TÜBİTAK

Turkish Journal of Chemistry

http://journals.tubitak.gov.tr/chem/

Research Article

Turk J Chem
(2013) 37: 1007 – 1013

doi:10.3906/kim-1304-72

N-functionalized benzimidazol-2-ylidene silver complexes: synthesis, characterization, and antimicrobial studies

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Received: 25.04.2013 • **Accepted:** 04.07.2013 • **Published Online:** 04.11.2013 • **Printed:** 29.11.2013

Abstract: 2-Methoxyethyl, 2-diethylaminoethyl, and 2-phenylethyl-substituted N-heterocyclic carbene (NHC) precursors were treated with Ag_2CO_3 to yield silver(I)-NHC complexes (**1a**–**g**) in dichloromethane as a solvent at room temperature. The 7 new silver-NHC complexes were fully characterized by means of ^{1}H NMR, ^{13}C NMR, and elemental analysis techniques. Using the agar dilution procedure recommended by the Laboratory and Clinical Standards Institute, the antimicrobial activities of all the silver-NHC complexes were studied against 2 gram-negative bacterial strains (*Pseudomonas aeruginosa* and *Escherichia coli*), 2 gram-positive bacterial strains (*Enterococcus faecalis* and *Staphylococcus aureus*), and 2 fungi (*Candida tropicalis* and *Candida albicans*).

Key words: N-Heterocyclic carbene, benzimidazol-2-ylidene, silver complex, antimicrobial activity, medical inorganic chemistry

1. Introduction

The transition metal complexes of N-heterocyclic carbenes (NHCs) have been significantly developed in organometallic chemistry and homogeneous catalysis since discovered by Wanzlick, Öfele, and Arduengo, and have become extremely popular.[1–3] In comparison, metal-NHC complexes have shown better catalytic activity than the corresponding phosphine–metal complexes in various organic transformation methods, not only due to their high σ-basicity and low π-acidity abilities but also because of the ease of controlling steric effects on nitrogen atoms.[4–9] The silver-NHC complexes, which were used as convenient carbene transfer reagents for the synthesis of some metal-NHC complexes, have received continuous attention.[10,11] More recently, the silver-NHC complexes exhibiting antimicrobial activity have also found applications, in particular as catalysts, nanomaterials, and anticancer agents.[12–19] There are 3 different procedures for the synthesis of silver-NHC complexes: (i) under basic phase transfer conditions, the reaction of silver salts with azolium salts; (ii) the reaction of silver bases such as AgOAc, Ag_2CO_3, and Ag_2O with azolium salts; (iii) the reaction of free NHC silver salts.[20,21] Route (ii) is the most commonly employed among these procedures.

We present herein the synthesis, characterization, and antimicrobial studies of 7 new 2-methoxyethyl-substituted, 2-diethylaminoethyl-substituted, and 2-phenylethyl-substituted silver-NHC complexes. All silver-NHC complexes showed antibacterial activity against the tested bacterial and fungal strains.

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2. Experimental

2.1. Materials and methods

Under an inert atmosphere of argon using standard Schlenk techniques, all reactions for the synthesis of chloro-(1,3-dialkylbenzimidazol-2-ylidene)silver(I) complexes were carried out. All chemicals were bought from Aldrich, Fluka, and Merck. The solvents, dichloromethane over P_4O_{10} and hexane over Na, were distilled prior to use. The ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AC300P FT spectrometer operating at 75.47 MHz (^{13}C) and 300.13 MHz (H^1). The chemical shifts (δ) were given in ppm relative to TMS coupling constants (J) in hertz. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus. Microanalyses were performed by the TÜBİTAK (Ankara, Turkey) analyses center.

The minimal inhibitory concentration for each compound was investigated against standard bacterial strains: *Enterococcus faecalis* (ATCC 29212), *Staphylococcus aureus* (ATCC 29213), *Pseudomonas aeruginosa* (ATCC 27853), and *Escherichia coli* (ATCC 25922). These were obtained from the American Type Culture Collection (Rockville, MD, USA). The fungal strains *Candida tropicalis* and *Candida albicans* were acquired from the Department of Microbiology, Faculty of Medicine, Ege University (Turkey). Bacterial strains were subcultured on Mueller Hinton broth (HiMedia Laboratories Pvt. Ltd, Mumbai, India) and fungal strains were also subcultured on RPMI 1640 broth (Sigma-Aldrich Chemie GmbH Taufkirchen, Germany).

