

**SILVER(I) AND GOLD(I) MONO-, BIS- AND
TETRA-N-HETEROCYCLIC CARBENE
COMPLEXES: SYNTHESIS,
CHARACTERIZATION, ANTIBACTERIAL AND
PHOTOPHYSICAL STUDIES**

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by

UMIE FATIHAH BINTI MOHAMAD HAZIZ

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TABLE OF CONTENTS

ACKNOWLEDGEMENT.....	ii
TABLE OF CONTENTS.....	iv
LIST OF TABLES.....	xiii
LIST OF FIGURES.....	xvi
LIST OF SCHEMES.....	xxii
LIST OF ABBREVIATIONS AND SYMBOLS.....	xxv
ABSTRAK.....	xxvii
ABSTRACT.....	xxix
CHAPTER 1 INTRODUCTION.....	1
1.1 Carbene.....	1
1.2 <i>N</i> -heterocyclic carbene.....	2
1.2.1 Stability of NHC.....	2
1.3 Benzimidazolium salts: Promising NHC ligand.....	3
1.4 Metal-NHC complexes.....	5
1.5 Silver(I)-NHC complexes.....	6
1.5.1 Convenient synthetic method: <i>In-situ</i> deprotonation.....	6
1.5.2 Classes on NHC and respective silver(I)-NHC complexes..	7
1.5.3 Focused application: Antibacterial study.....	8
1.5.4 Focused application: Silver(I)-NHC complexes as ligand transfer agent.....	9
1.6 Gold(I)-NHC complexes.....	9
1.6.1 Convenient synthetic method: Transmetalation and structural variation.....	9
1.6.1 Focused application: Photophysical properties.....	10
1.7 Problem statements.....	11

1.8	Objectives.....	12
1.9	Scope of works.....	12
CHAPTER 2 LITERATURE REVIEWS.....		16
2.1	Carbene and <i>N</i> -heterocyclic carbene.....	16
2.2	Metal-NHC complexes.....	17
2.2.1	General synthetic methods.....	17
2.3	Silver(I)-NHC complexes.....	21
2.3.1	Classes on NHC and respective silver(I)-NHC complexes..	21
2.3.2	Focused application: Antibacterial study.....	33
2.3.3	Focused application: Silver(I)-NHC complexes as ligand transfer agent.....	35
2.4	Gold(I)-NHC complexes.....	36
2.4.1	Convenient synthetic method: Transmetalation and structural variation.....	36
2.4.2	Focused application: Photophysical properties.....	41
CHAPTER 3 METHODOLOGY.....		42
3.1	Materials.....	42
3.2	Instruments.....	43
3.3	Syntheses of monodentate benzimidazolium salts (1-7).....	44
3.3.1	1-butyl-3-methylbenzimidazolium bromide (1).....	44
3.3.2	1-butyl-3-ethylbenzimidazolium bromide (2).....	45
3.3.3	1-butyl-3-propylbenzimidazolium bromide (3).....	46
3.3.4	3-butyl-1-pentylbenzimidazolium bromide (4).....	47
3.3.5	3-butyl-1-hexylbenzimidazolium bromide (5).....	48
3.3.6	3-butyl-1-heptylbenzimidazolium bromide (6).....	49
3.3.7	1-benzyl-3-butylbenzimidazolium bromide (7).....	50
3.4	Syntheses of symmetrical bidentate benzimidazolium salts (8-13).....	51

3.4.1	3,3'-(ethane-1,2-diyl)-1,1'-bisethylbenzimidazolium dibromide (8).....	51
3.4.2	3,3'-(ethane-1,2-diyl)-1,1'-bispropylbenzimidazolium dibromide (9).....	52
3.4.3	3,3'-(ethane-1,2-diyl)-1,1'-bisbutylbenzimidazolium dibromide (10).....	53
3.4.4	3,3'-(ethane-1,2-diyl)-1,1'-bisbenzylbenzimidazolium dibromide (11).....	54
3.4.5	3,3'-(propane-1,3-diyl)-1,1'-bisbenzylbenzimidazolium dibromide (12).....	55
3.4.6	3,3'-(butane-1,4-diyl)-1,1'-bisbenzylbenzimidazolium dibromide (13).....	56
3.5	Syntheses of non-symmetrical bidentate benzimidazolium salts (14-20).....	57
3.5.1	3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'-methylbenzimidazolium dibromide (14).....	57
3.5.2	3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'-ethylbenzimidazolium dibromide (15).....	58
3.5.3	3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'-propylbenzimidazolium dibromide (16).....	59
3.5.4	3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'-pentylbenzimidazolium dibromide (17).....	60
3.5.5	3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'-hexylbenzimidazolium dibromide (18).....	61
3.5.6	3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'-heptylbenzimidazolium dibromide (19).....	62
3.5.6	3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'-benzylbenzimidazolium dibromide (20).....	63
3.6	Syntheses of tetrabenzimidazolium salt precursors: 3-(2-bromoethyl)-1-substituted benzimidazolium bromide.....	64
3.6.1	3-(2-bromoethyl)-1-ethylbenzimidazolium bromide (i).....	64
3.6.2	3-(2-bromoethyl)-1-propylbenzimidazolium bromide (ii).....	65

3.7	Syntheses of tetradentate NHC ligand salts (21-28).....	66
3.7.1	Ethylsubstituted tetrakisbenzimidazolium tetrabromide with butyl bridge (21).....	66
3.7.2	<i>N</i> -propylsubstituted tetrakisbenzimidazolium tetrabromide with butyl bridge (22).....	67
3.7.3	<i>N</i> -butylsubstituted tetrakisbenzimidazolium tetrabromide with butyl bridge (23).....	68
3.7.4	<i>N</i> -benzylsubstituted tetrakisbenzimidazolium tetrabromide with butyl bridge (24).....	69
3.7.5	Ethylsubstituted tetrakisbenzimidazolium tetrabromide with metaxylyl bridge (25).....	70
3.7.6	<i>N</i> -propylsubstituted tetrakisbenzimidazolium tetrabromide with metaxylyl bridge (26).....	71
3.7.7	<i>N</i> -butylsubstituted tetrakisbenzimidazolium tetrabromide with metaxylyl bridge (27).....	72
3.7.8	<i>N</i> -benzylsubstituted tetrakisbenzimidazolium tetrabromide with metaxylyl bridge (28).....	73
3.8	Syntheses of mono-NHC mononuclear silver(I) complexes (Ag1-Ag7).....	74
3.8.1	[Bis(1-butyl-3-methylbenzimidazolium)silver(I)] hexafluorophosphate (Ag1).....	74
3.8.2	[Bis(1-butyl-3-ethylbenzimidazolium)silver(I)] hexafluorophosphate (Ag2).....	75
3.8.3	[Bis(1-butyl-3-propylbenzimidazolium)silver(I)] hexafluorophosphate (Ag3).....	76
3.8.4	[Bis(1-butyl-3-pentylbenzimidazolium)silver(I)] hexafluorophosphate (Ag4).....	77
3.8.5	[Bis(1-butyl-3-hexylbenzimidazolium)silver(I)] hexafluorophosphate (Ag5).....	78
3.8.6	[Bis(1-butyl-3-heptylbenzimidazolium)silver(I)] hexafluorophosphate (Ag6).....	79
3.8.7	[Bis(1-butyl-3-benzylbenzimidazolium)silver(I)]	

	hexafluorophosphate (Ag7).....	80
3.9	Syntheses of bis-NHC dinuclear silver(I) complexes (Ag8-Ag20).....	81
3.9.1	[Bis(3,3'-(ethane-1,2-diyl)-1,1'-bisethylbenzimidazolium disilver(I)) dihexafluorophosphate (Ag8).....	81
3.9.2	[Bis(3,3'-(ethane-1,2-diyl)-1,1'-bispropylbenzimidazolium disilver(I)) dihexafluorophosphate (Ag9).....	82
3.9.3	[Bis(3,3'-(ethane-1,2-diyl)-1,1'-bisbutylbenzimidazolium disilver(I)) dihexafluorophosphate (Ag10).....	83
3.9.4	[Bis(3,3'-(ethane-1,2-diyl)-1,1'-bisbenzylbenzimidazolium disilver(I)) dihexafluorophosphate (Ag11).....	84
3.9.5	[Bis(3,3'-(propane-1,3-diyl)-1,1'-bisbenzylbenzimidazolium disilver(I)) dihexafluorophosphate (Ag12).....	85
3.9.6	[Bis(3,3'-(butane-1,4-diyl)-1,1'-bisbenzylbenzimidazolium disilver(I)) dihexafluorophosphate (Ag13).....	86
3.9.7	[Bis(3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'-methylbenzimidazolium) disilver(I)] dihexafluorophosphate (Ag14).....	87
3.9.8	[Bis(3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'-ethylbenzimidazolium) disilver(I)] dihexafluorophosphate (Ag15).....	88
3.9.9	[Bis(3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'-propylbenzimidazolium) disilver(I)] dihexafluorophosphate (Ag16).....	89
3.9.10	[Bis(3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'-pentylbenzimidazolium) disilver(I)] dihexafluorophosphate (Ag17).....	90
3.9.11	[Bis(3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'-hexylbenzimidazolium) disilver(I)] dihexafluorophosphate (Ag18).....	91
3.9.12	[Bis(3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'-heptylbenzimidazolium) disilver(I)] dihexafluorophosphate (Ag19).....	92
3.9.13	[Bis(3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'-benzylbenzimidazolium) disilver(I)] dihexafluorophosphate	

