Catalysis Letters
https://doi.org/10.1007/s10562-019-02804-9

Synthesis, Characterization and Biological and Catalytic Activities of Propionitril: Ligated Transition Metal Complexes with $[B(C_6F_5)_4]$ as Counter Anion

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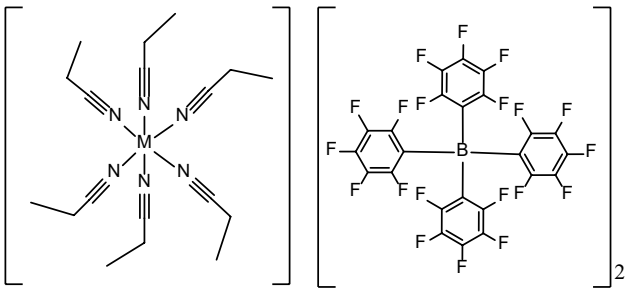
Received: 31 January 2019 / Accepted: 28 April 2019

Abstract

A series of new metal complexes of the general formula $[M(NCCH_2CH_3)_6][B(C_6F_5)_4]_2$, where M: Cu, Fe, Co, Ni, Zn, Mn, have been synthesized. Resulting complexes have been characterized in different spectroscopic techniques such as: IR, TGA, NMR and Elemental Analysis. GC–MS have been used to determine the purity of the reactions and the yield of the final products. These complexes have been applied as catalysis on different olefins for cyclopropanation reaction in homogenous phase. Complex **1** $[Cu(CH_3CH_2CN)_6][B(C_6F_5)_4]_2$ which has the Cu as central atom has shown the highest activity on different olefins. Their biological activities against a number of pathogenic bacteria have been screened and most of the complexes have shown moderate activities against Gram positive and low activities against Gram negative.

Graphical Abstract



Keywords Non-coordinating anions · Organonitrile · Cyclopropanation · Catalysts · Antimicrobial

1 Introduction

Synthesis of metal organonitrile complexes has become quite popular in organometallic chemistry because of their beneficial applications such as inorganic materials and catalysis [1–6]. The advantage of these complexes results from the coordination mode of the nitrile ligands, which can be easily replaced by more strongly coordinating ligands therefore making the complexes proper starting materials for the synthesis of other complexes. Many of these nitrile complexes have been synthesized and found to be valuable in many applications [7]. The acetonitrile complexes of the type $[M^{II}(NCCH_3)_6][X]_2$ (M = Cu, Fe, Co, Ni, Zn, and Mn and X = BF_{4-}, $B(C_6F_5)_4$ and $B\{C_6H_3(m\text{-}CF_3)_2\}_4^-$) have found

Electronic supplementary material The online version of this article (doi:https://doi.org/10.1007/s10562-019-02804-9) contains supplementary material, which is available to authorized users.

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Published online: 08 May 2019

to be catalytically active towards many reactions such as cyclopropanation and aziridination of olefins [8, 9], polymerization [10, 11], and aldehyde olefination reaction [12–16].

Cyclopropanes are essential subunits of many natural products, and a large number of synthetic compounds that carry a cyclopropane unit possess biological activities [17, 18]. As a consequence, considerable efforts have been made to develop efficient methods for the synthesis of these small ring motifs and to incorporate them into pharmacologically active ingredients [19]. The most important strategy for constructing three-membered rings start from olefins is Michael-reaction-initiated ring closure (MIRC) [20]. This method involves a sequence of a nucleophilic addition and a ring closure and requires the presence of both electron-withdrawing and leaving groups in the reaction partners [21]. The use of complexes with the type of $[M^{II}(NCCH_3)_6][X]_2$ (M = Mn and Cu and X = BF_{4-}, $B(C_6F_5)_4$ and $B\{C_6H_3(m\text{-}CF_3)_2\}_4^-$) can play a positive role on the catalytic activity of cyclopropanation reactions. Several studies have been reported using these types of complexes toward the decomposition of ethyl diazoacetate (EDA) in the presence of both terminal and internal olefins to yield cyclopropane products [22–24]. It is generally accepted that transition metal catalyzed cyclopropanation reactions involve the existence of a metal-carbene complex, [25, 26]. Furthermore, many fluorinated compounds are synthesized routinely in pharmaceutical research and are widely used in the treatment of diseases [27]. Introducing fluorine atoms into ligands would improve metabolic stability, alter physicochemical properties because of its electronegativity as well as increase the binding affinity [28]. Herein, we report the synthesis and spectroscopic characterization of propeonitrile complexes of the type $[M(C_3H_5N)_6][B(C_6F_5)_4]_2$, Where M = Cu(II),Mn(II),Ni(II),Co(II),Zn(II),Fe(II). The synthesized compounds were also examined for their catalytic cyclopropanation and biological properties. The biological activities have been investigated by evaluating the antibacterial behavior of the synthesized complexes against various pathogenic bacterial strains.