2.2. General method for the preparation of silver-*N*-heterocyclic carbene complexes

1,3-Dialkylbenzimidazolium chloride (1.0 mmol), Ag_2CO_3 (0.5 mmol), and activated 4-Å molecular sieves were stirred in dichloromethane (20 mL) at room temperature for 24 h. The Schlenk-type flask was covered with aluminum foil to avoid light exposure. The resulting solution was filtered through Celite and the solvent was removed under reduced pressure. The crude product was crystallized from hexane/dichloromethane at room temperature.

Chloro-[1,3-di(2-methoxyethyl)benzimidazol-2-ylidene]silver(I), 1a

Yield: 83%; mp: 181–182 °C. ^{1}H NMR (300.13 MHz, DMSO-d^6), δ: 3.23 (s, 6 H, $CH_2CH_2OCH_3$); 3.78 (t, J: 6.4 Hz, 4 H, $CH_2CH_2OCH_3$); 4.65 (t, J: 6.4 Hz, 4 H, $CH_2CH_2OCH_3$); 7.42–7.83 (m, 4 H, Ar-H). ^{13}C NMR (75.47 MHz, DMSO-d^6), δ: 48.9 ($CH_2CH_2OCH_3$); 58.8 ($CH_2CH_2OCH_3$); 71.3 ($CH_2CH_2OCH_3$); 112.7, 124.3, and 134.1 (C_6H_4-N_2); 187.9 (2-C). Anal. Calcd. for $C_{13}H_{19}N_2O_2AgCl$: C, 41.24; H, 5.06; N, 7.40. Found: C, 41.31; H, 4.99; N, 7.45%.

Chloro-[1-(2-methoxyethyl)-3-(2-morpholinoethyl)benzimidazol-2-ylidene)]silver(I), 1b

Yield: 86%, mp: 145–146 °C. ^{1}H NMR (300.13 MHz, DMSO-d^6), δ: 2.43 [t, J: 4.5 Hz, 4 H, $N(CH_2CH_2)_2O$]; 2.47 [t, J: 6.0 Hz, 2 H, $NCH_2CH_2N(CH_2CH_2)_2O$]; 3.21 (s, 3 H, OCH_3); 3.55 [t, J: 4.5 Hz, 4 H, $N(CH_2CH_2)_2O$]; 3.77 (t, J: 4.8 Hz, 2 H, $NCH_2CH_2OCH_3$); 4.55 [t, J: 6.0 Hz, 2 H, $NCH_2CH_2N(CH_2CH_2)_2O$]; 4.63 (t, J: 4.8 Hz, 2 H, $NCH_2CH_2OCH_3$); 7.42–7.82 (m, 4 H, Ar-H). ^{13}C NMR (75.47 MHz, DMSO-d^6), δ: 46.6 and 48.9 [$(NCH_2CH_2N(CH_2CH_2)_2O$]; 54.1 [$(NCH_2CH_2N(CH_2CH_2)_2O$]; 58.2 [$(NCH_2CH_2N(CH_2CH_2)_2O$]; 58.8 ($NCH_2CH_2OCH_3$); 66.6 ($NCH_2CH_2OCH_3$); 71.3 ($NCH_2CH_2OCH_3$); 112.4, 112.8, 124.3, 133.7, and 134.0 (C_6H_4-N_2); 188.9 (2-C). Anal. Calcd. for $C_{16}H_{24}N_3O_2AgCl$: C, 44.31; H, 5.58; N, 9.69. Found: C, 44.38; H, 5.49; N, 9.73%.

Chloro-[1-(2-methoxyethyl)-3-(4-methylbenzyl)benzimidazol-2-ylidene]silver(I), 1c

Yield: 79%, mp: 223–224 °C. ^{1}H NMR (300.13 MHz, DMSO-d^6), δ: 2.09 (s, 3 H, $CH_2C_6H_4CH_3$); 3.21