	(Ag20).....	93
3.10	Syntheses of tetra-NHC dinuclear silver(I) complexes (Ag21-Ag28)	94
3.10.1	Ethyl substituted tetra NHC-silver(I) complex with butyl bridge (Ag21).....	94
3.10.2	V-propyl substituted tetra NHC-silver(I) complex with butyl bridge (Ag22).....	95
3.10.3	<i>N</i> -butyl substituted tetra NHC-silver(I) complex with butyl bridge (Ag23).....	96
3.10.4	<i>N</i> -benzyl substituted tetra NHC-silver(I) complex with butyl bridge (Ag24).....	97
3.10.5	Ethyl substituted tetra NHC-silver(I) complex with metaxylyl bridge (Ag25).....	98
3.10.6	<i>N</i> -propyl substituted tetra NHC-silver(I) complex with metaxylyl bridge (Ag26).....	99
3.10.7	<i>N</i> -butyl substituted tetra NHC-silver(I) complex with metaxylyl bridge (Ag27).....	100
3.10.8	<i>N</i> -benzyl substituted tetra NHC-silver(I) complex with metaxylyl bridge (Ag28).....	101
3.11	Syntheses of mono-NHC mononuclear gold(I) complexes (Au1-Au7).....	102
3.11.1	[Bis(1-butyl-3-methylbenzimidazolium)gold(I)] hexafluorophosphate (Au1).....	102
3.11.2	[Bis(1-butyl-3-ethylbenzimidazolium)gold(I)] hexafluorophosphate (Au2).....	103
3.11.3	[Bis(1-butyl-3-propylbenzimidazolium)gold(I)] hexafluorophosphate (Au3).....	104
3.11.4	[Bis(1-butyl-3-pentylbenzimidazolium)gold(I)] hexafluorophosphate (Au4).....	105
3.11.5	[Bis(1-butyl-3-hexylbenzimidazolium)gold(I)] hexafluorophosphate (Au5).....	106
3.11.6	[Bis(1-butyl-3-heptylbenzimidazolium)gold(I)] hexafluorophosphate (Au6).....	107

3.11.7	[Bis(1-butyl-3-benzylbenzimidazolium)gold(I)] hexafluorophosphate (Au7).....	108
3.12	Syntheses of bis-NHC dinuclear silver(I) complexes (Au14-Au20)....	109
3.12.1	[Bis(3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'- methylbenzimidazolium) digold(I)] dihexafluorophosphate (Au14).....	109
3.12.2	[Bis(3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'- ethylbenzimidazolium) digold(I)] dihexafluorophosphate (Au15).....	110
3.12.3	[Bis(3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'- propylbenzimidazolium) digold(I)] dihexafluorophosphate (Au16).....	111
3.12.4	[Bis(3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'- pentylbenzimidazolium) digold(I)] dihexafluorophosphate (Au17).....	112
3.12.5	[Bis(3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'- hexylbenzimidazolium) digold(I)] dihexafluorophosphate (Au18).....	113
3.12.6	[Bis(3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'- heptylbenzimidazolium) digold(I)] dihexafluorophosphate (Au19).....	114
3.12.7	[Bis(3,3'-(ethane-1,2-diyl)-1-butylbenzimidazolium-1'- benzylbenzimidazolium) disilver(I)] dihexafluorophosphate (Au20).....	115
3.13	Crystal structures analyses.....	116
3.14	Antibacterial study.....	119
3.14.1	Materials.....	119
3.14.2	Disc diffusion method.....	119
3.14.3	Broth dilution and colony formation methods.....	120
	CHAPTER 4 RESULTS AND DISCUSSIONS	121
4.1	Monodentate benzimidazolium salts, mononuclear silver(I)- and gold(I)-NHC complexes.....	121

4.1.1	Syntheses.....	121
4.1.2	IR study.....	124
4.1.3	NMR study.....	126
4.1.4	Structural analyses.....	133
4.2	Symmetrical bidentate benzimidazolium salt and dinuclear silver(I)-NHC complexes.....	136
3.2.1	Syntheses.....	136
3.2.2	NMR study.....	139
3.2.3	Structural analyses.....	144
4.3	Non-symmetrical bidentate benzimidazolium salt, dinuclear silver(I)- and gold(I)-NHC complexes.....	148
3.3.1	Syntheses.....	148
3.3.2	NMR study.....	150
3.3.3	Structural analyses.....	160
4.4	Tetradentate benzimidazolium salt and dinuclear silver(I)-NHC complexes.....	163
4.4.1	Syntheses.....	163
4.4.2	NMR study.....	167
4.4.3	Structural analyses.....	175
4.5	Antibacterial study.....	178
4.6	Photophysical properties.....	189
CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORKS.....		195
5.1	Conclusions.....	195
5.2	Recommendation for future works.....	196

REFERENCES..... 198

APPENDICES

LIST OF PUBLICATIONS AND ATTENDED CONFERENCES

LIST OF TABLES

		Page
Table 2.1	Antimicrobial activities of 2.30-2.31 evaluated by minimum inhibitory concentration (MIC; $\mu\text{g/ml}$) [122].....	35
Table 3.1	Crystal details of i, 8, Ag1 and Au3	117
Table 3.2	Crystal details of Ag11, Au18, Ag20, Ag23 and Ag27	118
Table 4.1	Selected Infrared (IR) absorption of functional groups [cm^{-1}] of 3, Ag3 and Au3	126
Table 4.2	^1H NMR chemical shifts of [δ/ppm] of 3, Ag3 and Au3	131
Table 4.3	^{13}C NMR chemical shifts of [δ/ppm] of 3, Ag3 and Au3	132
Table 4.4	^1H NMR chemical shifts of [δ/ppm] of bisbenzimidazolium salt 10 and dinuclear silver(I)-NHC complex, Ag10	143
Table 4.5	^{13}C NMR chemical shifts of [δ/ppm] of bisbenzimidazolium salt 10 and dinuclear silver(I)-NHC complex, Ag10	143
Table 4.6	^1H NMR chemical shifts of [δ/ppm] of iii, 11, 14, Ag11 and Au11	158
Table 4.7	^{13}C NMR chemical shifts of [δ/ppm] of 12, Ag12 and Au12 ..	159
Table 4.8	^1H NMR chemical shifts of [δ/ppm] of i and ii	172
Table 4.9	^{13}C NMR chemical shifts of [δ/ppm] of i and ii	172
Table 4.10	^1H NMR chemical shifts of [δ/ppm] of tetrabenzimidazolium salt, 28	173
Table 4.11	^{13}C NMR chemical shifts of [δ/ppm] of tetrabenzimidazolium salt 21 and silver(I)-NHC complex, Ag21	173
Table 4.12	Selected bond length [\AA] and angles [$^\circ$] for Ag23 and Ag27 ..	177
Table 4.13	Zone of inhibition of complexes Ag1-Ag28, 4.1-4.3 [127], 4.4 and 4.5 [227] against <i>E. coli</i> by disc diffusion method.....	180
Table 4.14	Zone of inhibition of complexes Ag1-Ag28 and 4.1-4.3 [127] against <i>S. aureus</i> by disc diffusion	