2 Experimental

All manipulations were carried out under nitrogen atmosphere using standard schlenk techniques. All solvents used were dried, kept under inert gas atmosphere (N_2 gas or Ar gas) and molecular sieves prior to use. Acetonitrile and propionitrile were pre dried over P_2O_5, distilled over CaH_2 and were kept over 3A° molecular sieves. Nuclear magnetic resonance spectra were recorded at 400 MHz on a Bruker (FT-NMR advance 400 MHz) spectrometer. (Bruker Corporation, United States). The ^1H and ^{11}B NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. The chemical shifts were measured in ppm in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Thermal analyses were performed using a PCT-2 A thermo balance analyser operating at a heating rate of 10 °C min^{-1} in the range 30 to 800 °C under nitrogen atmosphere. Electron paramagnetic resonance (EPR) spectra were recorded using a JEOL JES-FA 200 spectrometer at X-band frequency. The spectra were measured at a microwave frequency of approximately 9.25 GHz with a microwave power of 5 mW, modulation amplitude of 0.4 mT, sweep time of 4 min, time constant of 0.1 s and modulation frequency of 100 kHz. The microwave frequency was measured with a microwave frequency counter (Advantest R5372). The temperature was monitored with a JEOL ES DVT4 temperature controller equipped with a calibrated thermocouple. Measurements at 113 K were performed using liquid nitrogen for cooling. The g values were determined using Mn2 + (nuclear spin I = 5/2) embedded in MgO as a standard; experimental errors: $\Delta g \pm 0.001$. GC–MS analyses were performed using electronic impact ionization mode with a Varian Saturn 2000 ion trap spectrometer, interfaced with a Varian GC CP-3800 apparatus. Microanalyses for carbon, hydrogen and nitrogen were performed at the Microanalytical Laboratory of the Technical University of Munich. Carbon, nitrogen and hydrogen analyses were performed using aVario EL elemental analyzer. GC–MS analyses were performed using electronic impact ionization mode on a Varian Saturn 2000 ion trap spectrometer, interfaced with a Varian GC CP-3800 apparatus. The silver salt $[B(C_6F_5)_4]^-$ was prepared according to literature [29, 30].

2.1 Synthesis of Complexes

2.1.1 $[Cu(NCC_2H_5)_6][B(C_6F_5)_4]_2$ (1)

$CuCl_2$ (0.086 g, 0.64 mmol), was added to a solution of $Ag[B(C_6F_5)_4]$ (1.00 g, 1.27 mmol) in (20 ml) dry acetonitrile, the resulting mixture was stirred overnight in the dark. The precipitate was removed by filtration (used cannula filter) and the filtrate was concentrated by vacuum pump, then the solid was dissolved in 20 ml propionitrile and stirred overnight, the solution was concentrated by vacuum pump and kept at − 35 °C. The desired product was obtained as a light-green solid. Yield 0.78 g (87.5%). $C_{66}H_{30}B_2F_{40}CuN_6$ (1751.1): calc. C 45.27, H 1.67, N 4.80; found C 45.20, H 1.73, N 4.67. Selected IR (KBr): 2291, 2319 [ν (CN)].^1H: 1.11, 2.43 ppm. ^{11}B: − 19.27 ppm.

