated
as a purple powder. (Yield: 92%); m.p: 170°C; IR (cm⁻¹): ν
(BH) 2511, ν (CH) 2923.

(iii) Synthesis of Copper-Tp* Complex (H3)
Two methods were adopted in the synthesis of complex
(H3):
Method A (reflux):
A solution of 0.5954g of KTp* (1.77mmole, 10ml MeOH)
was added drop wise to a stirred solution of 0.3416g of copper
(II) chloride (2.00mmole, 10ml MeOH) in a 50 mL round
bottom flask. The flask was fitted with a condenser and the
mixture was stirred at room temperature for 5h. A green
precipitate was obtained. Recrystallization of the product was
carried out in chloroform. Dark-green crystalline solid was
obtained, 80% yield. (m.p: 295°C); IR (cm⁻¹): ν (BH) 2513.10, ν (CH) 2922.88. MS: m/z: 391[M]⁺, 95[C₅H₇N₂]⁻, 107[BH(C₅H₇N₂)]⁻, 360[BH(C₅H₇N₂)₃Cu]⁻.
Method B (microwave):
A powder mixture of copper (II) chloride (0.3416g,
2.00mmole) and KTp* (0.5954g, 1.77mmole) was heated in a
glass tube in TFM vessel on the rotating balance plate inside
the microwave at 750 watt and 80°C for 17min. The rotor
was cooled to room temperature. Chloroform was added to
the reaction mixture and the product was washed several
times with chloroform and filtered. The product was isolated
as a dark-green powder. (Yield: 90%); m.p: 295°C; IR
(cm⁻¹): ν (BH) 2513, ν (CH) 2922.

3. Results and Discussion

3.1. Metal-Tp* Complexes
The Co, Ni, Cu complexes (H1 to H3) were synthesized by
reaction of the ligand (KTp*) with the appropriate metal (II)
chloride by using conventional reflux methods and
microwave methods as shown in figure 1. In the conventional
reflux method, all reactions were carried out in methanol
where the ligand-metal ratio was 1:1 at room temperature.
The complexes were obtained in high yield percentage.

![Figure 1. Synthesis of Tp* Complexes (H1 to H3).](image-url)
Table 2 shows a comparison between the reflux method and the microwave method in the synthesis of various compounds prepared in this work. This comparison is made in terms of reaction yield and reaction time. As can be seen from the table, it is evident that the microwave method gives higher yields and takes less time. In addition, the microwave method required no solvents. This made the reactions cleaner and the time required to evaporate has been saved.

| Compound | Microwave | Reflux |
|----------|-----------|--------|
|          | Reaction Time | %Yield | Reaction Time | %Yield |
| H1 - BH(C₅H₇N₂)₃CoCl | 17min | 92% | 5h | 83% |
| H2 – BH(C₅H₇N₂)₃NiCl | 17min | 92% | 5h | 78% |
| H3 – BH(C₅H₇N₂)₃CuCl | 17min | 90% | 5h | 80% |

3.2. IR Spectroscopy

Infrared spectroscopy was used in characterization of all compounds synthesized in this work. The IR spectrum of compound (KTp*), figure 2, shows a band at 2436cm⁻¹ that was assigned to the stretching vibration, ν(B-H), of the B-H group. The C= N group stretching frequency, ν(C= N), occurs at 1537cm⁻¹, and the C-N group stretching frequency, ν(C=N), occurs at 1028cm⁻¹. At 978cm⁻¹ band due to N-N group stretching frequency, ν(N=N). The bands at 2862, 2925 and 2960cm⁻¹ can be attributed to the stretching vibrations of the aliphatic and aromatic C-H groups.

The IR spectra of Tp* complexes, H1 to H3, figures 3, 4 and 5, respectively, are characterized an absorption band that occurs in the range 2507-2513cm⁻¹, as a single neat peak, due to ν(B-H) stretching, table 3. The bands due to the ‘breathing’ of the pyrazole rings in the complexes occurred at unusually high frequencies, in the range between 1540 and 1630cm⁻¹. The ν(M=N) and ν(M-Cl) stretching absorptions expected between 200 and 400cm⁻¹ were not observed because the infrared spectra were recorded from 600 to 4000cm⁻¹.

| Complex | ν(B-H) | ν(C=N) | ν(C-N) | ν(N-N) |
|---------|--------|--------|--------|--------|
| KTp* - K BH(C₅H₇N₂)₃ Ligand | 2436 | 1537 | 1028 | 978 |
| H1 - BH(C₅H₇N₂)₃CoCl | 2511 | 1541 | 1056 | 981.8 |
| H2 - BH(C₅H₇N₂)₃NiCl | 2512 | 1542 | 1055 | 981.3 |
| H3 - BH(C₅H₇N₂)₃CuCl | 2513 | 1541 | 1058 | 978.8 |

Figure 2. Infrared spectrum of (KTp*) At 1000 and 900watt.
Figure 3. Infrared spectrum of (Tp*- Co) complex (H1).

Figure 4. Infrared spectrum of (Tp*- Ni) complex (H2).
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3.3. Elemental Analysis Data

Elemental analysis of carbon, hydrogen and nitrogen was used in the characterization of all of the complexes synthesized in this work. The experimental and calculated C, H and N contents for these complexes are presented in the table 4.

Table 4. Elemental analysis data of complexes H1 to H3.

| Complex          | Elemental analysis | C  | H  | N  |
|------------------|--------------------|----|----|----|
| H1 - BH(C5H7N2)3CoCl | Cal.               | 46.01 | 5.66 | 21.46 |
|                  | Found              | 46.03 | 5.75 | 21.58 |
| H2 - BH(C5H7N2)3NiCl | Cal.               | 46.04 | 5.67 | 21.48 |
|                  | Found              | 46.04 | 5.67 | 21.48 |
| H3 - BH(C5H7N2)3CuCl | Cal.               | 45.47 | 5.60 | 21.21 |
|                  | Found              | 46.09 | 5.69 | 21.22 |

4. Conclusion

The synthetic and characterization results obtained in this work lead to the conclusion that the (Tp* complexes) can be synthesized in a solid form using reflux and microwave method in a 1:1 ratio between metal chloride and (KTp*). The microwave method was easier than reflux method and it gives higher percentage yield, and saves time and solvent.

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