(s, 3 H, $CH_2CH_2OCH_3$); 3.75 (t, J: 5.7 Hz, 2 H, $CH_2CH_2OCH_3$); 4.66 (t, J: 5.7 Hz, 2 H, $CH_2CH_2OCH_3$); 5.61 (s, 2 H, $CH_2C_6H_4CH_3$); 7.40–7.78 (m, 8 H, Ar-H). ^{13}C NMR (75.47 MHz, DMSO-d^6), δ: 21.1 ($CH_2C_6H_4CH_3$); 49.0 ($CH_2CH_2OCH_3$); 52.1 ($CH_2CH_2OCH_3$); 58.8 ($CH_2C_6H_4CH_3$); 71.3 ($CH_2CH_2OCH_3$); 112.7, 112.9, 124.5, 127.8, and 129.8 (C_6H_4-N_2); 133.5, 133.7, 134.3, and 137.9 ($CH_2C_6H_4CH_3$); the carbene carbon was not detected. Anal. Calcd. for $C_{18}H_{21}N_2OAgCl$: C, 50.91; H, 4.98; N, 6.60. Found: C, 50.83; H, 4.87; N, 6.55%.

Chloro-[1-(2-methoxyethyl)-3-(naphthylmethyl)benzimidazol-2-ylidene]silver(I), 1d

Yield: 87%, mp: 204–205 °C. ^{1}H NMR (300.13 MHz, DMSO-d^6), δ: 3.45 (s, 3 H, $CH_2CH_2OCH_3$); 3.71 (t, J: 4.5 Hz, 2 H, $CH_2CH_2OCH_3$); 4.62 (t, J: 4.5 Hz, 2 H, $CH_2CH_2OCH_3$); 6.20 (s, 2 H, $CH_2C_{10}H_7$); 6.90–8.19 (m, 11 H, Ar-H). ^{13}C NMR (75.47 MHz, DMSO-d^6) δ: 49.2 ($CH_2CH_2OCH_3$); 50.1 ($CH_2C_{10}H_7$); 58.7 ($CH_2CH_2OCH_3$); 71.2 ($CH_2CH_2OCH_3$); 112.6, 113.0, 123.6, 124.6, 128.9, and 129.2 (C_6H_4-N_2); 125.9, 126.8, 127.2, 130.7, 132.4, 133.8, 134.1, and 134.2 ($CH_2C_{10}H_7$); 190.1 (2-C). Anal. Calcd. for $C_{21}H_{21}N_2OAgCl$: C, 54.75, H, 4.59, N, 6.08. Found: C, 54.88, H, 4.49; N, 6.10%.

Chloro-[1-(2-methoxyethyl)-3-(isopropyl)benzimidazol-2-ylidene)]silver(I), 1e

Yield: 84%, mp: 147–148 °C. ^{1}H NMR (300.13 MHz, DMSO-d^6), δ: 1.68 [d, J: 6.9 Hz, 6 H, $CH(CH_3)_2$]; 3.23 (s, 3 H, $CH_2CH_2OCH_3$); 3.78 (t, J: 5.1 Hz, 2 H, $CH_2CH_2OCH_3$); 4.64 (t, J: 5.1 Hz, 2 H, $CH_2CH_2OCH_3$); 5.09 [h, J: 6.9 Hz, 1 H, $CH(CH_3)_2$]; 7.42–7.94 (m, 4 H, Ar-H). ^{13}C NMR (75.47 MHz, DMSO-d^6), δ: 22.9 [$CH(CH_3)_2$]; 49.3 [$CH(CH_3)_2$]; 52.5 ($CH_2CH_2OCH_3$); 58.8 ($CH_2CH_2OCH_3$); 71.3 ($CH_2CH_2OCH_3$); 112.9, 113.0, 124.2, 124.4, 132.7, and 134.4 (C_6H_4-N_2); 186.4 (2-C). Anal. Calcd. for $C_{13}H_{19}N_2AgCl$: C, 45.05; H, 5.52; N, 8.08. Found: C, 45.14; H, 5.49; N, 8.01%.

Chloro-[1-(2-diethylaminoethyl)-3-(isopropyl)benzimidazol-2-ylidene)]silver(I), 1f