2.1.2 $[Mn(NCC_2H_5)_6][B(C_6F_5)_4]_2$ (2)

Yield 0.83 g (84.3%). $C_{66}H_{30}B_2F_{40}MnN_6$ (1742.5): calc. C 45.49, H 1.68, N 4.82; found C 45.73, H 1.83, N 4.73. Selected IR (KBr): 2281, 2322 [ν (CN)].^1H: 1.14, 2.50 ppm. ^{11}B: − 16.67 ppm.

2.1.3 $[Zn(NCC_2H_5)_6][B(C_6F_5)_4]_2$ (3)

Yield 0.79 g (88.7%). $C_{66}H_{30}B_2F_{40}ZnN_6$ (1753): calc. C 45.22, H 1.67, N 4.79; found C 45.4, H 1.80, N 4.71. Selected IR (KBr): 2271, 2291 [ν (CN)]. ^{1}H: 1.31, 2.42 ppm. ^{11}B: − 19.24 ppm.

2.1.4 $[Co(NCC_2H_5)_6][B(C_6F_5)_4]_2$ (4)

Yield 0.76 g (85.4%). $C_{66}H_{30}B_2F_{40}CoN_6$ (1746.5): calc. C 45.39, H 1.67, N 4.81; found C 45.61, H 1.75, N 4.76. Selected IR (KBr): 2289, 2319 [ν (CN)]. ^{1}H: 1.28, 2.63 ppm. ^{11}B: − 19.07 ppm.

2.1.5 $[Ni(NCC_2H_5)_6][B(C_6F_5)_4]_2$ (5)

Yield 0.77 g (84.78%). $C_{66}H_{30}B_2F_{40}NiN_6$ (1746.3): calc. C 45.40, H 1.67, N 4.81; found C 45.62, H 1.91, N 4.79. Selected IR (KBr): 2272, 2340 [ν (CN)]. ^{1}H: 1.12, 2.44 ppm. ^{11}B: − 19.23 ppm.

2.1.6 $[Fe(NCC_2H_5)_6][B(C_6F_5)_4]_2$ (6)

Yield 0.65 g (76.1%). Selected IR (KBr): 2278, 2305 [ν (CN)]. ^{1}H: 1.14, 2.46 ppm. ^{11}B: − 19.25 ppm.

2.2 Antimicrobial Activity

The preparation of antimicrobial susceptibility cultures and Minimum Inhibitory concentrations (MIC, µg/ml) testing for the complexes were performed as described in previous work [29]. The clinical isolates were *Escherichia coli*; *Klebsiella pneumonia*; *Proteus mirabilis*; *Pseudomonas aeruginosa* (as Gram-negative) and *Staphylococcus aureus*; *Streptococcus pyogenes* (as Gram-positive).

2.3 Cyclopropanation

EDA (0.114 g, 1.0 mmol) in (20 ml) propionitrile was slowly added (addition time 1 h) to a 4.0 ml propionitrile solution of an olefin (2.0 mmol) and catalyst (0.02 mmol). The reaction was stirred for up to 24 h at room temperature. The course of each reaction was monitored by GC–MS analysis.

3 Results and Discussion

3.1 Synthesis of the Complexes

The metal complexes (Fig. 1) were synthesized by reacting metal (II) halides with the silver salts of the corresponding anion in acetonitrile (Scheme 1) [31]. The propionitrile is exchanged with acetonitrile by adding excess of propionitrile

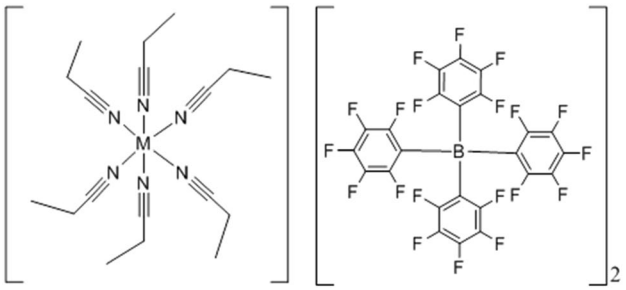
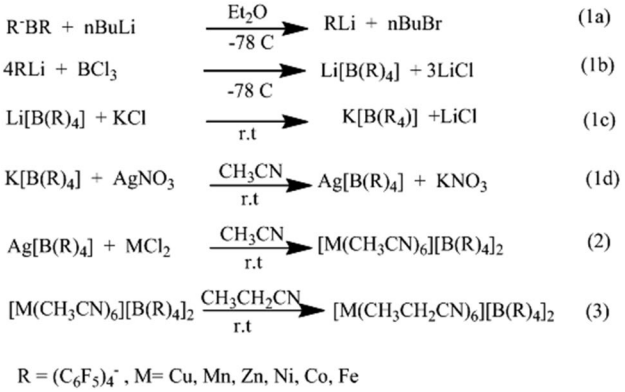