	method.....	181
Table 4.15	MIC and MBC of complexes Ag1-Ag28 against <i>E. coli</i> and <i>S. aureus</i>	182
Table A1.1	Selected infrared (IR) absorption of functional groups [cm ⁻¹] of benzimidazolium salts 1, 2, and 4-7	222
Table A1.2	Selected infrared (IR) absorption of functional groups [cm ⁻¹] of salts silver(I)-NHC complexes Ag1, Ag2, and Ag4-Ag7	222
Table A1.3	Selected infrared (IR) absorption of functional groups [cm ⁻¹] of salts gold(I)-NHC complexes Au1, Au2, and Au4-Au7	223
Table A1.4	Selected infrared (IR) absorption of functional groups [cm ⁻¹] of salts benzimidazolium salts 8-14	223
Table A1.5	Selected infrared (IR) absorption of functional groups [cm ⁻¹] of salts silver(I)-NHC complexes Ag8-Ag14	224
Table A1.6	Selected infrared (IR) absorption of functional groups [cm ⁻¹] of salts gold(I)-NHC complexes Au8-Au14	224
Table A1.7	Selected infrared (IR) absorption of functional groups [cm ⁻¹] of salts benzimidazolium salts 15-20	225
Table A1.8	Selected infrared (IR) absorption of functional groups [cm ⁻¹] of salts silver(I)-NHC complexes Ag15-Ag20	225
Table A1.9	Selected infrared (IR) absorption of functional groups [cm ⁻¹] of salts i and ii	226
Table A1.10	Selected infrared (IR) absorption of functional groups [cm ⁻¹] of salts benzimidazolium salts 21-28	226
Table A1.11	Selected infrared (IR) absorption of functional groups [cm ⁻¹] of salts silver(I)-NHC complexes Ag21-Ag28	227
Table A2.1	¹ H NMR chemical shifts of [δ/ppm] of salts benzimidazolium salts 1, 2 and 4-7	228
Table A2.2	¹³ C NMR chemical shifts of [δ/ppm] of salts benzimidazolium salts 1, 2 and 4-7	229
Table A2.3	¹ H NMR chemical shifts of [δ/ppm] of silver(I)-NHC complexes, Ag1-Ag2 and Ag4-Ag7	230
Table A2.4	¹³ C NMR chemical shifts of [δ/ppm] of silver(I)-NHC	

	complexes Ag1, Ag2 and Ag4-Ag7	231
Table A2.5	¹ H NMR chemical shifts of [δ /ppm] of gold(I)-NHC complexes, Au1, Au2 and Au4-Au7	232
Table A2.6	¹³ C NMR chemical shifts of [δ /ppm] of gold((I)-NHC complexes Au1, Au2 and Au4-Au7	233
Table A2.7	¹ H NMR chemical shifts of [δ /ppm] of salts bisbenzimidazolium salts 8, 9 and 11-13	234
Table A2.8	¹³ C NMR chemical shifts of [δ /ppm] of salts bisbenzimidazolium salts 8, 9 and 11-13	235
Table A2.9	¹ H NMR chemical shifts of [δ /ppm] of silver(I)-NHC complexes, Ag8, Ag9 and Ag11-Ag13	236
Table A2.10	¹³ C NMR chemical shifts of [δ /ppm] of silver((I)-NHC complexes Ag8, Ag9 and Ag11-Ag13	237
Table A2.11	¹ H NMR chemical shifts of [δ /ppm] of salts bisbenzimidazolium salts 14-16, 18 and 19	238
Table A2.12	¹³ C NMR chemical shifts of [δ /ppm] of salts bisbenzimidazolium salts 14-17, 19 and 20	239
Table A2.13	¹ H NMR chemical shifts of [δ /ppm] of silver(I)-NHC complexes, Ag14-Ag16 and Ag18-Ag20	240
Table A2.14	¹³ C NMR chemical shifts of [δ /ppm] of silver((I)-NHC complexes Ag14-Ag17, Ag19 and Ag20	241
Table A2.15	¹ H NMR chemical shifts of [δ /ppm] of gold(I)-NHC complexes, Au14-Au16 and Au18-Au20	242
Table A2.16	¹³ C NMR chemical shifts of [δ /ppm] of gold((I)-NHC complexes Au14-Au17, Au19 and Au20	243
Table A2.17	¹ H NMR chemical shifts of [δ /ppm] of salts tetrabenzimidazolium salts 21-27	244
Table A2.18	¹³ C NMR chemical shifts of [δ /ppm] of salts tetrabenzimidazolium salts 22-28	246
Table A2.19	¹³ C NMR chemical shifts of [δ /ppm] of silver((I)-NHC complexes Ag22-Ag28	247

LIST OF FIGURES

		Page
Figure 1.1	The general representative of carbene.....	1
Figure 1.2	Electronic configuration for singlet and triplet free carbene.....	2
Figure 1.3	Pull and push interaction in NHCs.....	2
Figure 1.4	The numbering in benzimidazole.....	3
Figure 1.5	Bonding in NHC complexes.....	6
Figure 1.6	The targeted benzimidazolium salts 1-28	15
Figure 2.1	Bonding in (a) Fischer carbene complexes [6] and; (b) Schröck carbene complexes [7].....	16
Figure 2.2	The mononuclear silver(I)-NHC complexes 2.9-2.11 , with different structures [55,57,60].....	22
Figure 2.3	An example of symmetrical homo-di-NHC precursors, 2.14 [65] and 2.15 [67], respectively.....	24
Figure 2.4	(a) Palladium(II)-NHC complex bearing di-hetero-carbene, 2.16 and; (b) the crystal structure of 2.16 . Hydrogen atoms were omitted for clarity [70].....	25
Figure 2.5	Structure of complex 2.17 (a) side view and (b) parallel view showing only two imidazolium NHC site were activated and bonded to one silver while the other one remained protonated. Hydrogen atoms were omitted for clarity [77].....	26
Figure 2.6	(a) Trinuclear silver(I)-NHC complex 2.18 bearing mixed triazol-2-ylidenes ligand; (b) the trinuclear silver(I)-NHC complex 2.19 bearing tribenzimidazol-2-ylidenes ligand and; (c) the selected part of ¹³ C NMR spectrum of compound 2.19 (d3-acetonitrile) highlighting the appearance of the resonance signal for two types of carbene-Ag bonds, indicated the successful synthesis of trinuclear silver(I)-NHC complex [78].....	27
Figure 2.7	Structures of (a) trinuclear silver(I)-NHC complex 2.23 ; (b) tetranuclear silver(I)-NHC complex 2.24 ; (c) hexanuclear silver(I)-NHC complex 2.25 silver(I)-NHC complexes from front perspective with sandwich-like structure and; (d) the	

	above perspective of complex 2.25 . All hydrogen atoms and anions were omitted for clarity [87,88].....	29
Figure 2.8	(a) The structure of dinuclear silver(I) tetra-NHC complex 2.28 containing tetrabenzimidazol-2-ylidene ligand by Fatima and co-workers and; (b) the crystal structure of 2.28 . All hydrogen atoms and anions were omitted for clarity [97].....	32
Figure 2.9	One of the first silver(I)-NHC complex, 2.29 for antimicrobial study by Youngs and co-workers [105].....	33
Figure 2.10	Silver(I)-NHC complexes 2.30-2.31 by Sakamoto co-workers [122].....	35
Figure 2.11	Structures of basket-shaped dinuclear complexes 2.41 and 2.42 with 50% probability thermal ellipsoids. Hydrogen atoms, solvent molecules and PF ₆ ⁻ anion molecules (one anion for 2.41 and both anions for 2.42) were omitted for clarity [152].....	40
Figure 2.12	The structures of luminescent gold(I)-NHC complex 2.43 and non-luminescent gold(I)-NHC complex 2.44 by Barnard and co-workers [181].....	41
Figure 4.1	Representative FT-IR spectra of (a) 3 ; (b) Ag3 and; (c) Au3 ..	126
Figure 4.2	Representative ¹ H NMR spectra of (a) 3 ; (b) Ag3 and (c) Au3	127
Figure 4.3	Representative ¹³ C NMR spectra of (a) 3 ; (b) Ag3 and (c) Au3	129
Figure 4.4	(a) Structure of Ag1 with ellipsoids shown at 50% probability. The hexafluorophosphate anion was omitted for clarity. Symmetry element use: $i = 1-x, 1-y, 1-z$. (b) The interdigitating arrangement of the molecule with the face-to-face π - π interactions.....	133
Figure 4.5	(a) Molecular structure of Au3 with ellipsoids shown at 50% probability. Selected bond lengths [Å] and angles [°]: Au1-C1 = 2.022(5); C1-N1 = 1.355(6); C1-N2 = 1.334(6); C1-Au1-C1 ⁱ = 178.8(2); N1-C1-Au1 = 125.5(4); N2-C1-Au1 = 128.0(3). Symmetry element used: $i = \frac{1}{2}-x, y, \frac{1}{2}-z$. The hexafluorophosphate anion was omitted for clarity. (b) Packing diagram of Au3 along the b-axis showing the π - π interactions. Closest separation between two adjacent	