Yield: 82%, mp: 129–130 °C. ^{1}H NMR (300.13 MHz, DMSO-d^6), δ: 0.78 [t, J: 6.0 Hz, 6 H, $CH_2CH_2N(CH_2CH_3)_2$]; 1.66 [d, J: 6.9 Hz, 6 H, $CH(CH_3)_2$]; 2.45 [q, J: 6.0 Hz, 4 H, $CH_2CH_2N(CH_2CH_3)_2$]; 2.78 [t, J: 5.1 Hz, 2 H, $CH_2CH_2N(CH_2CH_3)_2$]; 4.46 [t, J: 5.1 Hz, 2 H, $CH_2CH_2N(CH_2CH_3)_2$]; 5.08 [h, J: 6.9 Hz, 1 H, $CH(CH_3)_2$]; 7.41–7.92 (m, 4 H, Ar-H). ^{13}C NMR (75.47 MHz, DMSO-d^6), δ: 12.6 [$CH_2CH_2N(CH_2CH_3)_2$]; 22.9 [$CH(CH_3)_2$]; 47.4 [$CH_2CH_2N(CH_2CH_3)_2$]; 47.7 and 52.3 [$CH_2CH_2N(CH_2CH_3)_2$]; 48.9 [$CH(CH_3)_2$]; 112.6, 112.9, 124.1, 124.3, 132.6, and 134.2 (C_6H_4-N_2); 186.2 (2-C). Anal. Calcd. for $C_{16}H_{26}N_3AgCl$: C, 47.60; H, 6.49; N, 10.41. Found: C, 47.68; H, 6.43; N, 10.39%.

Chloro-[1,3-bis(2-diphenylethyl)benzimidazol-2-ylidene]silver(I), 1g

Yield: 79%, mp: 204–205 °C. ^{1}H NMR (300.13 MHz, DMSO-d^6) δ: 3.08 (t, J: 6.9 Hz, 4 H, $CH_2CH_2C_6H_5$); 4.63 (t, J: 6.9 Hz, 4 H, $CH_2CH_2C_6H_5$); 7.08–7.73 (m, 14 H, Ar-H). ^{13}C NMR (75.47 MHz, DMSO-d^6) δ: 50.4 and 55.4 ($CH_2CH_2C_6H_5$); 112.5, 124.3, and 129.0 (C_6H_4-N_2); 127.1, 129.3, 133.5, and 138.1 ($CH_2CH_2C_6H_5$); 185.8 (2-C). Anal. Calcd. for $C_{23}H_{23}N_2AgCl$: C, 58.68; H, 4.92; N, 5.95. Found: C, 58.79; H, 4.88; N, 5.97%.

2.3. Antimicrobial activity

Using the agar dilution procedure recommended by the Laboratory and Clinical Standards Institute, the antimicrobial activities of the synthesized silver-NHC complexes were determined.[22,23] The minimal inhibitory concentrations for each compound were investigated against the standard bacterial strains *E. faecalis*, *S. aureus*, *P. aeruginosa*, and *E. coli* and the fungal strains *C. tropicalis* and *C. albicans*. Their turbidities matched that

of a McFarland no. 0.5 turbidity standard. The stock solution of all compounds was prepared in DMSO. With distilled water, all of the dilutions were carried out. The concentrations of the tested compounds were 6.25, 12.5, 25, 50, 100, 200, 400, and 800 μg/mL. Ciprofloxacin and ampicillin were used as the antibacterial standard drugs while fluconazole was used as antifungal standard drug, whose minimum inhibitory concentration (MIC) values are provided. A loopful (0.01 mL) of the standardized inocula of the yeasts and bacteria (10^6 CFUs/mL) was spread over the surface of agar plates. All were inoculated after 16–20 h of incubation for bacteria and 48 h for yeasts. The lowest concentration of the compounds that prevented visible growth was considered to be the MIC.