Fig. 1 Proposed structure for the catalyst, M = Cu (complex 1), Zn (complex 2), Mn (complex 3), Co (complex 4), Ni (complex 5), Fe (complex 6)



Scheme 1 The synthetic route to complexes 1-6

solvent. The complexes are moderately air stable and can be handled in laboratory atmosphere for brief periods of time. For storage over longer periods, the compounds have to be kept under an inert gas (N_2 or Ar gas) atmosphere at low temperature (− 30 °C). All synthesized compounds were characterized by using IR spectroscopy, ^{1}H-NMR ^{11}B NMR spectroscopy, Thermogravimmetry analysis (TGA), Elemental analysis.

3.2 Elemental Analysis

Table 1 lists the elemental analysis data and yields for all the complexes. The elemental contents (C, H, N) of the complexes are relatively close to those calculated based on the proposed molecular formula.

3.3 Infrared Spectra

The infrared (IR) spectra of all the complexes are recorded in a KBr matrix and listed in Table 2. Figure 2 shows the IR spectra for $[Mn(NCC_2H_5)_6][B(C_6F_5)_4]_2$ **2** and $[Co(NCC_2H_5)_6][B(C_6F_5)_4]_2$ **5** complexes. Complex **2** exhibits two sharp ν(CN) absorptions at approximately 2291 cm^{-1}

Table 1 Analytical data for the complexes 1–5

Complexes	C (%) found (calc.)	H (%) found (calc.)	N (%) found (calc.)	Yields %
1	45.20 (45.27)	1.73 (1.67)	4.67 (4.80)	87.50
2	45.20 (45.22)	1.80 (1.67)	4.71 (4.79)	88.76
3	45.73 (45.49)	1.83 (1.68)	4.73 (4.82)	84.33
4	45.61 (45.39)	1.75 (1.67)	4.76 (4.81)	85.40
5	45.62 (45.40)	1.91 (1.67)	4.79 (4.81)	84.78

Table 2 Major infrared spectra data for the complexes 1–6

Complexes	v(CN)		v (Ar-(C=C))		v (Ar-(C-F))		
1 Cu	2291	2319	1645	1472	1383	1264	1082
2 Mn	2271	2291	1646	1518	1383	1270	1090
3 Zn	2281	2322	1642	1446	1384	1271	1081
4 Ni	2289	2319	1643	1474	1383	1271	1088
5 Co	2272	2340	1646	1516	1383	1272	1089
6 Fe	2278	2305	1645	1471	1384	1264	1082