	gold(I)ions	is	7.977(3)	135
	Å.....			
Figure 4.6	¹ H NMR spectra of (a) 10 showing the carbene proton peak at δ 10.02 ppm and; (b) Ag10 with no peak around ~ δ 10 ppm, indicating the absence of carbene proton.....			139
Figure 4.7	¹³ C NMR spectra of (a) 10 showing carbene carbon peak at 143.46 ppm; (b) Ag10 and; (b) doublets in two peaks in spectrum of Ag10 attributed to ¹³ C _(carbene) - ¹⁰⁷ Ag (d, J = 180.8 Hz) and ¹³ C _(carbene) - ¹⁰⁹ Ag (d, J = 208.0 Hz).....			141
Figure 4.8	Structure of 8 with ellipsoid shown at 50% probability. Symmetry element used: $i = 3/2-x, 1/2-y, 1-z$. Selected bond length [Å] and angles [°] C1-N1: 1.307 (4); C1-N2: 1.315(4); N1-C1-N2: 125.3(3).....			144
Figure 4.9	(a) Structure of cationic in complex Ag11 with the ellipsoids shown at 50% probability. Hydrogen atoms and hexafluorophosphate anions in the lattice omitted for clarity. Symmetry element used: $i = 1-x, 1-y, 1-z$. (b) The view along the c-axis of complex Ag11 showing the face-to-face π-π stacking interactions.....			145
Figure 4.10	Perspective view of reported Ag19 and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms and hexafluorophosphate anions have been omitted for clarity. Selected bond length (Å) and angle (°): Ag(1)-C(1) 2.091(9), Ag(1)-C(1A) 2.091(9); C(1)-Ag(1)-C(1A) 174.1(4), N(1)-C(1)-N(2) 107.3(7), Ag...Ag 6.356(1) [196].....			147
Figure 4.11	¹ H NMR spectra of (a) iii showing the present of CH ₂ Br peak at δ 4.085 ppm and (b) 17 , with no CH ₂ Br peak.....			151
Figure 4.12	¹ H NMR spectrum of salt 20 , with most of the peaks belong to same type of protons split into two different peaks; especially the most downfield carbenic proton NCHN peaks...			152
Figure 4.13	Representative ¹ H NMR spectra of (a) silver(I)-NHC complex, Ag17 and (b) gold(I)-NHC complex Au17 with no carbenic NCHN peaks; suggested successful complexation with respective metal.....			153
Figure 4.14	Representative spectra show (a) peak at ca ~ δ 143 ppm			

	belong to carbene carbon in the spectrum of 18 and; (b) doublet peak in the range of δ 187-190 ppm in the spectrum of Ag18 belong to $C_{(\text{carbene})}$ -Ag bond.....	155
Figure 4.15	The most downfield region of ^{13}C NMR spectra of (a) Ag16 shows two peaks belong to $^{13}\text{C}_{(\text{carbene})}\text{Ag}$ (d, $J = 180.8$ Hz) and (b) Ag20 shows four peaks corresponding to $^{13}\text{C}_{(\text{carbene})}$ -Ag (d, $J = 193.8$ Hz).....	156
Figure 4.16	Representative spectra show sharp singlet peak at δ 190.3 ppm in the spectrum of Au18 , suggesting the present of $C_{(\text{carbene})}$ -Au bond.....	157
Figure 4.17	Structure of dinuclear silver(I) complex Ag20 bearing non-symmetrical di-carbene ligand with ellipsoids shown at 50% probability. Symmetry elements used: $i = -x, 1-y, -z$. Hydrogen atoms and hexafluorophosphate ions in the lattice were omitted for clarity. Selected bond lengths [\AA] and angle [$^\circ$]: Ag1-C1 2.097(9), Ag1-C14 2.096(9) and C1-Ag1-C14 177.52(9).....	161
Figure 4.18	Structure of dinuclear gold(I)-NHC complex Au18 . Symmetry elements used: $i = 1-x, 1-y, 1-z$. Hydrogen atoms and hexafluorophosphate ions in the lattice were omitted for clarity. Selected bond lengths [\AA] and angle [$^\circ$]: Au1-C1 2.033(8), Au1-C14 2.030(8) and C1-Ag1-C14 177.31(5).....	162
Figure 4.19	The structures of iii and iv reported in the literature [78, 98]...	164
Figure 4.20	The structures of 1,4-butylbenzimidazole and 1,3-bis(methylbenzimidazole)benzene reported in the literature.....	164
Figure 4.21	Representative (a) ^1H NMR spectra of ii showing CH_2Br proton peak at δ 4.069 ppm and (b) ^{13}C NMR spectra of ii showing CH_2Br carbon peak at δ 31.53 ppm.....	167
Figure 4.22	Representative ^1H NMR spectrum of 28	169
Figure 4.23	Representative ^{13}C NMR spectra of (a) 21 showing two peaks at ca $\sim \delta$ 143 ppm belongs to carbene carbons; (b) Ag21 and (c) eight peak in the range of δ 186-190 ppm in the spectrum of Ag21 belong to $C_{(\text{carbene})}$ -Ag bond.....	170
Figure 4.24	Structure of i with ellipsoid shown at 50% probability. Symmetry element used: $i = 2-x, 1-y, 1-z$. Selected bond length [\AA] and angles [$^\circ$], C1-N1: 1.306 (5); C1-N2: 1.305(5);	

	N1-C1-N2: 110.8(4).....	174
Figure 4.25	Structure of (a) Ag23 with ellipsoid shown at 50% probability; and (b) Ag27 with ellipsoid shown at 50% probability. In both structures, hydrogen atoms and hexafluorophosphate anions in the lattice were omitted for clarity.....	176
Figure 4.26	Antibacterial assay plates of Ag15 (a) against <i>E. coli</i> and; (b) against <i>S. aureus</i> : showing the biggest inhibition zones amongst all silver(I)-NHC complexes.....	183
Figure 4.27	Representative antibacterial assay tubes with the sample concentrations of 25.0 μM (Tube 4), 12.5 μM (Tube 5), 6.25 μM (Tube 6), 3.13 μM (Tube 7), 1.56 μM (Tube 8), 0.78 μM (Tube 9) and 0.39 (Tube 10) of Ag16 against <i>E. coli</i> with MIC level of 1.56 μM (Tube 8).....	183
Figure 4.28	Antibacterial assay plates of Ag16 (MBC level = 12.50 μM) against <i>E. coli</i> with the sample concentration of 25.0 μM (Plate 4), no. of colonies: 0 CFU; 12.50 μM (Plate 5), no. of colonies: 0 CFU; 6.25 μM (Plate 6), no. of colonies: 213; 3.13 μM (Plate 7), no. of colonies: TNTC; 1.56 μM (Plate 8), no. of colonies: TNTC (TNTC = too numerous to count).....	183
Figure 4.29	The structures of silver(I)-NHC complexes, 4.1-4.3 by Sharhan and co-workers [127] and 4.4 and 4.5 by Haque and co-workers [227].....	
Figure 4.30	Antibacterial assay plates of Ag4 (a) against <i>E. coli</i> and; (b) against <i>S. aureus</i> : showing the biggest inhibition zones amongst mononuclear silver(I)-NHC complexes but smaller than dinuclear silver(I)-NHC complexes.....	185
Figure 4.31	Inhibition zone of different volumes of complexes Ag11-Ag13 and Amoxicillin against (a) <i>E. coli</i> and (b) <i>S. aureus</i> with ampicillin as standard determined in disc diffusion method.....	187
Figure 4.32	Antibacterial assay plates of (a) Ag10 ; (b) Ag23 and; (c) Ag27 against <i>E. coli</i> : showing no vast difference in inhibition zones.....	188
Figure 4.33	Powder X-ray diffraction patterns for (a) Au3 and (b) Au18 ...	189

Figure 4.34	Luminescence spectrum for Au3 in the solid-state upon 320, 340 and 360 nm excitation at room temperature.....	190
Figure 4.35	Temperature-dependent luminescence spectrum for Au18 in the solid-state upon 340 nm excitation.....	191