3. Results and discussion

3.1. Synthesis and characterization of silver-*N*-heterocyclic carbene complexes, 1a–g

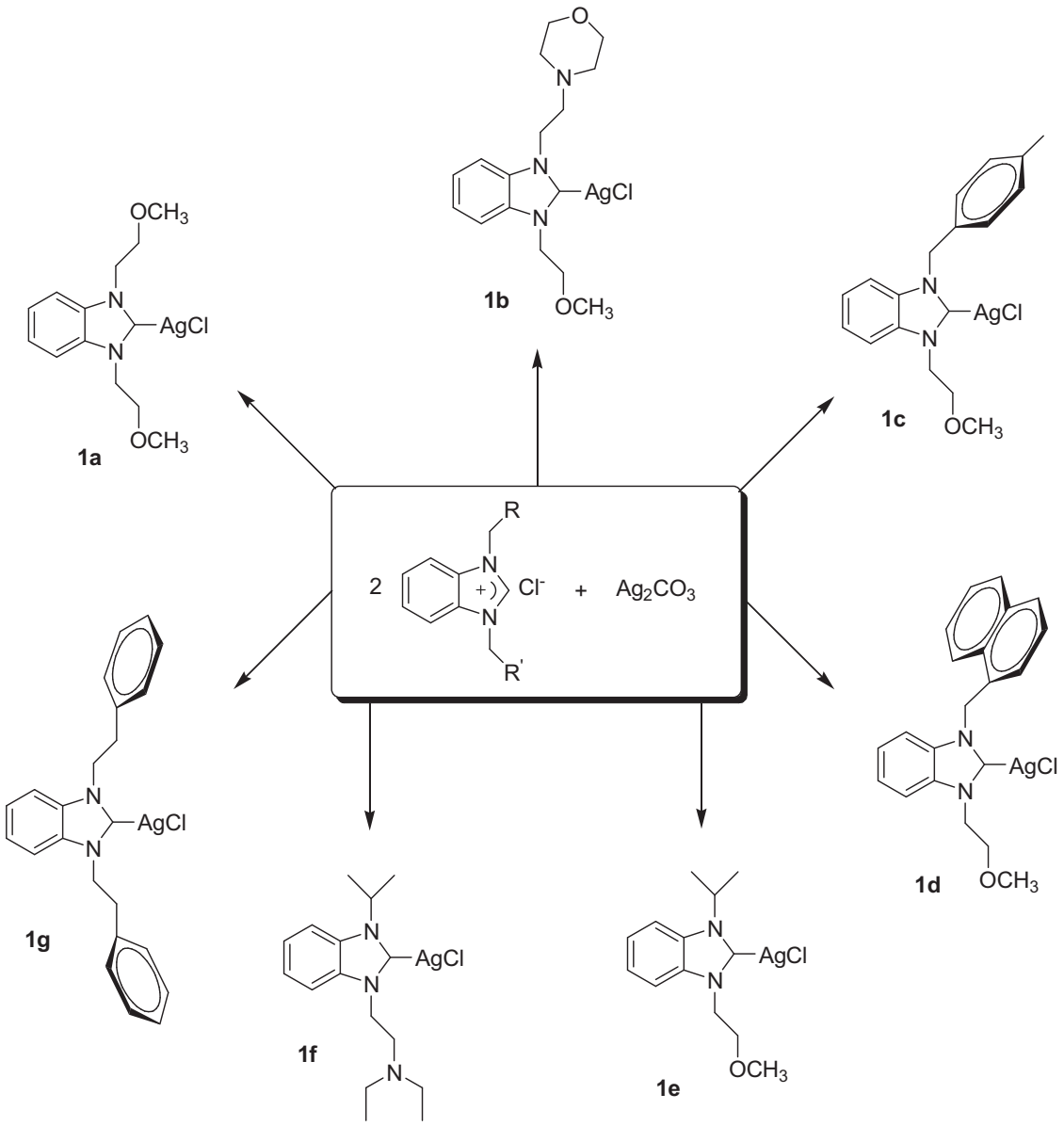
The carbene precursors 1-(2-methoxyethyl)-3-alkylbenzimidazolium salts, 1-(2-diethylaminoethyl)-3-isopropylbenzimidazolium salt, and 1,3-di(2-phenylethyl)benzimidazolium salt were prepared according to known methods.[24,25] Treatment of the benzimidazolium salts with 0.5 equiv. of Ag_2CO_3 in CH_2Cl_2 afforded quantitatively the expected carbene **1a–g** after 24 h (Scheme). The silver-NHCs **1a–g** were obtained as white solids in 79%–87% yields. While the silver carbene complexes (**1a–g**) were soluble in halogenated solvents, they were insoluble in nonpolar solvents. The structures of the silver-NHC complexes were characterized by spectroscopic and analytical techniques. Their ^{1}H and ^{13}C NMR spectra are consistent with the proposed formula. In the ^{1}H NMR and ^{13}C NMR spectra of these solid products in DMSO, loss of the benzimidazolium proton (NCHN) and benzimidazolium carbon (NCHN) signal suggests the formation of the silver complexes. The ^{13}C NMR spectra exhibit singlets at 187.9, 188.9, 186.4, 190.1, 186.2, and 185.8 ppm for **1a**, **1b**, **1d**, **1e**, **1f**, and **1g**, respectively, which is characteristic of the carbenic carbon resonance. In the **1c** complex, the resonance for carbene carbon was not detected, which has also been mentioned in the literature and has been given as a reason for the fluxional behavior of the NHC complexes.[26–28] The NMR values are similar to the results of other silver-NHC complexes.