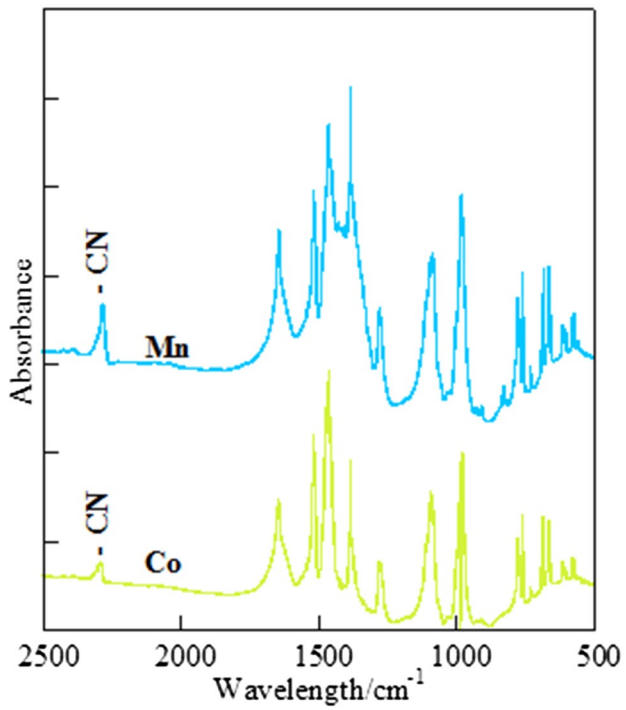


Fig. 2 FT-IR spectrum of [Mn (NCC_2H_5)6][B (C_6F_5)4]2 2 and [Co (NCC_2H_5)6][B(C_6F_5)4]2 5

and 2271 cm^{-1} and this is for stretching mode ν_2-CN and a combination mode ($\nu_3+\nu_4$) for complex respectively. Complex **5** also shows two sharp ν(CN) absorptions at approximately 2340 cm^{-1} and 2272 cm^{-1} [32]. For complexes **1**, **3**,**4** and **6**, the absorptions bands assigned to stretching mode ν_2-CN at 2319, 2322, 2319 and 2305 $cm^{-1,}$ respectively, and bands for combination mode ($\nu_3+\nu_4$) at 2291, 2281, 2289 and 2278 cm^{-1}, respectively. These results indicate that the CN group within all complexes. Higher energy for both types of vibration modes observed for all examined compounds in comparison to free propionitrile (ν (CN) = 2247 cm^{-1}) [33]. This energy change is due to the σ-donation of electron density from the lone pair of the nitrogen, which has some *anti*-bonding character [34].

3.4 Thermogravimmetric Analysis (TGA)

Thermogravimmetric (TG) and differential Thermogravimmetric (DTG) analysis for all complexes were carried out within a temperature range from 30 °C up to 800 °C under N_2 flow.

Thermal gravimetric curves TG and DTG complexes **1–6** showed similar thermal decompositions (Figs. S1, S2). The TGA/DrTG spectra of copper complex (Fig. 3) show that the first step decomposition started at 180 °C with 30.60 wt%, this mass loss back to loss six propionitrile ligands. The second step occurred at 210 °C with an estimated mass loss of 52.70% which may be due to decomposition of anion fragmentation $(B(C6F5)4)_2$. The final step involves the formation of metal fluoride as a final residue [35].

3.5 NMR Characterization

The ^{1}H-NMR spectra of the complexes were obtained in DMSO-d6 solution in the range 0–12 ppm. Figure 4 shows the chemical shifts of the propionitrile protons of $[Zn(NCC_2H_5)_6][B\ (C_6F_5)_4]_2$ complex which are observed as quartet and triplet peaks at 2.36 (q, 12H, CH_2) and 1.20 (t, 18H,CH_3) ppm, respectively. The ^{11}B-NMR spectra of all complexes were recorded in deuterium oxide (D_2O), in the range (−20, −10) ppm. Figure 5 shows the spectra for the Fe complex, a singlet peak observed at δ = − 19.25 ppm is