LIST OF SCHEMES

		Page
Scheme 1.1	The general route to synthesis benzimidazol-2-ylidene, v..	5
Scheme 1.2	The first silver(I)-NHC complex, 1.1 synthesized using silver(I) oxide by Wang and Lin [31].....	6
Scheme 1.3	General schematic diagram in the preparation of palladium(II)-NHC complexes from silver(I)-NHC complexes by Guinness and Cavell [123].....	9
Scheme 2.1	The synthesis of 1,3-di-(1-adamantyl)imidazol-2-ylidene, 2.1 from 1,3-di(adamantly)imidazolium chloride [11].....	17
Scheme 2.2	Palladium(II) acetate as a base and metal source in the formation of palladium(II)-NHC complex, 2.2 [30].....	18
Scheme 2.3	The example of <i>in-situ</i> deprotonation using external base, NaOAc to produce platinum(II)-NHC complex, 2.3 and palladium(II)-NHC complex, 2.4 [35].....	19
Scheme 2.4	The reaction between a free carbene, 2.5 with silver(I) triflate to facilitate the formation of first silver(I)-NHC complex, 2.6 by Arduengo and co-workers [14].....	20
Scheme 2.5	The first transmetallation reaction of NHC by Liu [37].....	20
Scheme 2.6	The silver(I)-NHC complex, 2.12 bearing zwitterion ligand [62].....	23
Scheme 2.7	The silver(I)-NHC complex, 2.13 bearing zwitterion ligand [63].....	23
Scheme 2.8	Preparation of mono and dinuclear silver(I)-NHC complexes 2.21 and 2.22 from a same macrocyclic tetra-NHC ligand salt, 2.20 [86].....	28
Scheme 2.9	The synthesis of silver(I) tetra-NHC complexes 2.26 and 2.27 containing tetraimidazol-2-ylidene ligand and their crystal structures (hydrogen atoms and anions were omitted for clarity) by Weiss and co-workers [94].....	31
Scheme 2.10	The synthesis of gold(I)- (2.32) and palladium(II)-NHC (2.33) complexes from the silver(I)-NHC complex 1.1 by	

	Wang and Lin [31].....	36
Scheme 2.11	The synthesis of 2.34 by Maftai and co-workers [133].....	37
Scheme 2.12	The formation of neutral gold(I)-NHC complex 2.35 and the respective crystal structure by Zhang and co-workers [145].....	38
Scheme 2.13	The formation of ionic gold(I)-NHC complex 2.37 and the respective crystal structure from the tranmetalation reaction of silver(I)-NHC complex 2.36 by Hussaini and co-workers [146].....	38
Scheme 2.14	The formation of coinage metal(I)-NHC complexes 2.39-2.40 with formula of [NHC-M(I)-NHC]·2PF ₆ (where M = Ag, Au, Cu) by Gierz and co-workers [151].....	39
Scheme 4.1	The synthesis of benzimidazolium salts 1-7	123
Scheme 4.2	The synthesis of mononuclear silver(I)-NHC complexes, Ag1-Ag7	124
Scheme 4.3	The synthesis of mononuclear gold(I)-NHC complexes Au1-Au7	125
Scheme 4.4	The synthesis of symmetrical bisbenzimidazolium salts 8-10	137
Scheme 4.5	The synthesis of symmetrical <i>n</i> -benzylsubstitute bisbenzimidazolium salts 11-13	137
Scheme 4.6	The synthesis of dinuclear silver(I)-NHC complexes Ag8-Ag13	138
Scheme 4.7	The synthesis of non-symmetrical bis-benzimidazolium salts 14-20	148
Scheme 4.8	The synthesis of dinuclear silver(I)-NHC complexes Ag14-Ag20	149
Scheme 4.9	The synthesis of dinuclear gold(I)-NHC complexes Au14-Au20	150
Scheme 4.10	The syntheses of ligand precursors and bisbenzimidazolium salts, 8 and 9 as minor product, respectively.....	164

Scheme 4.11	The synthesis of symmetrical tetrabenzimidazolium salts 21-24	165
Scheme 4.12	The synthesis of symmetrical tetrabenzimidazolium salts 25-28	165
Scheme 4.13	The synthesis of dinuclear tetra-NHC silver(I) complexes, Ag21-Ag24	166
Scheme 4.14	The synthesis of dinuclear tetra-NHC silver(I) complexes, Ag25-Ag28	167

LIST OF ABBREVIATION AND SYMBOLS

°	degrees
°C	degrees celcius
δ	chemical shift in ppm
σ	sigma
π	Pi
μg	microgram
μL	microliter
μM	micromolar
λ_{em}^{max}	maximum emission
¹ H NMR	proton nuclear magnetic resonance
¹³ C NMR	carbon-13 nuclear magnetic resonance
Å	Angstrom, 1×10^{-10} m
aliph	aliphatic
Anal.	analysis
arom	aromatic
ATCC	American type culture collection
Calcd.	calculated
cm	centimetre
d	doublet
DCM	dichloromethane
D _c	density
DMF	dimethylformamide
DMSO	dimethylsulfoxide
<i>d</i> ₃ -acetonitrile	deuterated acetonitrile
<i>d</i> ₆ -DMSO	deuterated dimethylsulfoxide

g	gram
h	hours
Hz	Hertz
IR	Infrared
<i>J</i>	nuclear spin-spin coupling constant through bonds
K	Kelvin
m	multiplet
<i>M</i>	molecular mass
MeCN	acetonitrile
MHz	megahertz
mL	millilitre
mmol	millimoles
mm	millimeter
mol	moles
NHC	<i>N</i> -heterocyclic carbene
nm	nanometer
OAc	acetate
s	singlet
SMe ₂	dimethylsulfide
t	triplet
T	temperature
THF	tetrahydrofuran
TMS	tetramethylsilane
TNTC	too numerous to count
<i>V</i>	volume
UV-Vis	Ultraviolet-Visible

**KOMPLEKS ARGENTUM(I) DAN AURUM(I) MONO-, BIS- DAN TETRA-
N-HETEROSIKLIK KARBENA: SINTESIS, PENCIRIAN, KAJIAN
ANTIBAKTERIA DAN FOTOFIZIKAL**

ABSTRAK

Penyelidikan ini menghuraikan sintesis garam benzimidazol yang simetri dan tidak simetri sebagai pelopor bagi kompleks argentum(I)-NHC (di mana NHC= N-heterisiklik karbena). Bagi siri yang pertama, tujuh garam *n*-butil-*n*'-alkilbenzimidazol bromida (di mana alkil = metil, etil, *n*-propil, *n*-pentil, *n*-heksil, *n*-heptil dan *n*-benzil), **1-7** telah berjaya disintesis. Siri yang kedua memaparkan garam **8-10** disintesis daripada *n*-alkilbenzimidazol (di mana *n*-alkil = etil, *n*-propil dan *n*-butil) dengan 1,2-dibromoetana, manakala **11-13** disintesis daripada *n*-benzilbenzimidazol dengan 1,*n*-dibromoalkana (di mana, *n* = 2,3,4; alkana = etana, propana dan butana). Sementara itu, melalui tindak balas antara garam 3-(2-bromoetil)-1-butylbenzimidazol bromida, **iii** dengan *n*-alkilbenzimidazol (di mana *n*-alkyl = metil, etil, *n*-propil, *n*-pentil, *n*-heksil, *n*-heptil dan *n*-benzil), tujuh garam bidentat benzimidazolium yang tidak simetri, **14-20** bagi siri yang ketiga boleh diperolehi. Bagi siri terakhir, garam benzimidazole tetridentat **21-28** telah berjaya disintesis melalui tindak balas antara garam 3-(2-bromoetil)-1-alkilbenzimidazol bromida (di mana alkil = etil, *n*-propil, *n*-butil dan *n*-benzil), **i-iv** dengan sama ada 1,4-butylbisbenzimidazol atau 1,3-bis(metilbenzimidazol)benzena. Garam **1-28** ditindakbalaskan dengan argentum(I) oksida melalui tindak balas deprotonasi *in-situ* untuk memudahkan pembentukan kompleks argentum(I)-NHC, **Ag1-Ag28**. Seterusnya, kompleks **Ag1-Ag7** dan **Ag14-Ag20** dipilih untuk menjadi ejen pemindahan ligan, bertindakbalas dengan kloro(dimetilsulfida)aurum(I) untuk