Table 1. MICs (μg mL^{-1}) of silver-NHCs for test microorganisms.

Compound	*E. coli*	*S. aureus*	*E. faecalis*	*P. aerug.*	*C. albicans*	*C. tropicalis*
1a	50	50	50	50	50	50
1b	100	100	100	100	100	100
1c	100	100	100	100	25	12.5
1d	100	200	200	100	100	100
1e	100	100	100	100	100	100
1f	100	100	100	100	100	100
1g	200	100	100	100	100	100
Ampicillin	3.12	3.12	1.56	-	-	-
Ciprofloxacin	1.56	0.39	0.78	3.12	-	-
Fluconazole	-	-	-	-	3.12	3.12

The antimicrobial activities of the silver(I) complexes were estimated by minimum inhibitory concentrations (MIC, μg mL^{-1}) using an agar dilution procedure. Antimicrobial activity against fungi and bacteria was observed in the silver complexes (**1a–g**) tested at 200–12.5 μg mL^{-1} concentrations and the results are given in Table 1. The silver carbene complexes showed effective activities against 2 gram-negative bacterial strains

(*Escherichia coli* and *Pseudomonas aeruginosa*), 2 gram-positive bacterial strains (*Enterococcus faecalis* and *Staphylococcus aureus*), and 2 fungi (*Candida tropicalis* and *Candida albicans*). The tested complexes were found to be effective in inhibiting the growth of bacteria with MIC values between 200 and 50 μg mL^{-1}. The silver carbene complex (**1a**) showed a better antibacterial activity than the other complexes. All of the other silver carbene complexes (**1b**–**g**) exhibited the same activities against all bacteria.



Scheme. Synthesis of silver-*N*-heterocyclic carbene complexes.

The silver carbene complexes exhibited antifungal activity with a range of MICs values between 100 and 12.5 μg mL^{-1}. Among the silver carbene complexes, **1a** and **1c** showed high activity against the fungi *C. tropicalis* and *C. albicans*. All of the other silver carbene complexes (**1b**, **1e**, **1f**, and **1g**) exhibited the same activity against all fungi. From the data obtained in this work it is suggested that the substituents on the *N*-atoms may play a crucial role in antimicrobial activity.

When compared with other studies, the antimicrobial activities of synthesized silver-NHC complexes showed higher activities than did the NHC ligands.[12,29]

Table 2. Concentration (%) of DMSO.

Test plate	(μg mL^{-1}) (1.6 mL substance + DMSO + MICs 0.4 mL distilled water)	DMSO concentration (%)
A	800	8
B	400	4
C	200	2
D	100	1
E	50	0.5
F	25	0.25
G	12.5	0.125
I	6.25	0.0625

When Table 2 is examined, it is seen in the forefront that due to the increase in the substance inflows into the cell, rather than DMSO's antimicrobial activity, DMSO provides an additional contribution. In our studies, the fact that antimicrobial activities are not seen in plates A and B supports this information. If 1% DMSO value were effective, antimicrobial activities could have always been observed in A, B, C, and D plates.

4. Conclusions

We synthesized and characterized 7 new silver-NHC complexes. The in vitro antimicrobial activities of the synthesized complexes were studied against 2 gram-positive bacterial strains (*Staphylococcus aureus* and *Enterococcus faecalis*), 2 gram-negative bacterial strains (*Pseudomonas aeruginosa* and *Escherichia coli*), and 2 fungal strains (*C. tropicalis* and *C. albicans*), which showed their inhibitory effect. The silver-NHC complexes (**1a**–**g**) showed high activity against all bacteria and fungi. In particular, complexes **1a** and **1c** exhibited significant activity, and showed the potential for their use as antimicrobial agents.

Acknowledgments

We would like to thank the Scientific and Technological and Research Council of Turkey (TÜBİTAK) [TBAG (107T419)] and İnönü University Research Fund (BAP 2011/35) for their financial support.