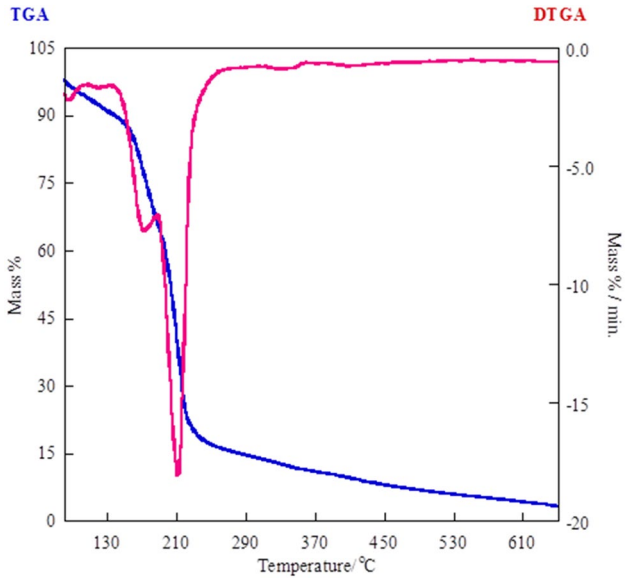


Fig. 3 TGA/DTG spectra of [Cu (NCC_2H_5)6][B (C_6F_5)4]2 1

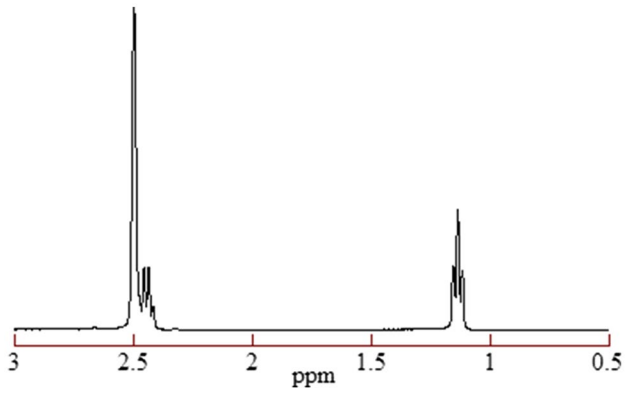


Fig. 4 1H NMR for structure of [Zn(NCC_2H_5)6][B (C_6F_5)4]2 3

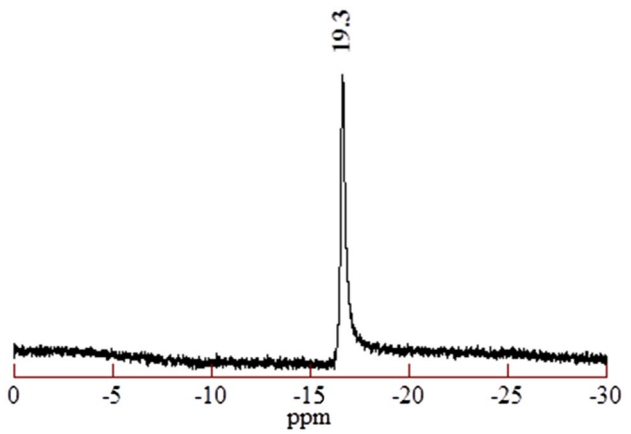


Fig. 5 11B NMR for structure of [Fe(NCC_2H_5)6][B (C_6F_5)4]2 6

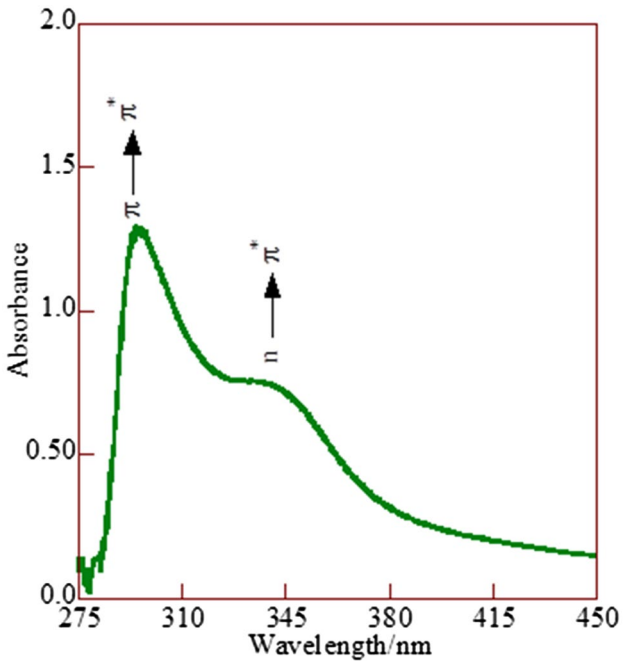


Fig. 6 UV–Vis absorption spectra for [Cu(NCC_2H_5)6][B (C_6F_5)4]2 1

assigned to boron of [$B(C_6F_5)_4$] [36]. The same peaks were observed in the same region for the other metal complexes.