menghasilkan masing-masing kompleks aurum(I)-NHC **Au1-Au7** and **Au14-Au20**. Kejayaan pengkompleksan dicadangkan melalui kehilangan puncak $H2'$ dalam 1H NMR dan kewujudan puncak $C_{\text{karbona-M}}$ dalam ^{13}C NMR bagi kompleks. Selain kajian NMR, pembentukan sebatian yang disintesis disokong dengan takat lebur, analisis unsur dan kajian IR. Teknik pembelauan sinaran-X hablur tunggal mendedahkan bahawa kompleks **Ag1**, **Ag11**, **Ag20**, **Au3** dan **Au18** mempunyai formula kimia seperti yang dijangka, $[M_n(\text{NHC})_2] \cdot n\text{PF}_6$ (di mana $M = \text{Ag}$ atau Au , $n = 1$ atau 2). Sementara itu, kompleks **Ag23** dan **Ag27** membentuk kompleks dinukleus argentum(I)-NHC dengan formula $[\text{Ag}_2(\mu_2\text{-NHC})] \cdot 2\text{PF}_6$. Aktiviti antibakteria bagi semua garam benzimidazol **1-28** dan kompleks argentum(I)-NHC, **Ag1-Ag28** dikajikan. Semua kompleks menunjukkan aktiviti rendah sehingga tinggi terhadap *E. coli* (ATCC 25922) dan *S. aureus* (ATCC 12600) berbanding antibiotik standard, Ampicillin. Sifat fotofizikal bagi hablur kompleks aurum(I)-NHC, **Au3** and **Au18** ditentukan dengan menggunakan teknik fotopendarcahaya dalam keadaan pepejal. Di dalam ketiadaan interaksi aurofilik yang ketara dalam kompleks **Au3**, jalur pemancaran dikaitkan dengan pemindahan cas logam kepada ligan (MLCT). Manakala, kompleks **Au18** menunjukkan tingkahlaku fotopendarcahaya bergantung pada suhu yang menarik, akibat daripada kehadiran interaksi aurofilik dalam kompleks tersebut.

**SILVER(I) AND GOLD(I) MONO-, BIS- AND TETRA-*N*-HETEROCYCLIC
CARBENE COMPLEXES: SYNTHESIS, CHARACTERIZATION,
ANTIBACTERIAL AND PHOTOPHYSICAL STUDIES**

ABSTRACT

This work describes the synthesis of symmetrical and non-symmetrical benzimidazolium salts as a precursor for the silver(I)-NHC complexes (where NHC = *N*-heterocyclic carbene). For the first series, seven *n*-butyl-*n*'-alkylbenzimidazolium bromide salts (where alkyl = methyl, ethyl, *n*-propyl, *n*-pentyl, *n*-hexyl, *n*-heptyl and *n*-benzyl), **1-7** were successfully synthesized. The second series, salts **8-10** were synthesized from *n*-alkylbenzimidazole (where *n*-alkyl = ethyl, *n*-propyl and *n*-butyl) with 1,2-dibromoethane, while salts **11-13** were synthesized from *n*-benzylbenzimidazole with 1,*n*-dibromoalkane (where alkane = ethane, propane and butane). Meanwhile, through the reaction of 3-(2-bromoethyl)-1-butylbenzimidazole bromide, **iii** with *n*-alkylbenzimidazole (where *n*-alkyl = methyl, ethyl, *n*-propyl, *n*-pentyl, *n*-hexyl, *n*-heptyl and *n*-benzyl), seven unprecedented non-symmetry dibenzimidazolium bromide salts, **14-20** were successfully obtained in the third series. The last series, tetradentate benzimidazolium salts **21-28** were successfully synthesized through the reaction of 3-(2-bromoethyl)-1-alkylbenzimidazole bromide salts (where alkyl = ethyl, *n*-propyl, *n*-butyl and *n*-benzyl), **i-iv** with either 1,4-butylbisbenzimidazole or 1,3-bis(methylbenzimidazole)benzene. Salts **1-28** were reacted with silver(I) oxide in appropriate molar ratio *via in-situ* deprotonation reaction to facilitate the formation of silver(I)-NHC complexes **Ag1-Ag28**, respectively. Furthermore, **Ag1-Ag7** and **Ag14-Ag20** were selected as ligand transfer agents, reacted with

chloro(dimethylsulfide)gold(I) to yield gold(I)-NHC complexes, **Au1-Au7** and **Au14-Au20**, respectively. The successful complexation was suggested by the disappearance of $H2'$ peaks in 1H NMR and the presence of $C_{\text{carbene}}-M$ peaks in the ^{13}C NMR of the complexes. Besides NMR study, the formation of the synthesized compounds were supported by melting points, elemental analysis and IR studies. The single crystal X-ray diffraction analysis has revealed that complexes **Ag1**, **Ag11**, **Ag20**, **Au3** and **Au18** having the expected chemical formula of $[M_n(\text{NHC})_2] \cdot n\text{PF}_6$ (where $M = \text{Ag}$ or Au , $n = 1$ or 2). On the other hand, the silver(I)-NHC complexes with tetrabenzimidazol-2-ylidene ligands, **Ag23** and **Ag27** formed the dinuclear silver(I)-NHC complexes with formula of $[\text{Ag}_2(\mu\text{-NHC})] \cdot 2\text{PF}_6$. Antibacteria activity for all benzimidazolium salts **1-28** and silver(I)-NHC complexes, **Ag1-Ag28** were evaluated. All silver(I)-NHC complexes show lower to higher activities against *E. coli* (ATCC 25922) and *S. aureus* (ATCC 12600) compared to the standard antibiotic drug, Ampicillin. The photophysical properties of crystallized gold(I)-NHC complexes, **Au3** and **Au18** were determined using photoluminescence technique in solid state. In the absence of significant aurophilic interaction in **Au3**, the emission band is attributed to the metal-to-ligand charge transfer (MLCT). Meanwhile, **Au18** shows interesting temperature-dependent photoluminescence behaviours resulted from aurophilic interaction in the complex.

CHAPTER 1

INTRODUCTION

1.1 Carbene

Carbene is a type of neutral carbon intermediates that bearing divalent carbon atom with two single covalent bonds, bonded to adjacent groups and two unshared electrons (Figure 1.1) [1]. The presence of these three groups can form the carbene carbon with either sp or sp^2 hybridization, with either linear or bent geometry shape, respectively. The sp^2 hybridized carbene carbon is energetically more stable as compared to sp hybridized carbon, thus most of the carbene is possessing the sp^2 hybridization [2].



Figure 1.1: The general representative of carbene.

Furthermore, depending on the relative energies of the orbitals, the sp^2 free carbenes can be distinguished as either singlet or triplet carbene. If the energy difference in the frontier orbitals is large, the singlet state become favourable. In this state, the two nonbonding electrons are present in the same orbital with antiparallel spin. On the other hand, if the energy difference is low, triplet state carbene is formed with two nonbonding electrons end up being in two different orbitals with parallel spin (Figure 1.2) [3]. The other factor to determine the state of carbene is by the type of heteroatoms present. If the heteroatoms are donor electron species, the triplet state is favoured. Meanwhile, singlet state is favoured if the heteroatoms are from electron withdrawing groups [3,4].

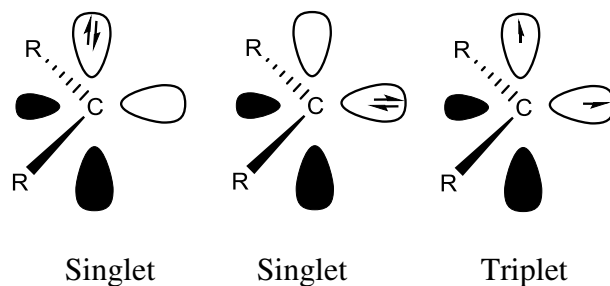


Figure 1.2: Electronic configuration for singlet and triplet free carbene.

1.2 N-heterocyclic carbene

N-heterocyclic carbene (NHC) or Arduengo's carbene is the third type of carbene. NHCs present as a neutral heterocyclic species containing at least one nitrogen atom and carbene carbon atom within the ring structure [5].

1.2.1 Stability of NHC

The stability of a singlet carbene is affected by several factors. The first stabilizing factor is the electronic contribution, and this can be achieved by the presence of heteroatoms such as N, S or O that can be considered as electron donating groups for the vacant *p* orbital in carbene carbon [6,7]. NHCs possess a potent stability due to the two adjacent nitrogen atoms that lead to a unique electronic structure [8]. The interaction between the electronegative nitrogen atoms and carbene carbon forms an interaction called pull and push stabilization (Figure 1.3) [9].

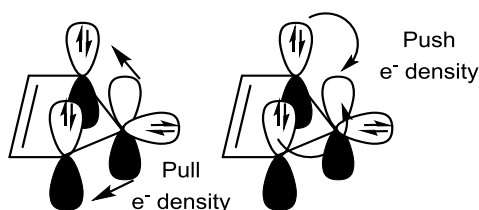


Figure 1.3: Pull and push interaction in NHCs.