References

1. Öfele, K. *J. Organomet. Chem.* **1968**, *12*, 42–43.
2. Wanzlick, H. W.; Schönherr H. W. *Angew. Chem. Int. Ed.* **1968**, *7*, 141–142.
3. Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
4. Karthikeyan, P.; Muskawar, P. N.; Aswar, S. A.; Bhagat, P. R.; Sythana, S. K. *Arabian J. Chem.* **2012**, *26*, 562–569.
5. Wiedemann, S. H.; Lewis, J. C.; Elman, J. A.; Bergman, R. G. *J. Am. Chem. Soc.* **2006**, *128*, 2452–2462.
6. Özdemir, İ.; Gök, Y.; Özeroğlu, Ö.; Kaloğlu, M.; Doucet, H. *Eur. J. Inorg. Chem.* **2010**, *12*, 1798–1805.
7. Özdemir, İ.; Gürbüz, N.; Gök, Y.; Çetinkaya, B.; Çetinkaya, E. *Trans. Metal Chem.* **2005**, *30*, 367–371.
8. Tyrrell, E.; Whiteman, L.; Williams, N. *J. Organomet. Chem.* **2011**, *696*, 3465–3472.

9. Danopoulos, A. A.; Tsoureas, N.; Macgregor, S. A.; Smith, C. *Organometallics* **2007**, *26*, 253–263.
10. Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972–975.
11. Arnold, P. L. *Heteroatom. Chem.* **2002**, *13*, 534–539.
12. Yiğit, B.; Gök, Y.; Özdemir, İ.; Günal, S. *J. Coord. Chem.* **2012**, *3(65)*, 371–379.
13. Cheng, C-H.; Chen, D-F.; Song, H-B.; Tang, L-F. *J. Organomet. Chem.* **2013**, *726*, 1–88.
14. Akkurt, M.; Akkoç, S.; Gök, Y.; Dağdemir, Y.; Tahir, M. N. *Acta Cryst.* **2012**, *E68*, 590–591.
15. Patil, S.; Deally, A.; Gleeson, B.; Hackenberg, F.; Müller-Bunz, H.; Paradisi, F.; Tacke, M. *M. Z. Anorg. Allg. Chem.* **2011**, *637*, 386–396.
16. Patil, S.; Deally, A.; Gleeson, B.; Hackenberg, F.; Müller-Bunz, H.; Paradisi, F.; Tacke, M. *Metallomics* **2011**, *3*, 74–88.
17. Hackenberg, F.; Lally, G.; Müller-Bunz, H.; Paradisi, F.; Quaglia, D.; Streciwilk, W.; Tacke, M. *Inorg. Chim. Acta* **2013**, *395*, 135–144.
18. Haque, R. A.; Ghdhayeb, M. Z.; Salman, A. W.; Budagumpi, S.; Ahamed, M. B. K.; Majid, A. M. S. *Inorg. Chem. Commun.* **2012**, *22*, 113–119.
19. Youngs, W. J.; Knapp, A. R.; Wagers, P. O.; Tessier, C. A. *Dalton Trans.* **2012**, *41*, 327–336.
20. Lee, C. K.; Lee, K. M.; Lin, I. J. B. *Organometallics* **2002**, *21*, 10–12.
21. Lin, I. J. B.; Vasam, C. S. *Coord. Chem. Rev.* **2007**, *251*, 642–670.
22. National Clinical and Laboratory Standards Institute. Methods for Dilution Antimicrobial Susceptibility Tests for Bacteria that Grow Aerobically: Approved Standard, 7th ed. CLSI Document M7-A7; National Clinical and Laboratory Standard Institute: Wayne, PA, USA (2003).
23. Clinical and Laboratory Standards Institute. Reference Method for Broth Dilution Antifungal Susceptibility Testing of Yeasts: Approved Standard, 2nd ed. NCCLS document M27-A2; National Clinical and Laboratory Standards Institute: Wayne, PA, USA (2002).
24. Gök, Y.; Gürbüz, N.; Özdemir, İ.; Çetinkaya, B.; Çetinkaya, E. *Appl. Organometal. Chem.* **2005**, *19*, 870–874.
25. Özdemir, İ.; Gürbüz, N.; Gök, Y.; Çetinkaya, E.; Çetinkaya, B. *Synlett* **2005**, *15*, 2394–2396.
26. Nielsen, D. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2003**, *352*, 143–150.
27. Pytkowicz, J.; Roland, S.; Mangeney, P. *J. Organomet. Chem.* **2001**, *631*, 157–163.
28. Lee, H. M.; Chiu, P. L.; Hu, C. H.; Lai, C. L.; Chou, Y. C. *J. Organomet. Chem.* **2005**, *690*, 403–414.
29. Günal, S.; Kaloğlu, N.; Özdemir, İ.; Demir, S.; Özdemir, İ. *Inorg. Chem. Commun.* **2012**, *21*, 142–146.