3.6 UV–Visible Spectroscopy

The UV–Vis absorption spectra of the complexes **1–6** were carried out in methanol solvent at room temperature. Figure 6 shows the UV–Vis absorption spectra for [Cu(NCC_2H_5)$_6$][B (C_6F_5)$_4$]$_2$ **1**. The absorption band centered at 293 nm may be attributed to the π–π^* transitions in the aromatic ring and the absorption bands between 326 and 340 nm corresponds to the n–π^* transitions.

3.7 Determination of MIC

The minimum inhibition concentration (MIC) of the complexes against different types of Gram-positive and Gram-negative bacteria, as well as fungi were determined and tabulated in Table 3. The synthesized complexes possessed poor antimicrobial activity against all the Gram-negative bacteria tested. The complexes showed moderate antimicrobial activity against *S. aureus* and *S. pyogenes*. The antifungal activities for all complexes were highly active against *C. tropicalis* and moderate activities against *C. albicans*. Ni complex has less active against *S. aureus* and moderate activity against *C. tropicalis* and poor activity against *C. albicans*. All complexes have similar geometry; its apparent from the present results that the nature of the coordinating ligands, this enhancement in the activity can be explained

Table 3 Minimum inhibitory concentrations (MIC, µg/ml) of all complexes against clinical isolates of some bacterial and Candida albicans using agar well diffusion

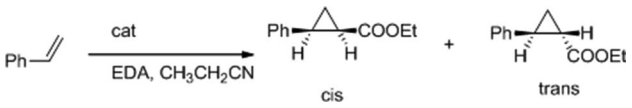
	Gram (−) bacteria			Gram (+) bacteria		Antifungal		
	Ec	Pm	Pa	Sp	Sa	Cr	Ca	Ct
Tested compounds								
1	256	256	512	64	32	N	64	4
2	256	256	512	128	32	N	64	8
3	256	256	256	64	32	N	32	8
4	256	256	512	128	64	N	128	8
5	256	256	512	64	256	N	256	32
DMSO (−ve control)	N	N	N	N	N	–	–	–
Oxytetracycline (+ve control)	8	8	16	16	4	–	–	–
Fluconazole (+ve control)	–	–	–	–	–	4	4	4

Ec Escherichia coli, *Pm Proteus mirabilis*, Pa *Pseudomonas aeruginosa*, Sa *Staphylococcus aureus*; pyogenes, *Sp Streptococcus pyogenes*, *Cc Candida cruzi*, *Ct Candida tropicalis*, *Ca Candida albicans*, *Fluconazole* antifungal positive control for Candida albicans

on the basis of chelation theory [37]. Chelation increases the lipophilic nature of the central metal atom, and the type of counter anion maybe responsible for a number of specific interactions with selected microorganisms, which enhances the penetration of the complexes into the lipid membrane of the microorganism cell wall and thus raising the activity of the complex and restricts the further growth of the organism [38]. The activity observed against the Gram positive bacteria can be explained by considering the effect on lipopolysaccharide (LPS), a major component of the surface of Gram positive [39]. LPS is an important entity in determining the outer membrane barrier function and the virulence of Gram negative pathogens. The complexes can permeate the bacterial cell membrane by coordination to LPS and this leads to the spoilage of outer cell membrane and inhibits the growth of the bacteria. However the chance of such coordination is low in Gram negative bacteria which contain a thin peptidoglycan layer adjacent to the cytoplasmic membrane.

3.8 Application to Catalytic Olefin Cyclopropanation

Weakly coordinated complexes based are easily displaceable ligands and have a positive effect on the catalytic activity, by rendering the intermediate species more accessible to substrate coordination [40]. Complexes **1–6** were evaluated as catalysts for cyclopropanation using trans-stilbene with ratio catalyst/olefin 1:250 using EDA in a propionitrile as a solvent at room temperature yielding a mixture of cis and trans isomers (Scheme 2). The catalytic runs of the complexes **1–6** with the trans-stilbene are summarized in Table 4. Compounds **1–6** exhibited to be active in internal olefin cyclopropanation as well. In fact, Complex **1** $[Cu(CH_3CH_2CN)_6][B(R)_4]_2$ exhibited the best among other metal catalysts toward the decomposition of ethyl diazoacetate, and the