The nitrogen atoms in NHC ring can pull the electron density from the electron rich carbene carbon by inductive effect while the lone pair of electrons from each nitrogen atom can be pushed or donated to the empty p -orbital of the carbene carbon by resonance effect [9]. Due to this electronic structure, NHC is recognized as a good σ -donor but poor π -acceptor ligand in organometallic chemistry [2]. Meanwhile, the steric factor is the second factor that can contribute to the stability of a carbene. This factor can be considered when some researchers observed changes in the stability of the NHC after changing the N -substituents with the bulk substituents [9,10].

1.3 Benzimidazolium salts: Promising NHC ligand

Benzimidazole moiety is one of the azole compounds other than imidazole, pyrazole, triazole and tetrazole [11]. This organic heterocyclic aromatic compound bearing a benzene ring fused with five membered rings containing two nitrogen atoms, which present at non-adjacent position (Figure 1.4) [12].

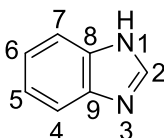


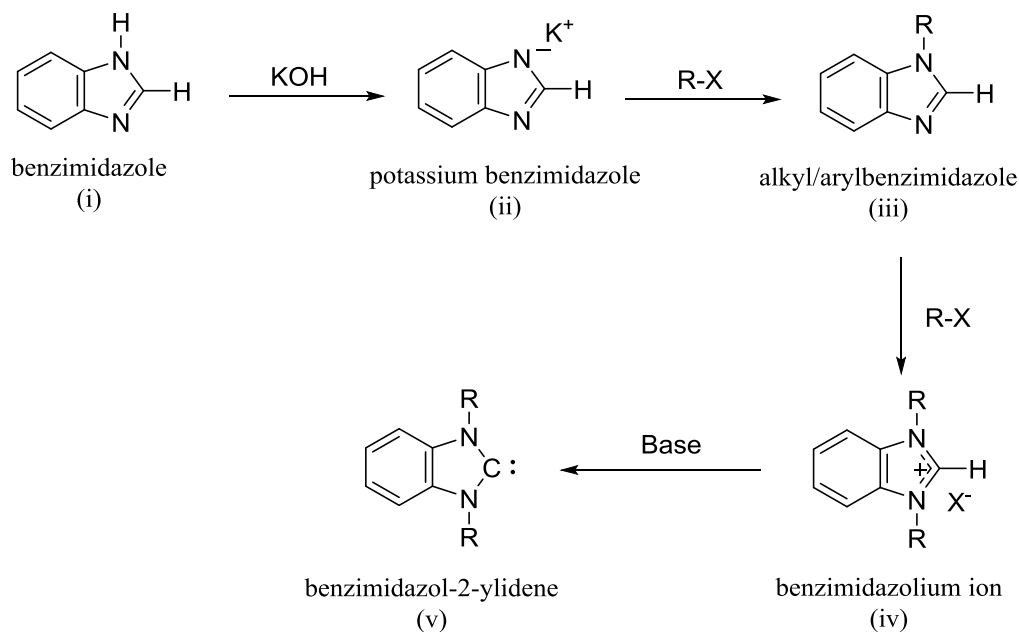
Figure 1.4: The numbering in benzimidazole.

Since the discovery of free NHC by Arduengo [13], different methods have been developed in order to isolate various heterocyclic carbene [14-17]. In general, there are two synthetic routes that can lead to the formation of azolium salts. The first unique route is the multicomponent one step reaction, involving a primary

amine and formaldehyde under acidic condition with Schiff base as an intermediate [18].

While the aforementioned route is only suitable for symmetrically imidazolium salts, the second route, namely, nucleophilic substitution is more accessible to synthesized benzimidazolium salts in high yield. This reaction is started from commercially available, in this case, benzimidazole as a starting material with several steps to attach the substituents onto the 1- and 3- positioned nitrogen atoms [19]. In a clearer description, benzimidazole will be reacted with strong base such as potassium hydroxide to yield a potassium benzimidazole as an intermediate compound (Scheme 1.1(i-ii)). Simultaneously, the presence of alkyl/aryl halide will allow the formation of alkyl/arylbenzimidazole, in which the alkyl/aryl is attached to one of the nitrogen atoms (Scheme 1.1(iii)) [20]. The attachment of the first substituent activates the other nitrogen atom which subsequently allows an addition reaction by another alkyl/aryl halide in a different reaction to yield a benzimidazolium salts (Scheme 1.1(iv)).

When an acidic proton from a benzimidazolium ion is removed by a strong base, the free NHC is formed. To name a free carbene compounds, the heterocyclic system is mentioned in the front, followed by the position of the carbene carbon in the NHC system. Furthermore, the addendum -ylidene will complete the systematical suffix. Noteworthy, the term “-ylidene” refers to a compound featuring the hydrogen atom replaced by a pair of electrons. For benzimidazole in NHC forms, the suffix is benzimidazol-2-ylidene, as depicted in Scheme 1.1(v).



Scheme 1.1: The general route to synthesis benzimidazol-2-ylidene, v.

1.4 Metal-NHC complexes

The ability of NHC as a strong nucleophile and excellent σ -donors encouraged researchers to synthesized various NHC complexes with main group or transition metal elements. The lone pair from carbene carbon or the σ -donations to the metal atoms plays an important role to form a strong covalent bond in metal-NHC entity. Therefore, the contribution of both metal π -back donation into the p -orbital of the carbene carbon and carbene π -donation are negligible because the π -contribution is limited to delocalise within the NHC ring and metal-NHC bonding resulting in a single rather than double bonds [9,21,22]. In summary, a single dative bond is formed from the donation of the electron pair in the σ -orbital of carbene carbon to the metal. Moreover, the resulting empty p -orbital of carbene carbon is filled with the electron density from a lone pair electron of both adjacent nitrogen atoms (Figure 1.5) [23].

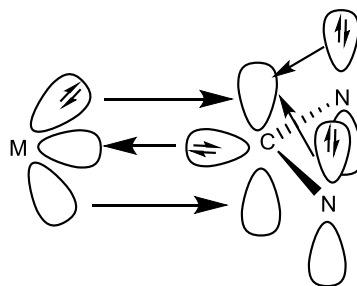
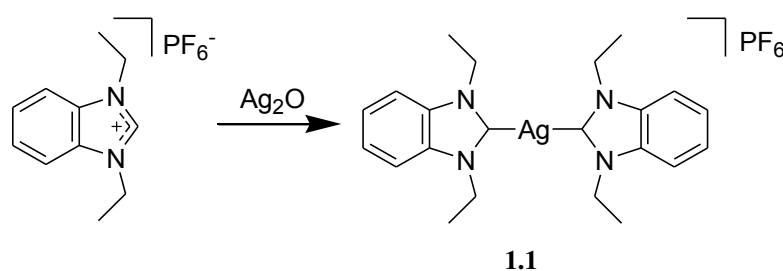


Figure 1.5: Bonding in NHC complexes.

1.5 Silver(I)-NHC Complexes

1.5.1 Convenient synthetic method: In-situ deprotonation

The silver(I)-NHC complexes can be prepared *via* free carbene method, but some drawbacks from this method encouraged the chemists to widely use the *in-situ* deprotonation method to prepare the desired complexes. The use of silver(I) acetate as silver base was started in the reaction was in 1997 [24] and a year after, the uses of silver(I) oxide have been introduced by Wang and Lin for the synthesis of silver(I)-NHC complex, **1.1** (Scheme 1.2) [25]. In 2000, silver(I) carbonate was used as well to produce various silver(I)-NHC complexes [26].



Scheme 1.2: The first silver(I)-NHC complex, **1.1** synthesized using silver(I) oxide by Wang and Lin [25].

Among the above three silver sources, silver(I) oxide has received more attentions since this chemical is commercially accessible, and it is relatively stable. The *in-situ* deprotonation reaction using silver(I) oxide can be performed at ambient temperature with no external base required [27,28]. Besides, the resulting silver(I)-NHC complexes from this reaction are usually stable, high percentage yield and proven to be excellent carbene transfer agents in the preparation of other metal-NHC complexes. The product can be easily purified by removing the unreacted insoluble silver(I) oxide after the completion of reaction [29-31].

1.5.2 Classes on NHC and respective silver(I)-NHC complexes

The classification of the metal-NHC complexes can be divided into two; either by the number of metal centers per complex or by the number of NHC unit per ligand molecule. Moreover, the latter classes can be categorized into two major groups; mono-NHC and poly-NHC in which the poly-NHC can be further subdivided into few different types.