Scheme 2 Catalytic cyclopropanation of alkenes

Table 4 Catalytic cyclopropanation of trans-stilbene mediated by complexes 1–6

Entry	Catalyst	Yield[a]	Cis:trans[b]
1	1	82	28:72
2	2	66	30:70
3	3	72	32:68
4	4	71	31:69
5	5	73	30:70
6	6	70	38:62

Reactions performed at room temperature with 2.0 mmol of EDA

[a]Percentage of the product, based in EDA, determined by GC

[b]Determined by GC–MS

subsequent transfer of the carbene moiety to the C=C double bond [41]. As reported the literature in catalytic cyclopropanation reactions, Cu(II) complexes are reduced to Cu(I) derivatives during the catalytic cycle, lead to the general agreement that the active species is a Cu(I) species regardless the oxidation state of the copper complex used as a pre catalyst. A large excess of the olefin is not required for the reaction to proceed: even if equimolar amounts of EDA and olefin were used the cyclopropane products were obtained in reasonable yields. The cis:trans ratio is not affected to a large extent by changing the conditions and the cis:trans ratio ranging from 40:60 to 20:80. Several alkenes were employed to determine the substrate scope of the complex

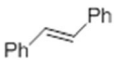
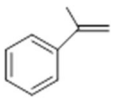
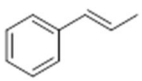
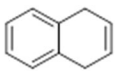
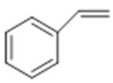
$[Cu(CH_3CH_2CN)_6][B(R)_4]_2$ as cyclopropanation catalyst. At a 1/EDA/olefin ratio of 1:1:250 at room temperature, the complex catalyzed the cyclopropanation of a range of substrates with quantitative conversion ranging from 68 to 89% Table 4. Styrene and α and β methyl styrene derivatives are employed as substrates. The catalyst could successfully convert these substrates to the desired cyclopropanes in good yields (entry 2, 3 and 7, Table 5). Steric hindrance at the position α does not hamper the reaction and good yields are obtained even with 1 α methyl styrene (entry 2, Table 5). Aliphatic double bonds are generally less reactive towards cyclopropanation, even though they gave good results (entry 4 and 6 Table 5).

4 Conclusions

Complexes of formula $[M^{II}(NCCH_2CH_3)_6][B(C_6F_5)_4]_2$ (M = Cu, Fe, Co, Ni, Mn and Zn) have been prepared and characterized. The complexes characterized by FT-IR, elemental analysis, ^{1}H-NMR, ^{11}B-NMR, TGA, UV–Vis. Upon thermolysis, solvent is lost from the coordination sphere together with abstraction of fluoride from the anion. All six propionitrile ligands are coordinated to M(II) in octahedral arrangement similar to the acetonitrile complex analog $[Cu(NCCH_2CH_3)_6][B(C_6F_5)_4]_2$. The complexes are structurally similar with six propionitrile ligand coordinated to M(II) in octahedral arrangement. All compounds are easily accessible and can be obtained in good yields. The antimicrobial and antifungal activities of all complexes were studied against different pathogens. The complexes have shown moderate activities against Gram positive and low activities against Gram negative.

The catalytic results indicate that these types of complexes are potentially interesting for cyclopropanation reaction. The copper(II) complex showed excellent catalytic activity in for various olefins at room temperature.

Table 5 Cyclopropanation of olefins with EDA catalyzed by complex 2 $[Cu(CH_3CH_2CN)_6][B(R)_4]_2$ after 24 h

Entry	Olefin[a]	Yield[b]	Cis:trans[c]
1		82	28:72
2		80	40:60
3		78	32:68
4		80	20:80
5		78	21:79
6		89	38:62
7		79	35:65

[a]Reactions performed at room temperature with 2:1 Olefin:EDA

[b]Percentage of the product, based in EDA, determined by GC

[c]Determined by GC–MS

Acknowledgements We gratefully acknowledge financial support from Jordan University of Science and Technology (Project No. 533/2015).

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