The mono-NHC ligands possess only one NHC moiety per molecule. Normally, the structures of silver(I)-NHC complexes can be easily studied through mono-NHC silver(I) complexes. The variation of structural motifs of the silver(I)-NHC complexes can be arose by many factors such as the ratio between ligand and metal salt, the types of the metal source, *N*-substituents on the NHC core, counter ions, solvents and temperature [32,33].

Meanwhile, polytopic ligands featuring more than one carbene unit including di-, tri-, tetra- and hexa-carbene have received more attentions as they lead to the synthesis of various organometallic compounds with numerous structural

architectures [34-38]. Poly-NHC as either chelating or bridging ligands allow complexes to be more stable and the topological properties such as chirality, bite angles and steric hindrance to be fine-tuned. In the present work, the classification based on the number of NHC centers per ligand is discussed and the focused metal complexes are silver(I)-NHC complexes.

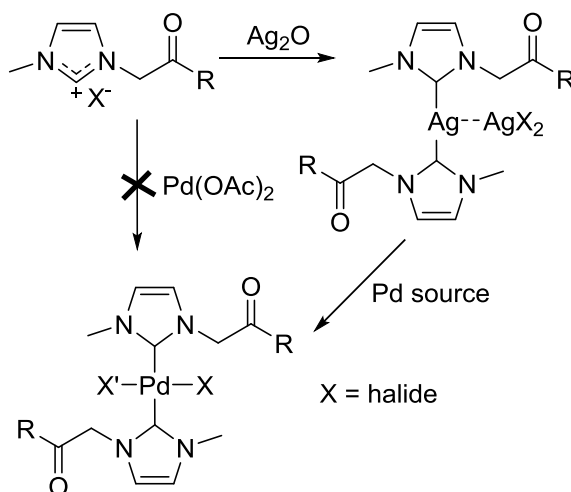
1.5.3 Focused application: Antibacterial study

The uses of silver as an antimicrobial agent can be traced since ancient times. The pure metal is inactive; however, silver complexes can readily release silver ions in the presence of moisture where antimicrobial activity can be observed [39]. Bioavailability is an important parameter that affect the activity of silver cations. The bioavailability of silver compounds is depending on the delivery methods, ionization rate of silver sources, solubility and the presence of biological ligands such as chloride, sulfides and proteins [40].

Aforementioned, in general, NHC ligands possess a dominant stability due to their high σ -donor and low π -acceptor ability, hence they can produce a stable metal-NHC complexes with strong metal-carbon bonds [41]. Furthermore, with this ability, silver(I)-NHC complexes could also achieve a slower release rate of silver ions compared to other coordinated silver complexes or current antimicrobial agents. This thus enhanced the ability of the former complexes to kill the bacteria over a sustained period of time [32]. In addition, the effect of substituent moiety at the nitrogen atoms that related to the lipophilicity of the complexes can also affect the antimicrobial activities of the complexes [42,43].

1.5.4 Focused application: Silver(I)-NHC complexes as ligand transfer agent

In the most cases, silver(I)-NHC complexes were used to transfer the NHC ligands with acidic functional groups, with the attempts to prepare similar complexes by using base as a part of the reaction were unsuccessful (Scheme 1.3) [44,45]. Furthermore, the uses of silver(I)-NHC complexes as transfer agent overcome the hurdles to isolate the unstable free heterocyclic carbenes. In addition, the rigidity of synthesis conditions in direct metalation of azolium salts with the metal salts can be avoided [46].



Scheme 1.3: General schematic diagram in the preparation of palladium(II)-NHC complexes from silver(I)-NHC complexes by Guinness and Cavell [44].

1.6 Gold(I)-NHC Complexes

1.6.1 Convenient synthetic method: Transmetalation and structural variation

Several synthesis methods for the preparation of gold(I)-NHC complexes have been described in the literature [47-49]. The free NHC method can be used to produce gold(I)-NHC complexes by reacting the generated free NHC with gold precursors such as [Au(SMe₂)Cl] or [Au(THT)Cl] (where SMe₂ = dimethylsulfide,

THT = tetrahydrothiophene) [50]. However, this method requires special conditions due to the high reactivity and the unstable nature of the free carbenes. Other than that, several works reported in the literature described the *in-situ* deprotonation method using gold(I) precursors and external base, usually K_2CO_3 [51-53].

Another approach in order to achieve gold(I)-NHC complexes is by using silver(I) and copper(I) transmetalation protocols. The potential of silver(I)-NHC complexes as NHC ligand transfer agents have been briefly described in the previous sections. Other than silver(I)-NHC complexes, copper(I)-NHC complexes can also be used to prepare the gold(I)-NHC complexes [54,55]. However, when observed from the growth of gold(I)-NHC complexes through silver(I) transmetalation protocols, the significant role of silver(I) as transfer agents are proven [56,57]. This method can be used to synthesize the complexes with various structural motifs, depending on several factors such as the molar ratio of the reactants, type of solvents, structure of silver(I)-NHC complexes and structure of azolium ligands used [58-62]. Among the factors, the type of solvents plays an important role in determining the structure of the gold(I)-NHC complexes.

1.6.2 Focused application: Photophysical properties

The photophysical and photochemical properties of transition metal complexes have been studied for a long time and the basic ideas about their excited states have been included into account since 30 years ago [63-67]. In the last 20 years, various parameters for efficient photoluminescence was designed by varying the structures of the complexes for possible applications such as optical devices, sensing applications and cell imaging applications [66-80].

In coinage metals, specific short metal-metal known as metallophilic d^{10} - d^{10} interactions have been observed in their complexes [81-85]. Moreover, in gold chemistry, the term “aurophilicity” is referred to the weak interaction between linearly coordinated gold(I) closed shell centres, introduced by Schmidbaur in early 1990s [85]. The intra- and intermolecular aurophilic interactions in gold(I) complexes play an important role in influencing the photophysical properties of the complexes by contributing towards metal-metal-to-ligand charge transfer (MMLCT) [86,87].

Studies of mononuclear and dinuclear gold(I)-NHC complexes have revealed that the complexes may have either red or blue emission profiles, depending on the ligands used [61,88,89]. Additional to that, several of the found complexes showed their ability to be highly emissive only as single crystals, which proved that their molecular stacking in the lattice gives a big impact on their luminescence properties [90].

1.7 Problem Statements

In the reports by Centre for Disease Control (CDC), World Health Organization (WHO) and the European Centre for Disease Prevention and Control (ECDC), the increasing cases of Antimicrobial Resistance (AMR) across the world has been highlighted in the past decade [91]. The major cause of AMR is due to the over-use of antimicrobials and the failure to develop new drugs [92]. In the efforts to overcome this problem, silver-based compounds have received a massive attention in developing new classes of antimicrobial drugs. Despite of this study, the antibacterial activity about complexes with tetra-NHC ligands is still scarced. Thus, a good plans to design tetrabenzimidazolium ligand lead to the formation of

bromide bearing benzimidazolium salts, an important compound in organic synthesis due to the presence of bromide atom attached to the molecule. This type of salts can be used in the formation of di-hetero-NHC ligands.

In the past few years, the luminescence properties of mono and polynuclear gold(I)-NHC complexes have been reported, just to study the relationship of intra- or intermolecular distance with their photoluminescent properties [92-99]. Despite the emerging of this study, only few structures of the complexes with clearly outstanding emission characteristics in the solid state have become prominent up to now, applicable for technological applications [100-103].

1.8 Objectives

- i. To synthesize and characterize new *N*-heterocyclic carbenes (NHC) precursor bearing mono-, bis- and tetradentate benzimidazolium salts.
- ii. To synthesize and characterize novel silver(I)- and gold(I)-NHC complexes *via in-situ* deprotonation and transmetalation method, respectively.
- iii. To evaluate the antibacterial activities of the synthesized silver(I)-NHC complexes *via* disc diffusion and MIC and MBC levels determination methods.
- iv. To study the photophysical properties of the selected gold(I)-NHC complexes using photoluminescence study in solid state.

1.9 Scope of works

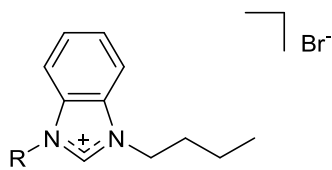
In this current study, benzimidazole was used instead of otherazole compounds due to structure stability and commercial availability. The targeted benzimidazolium salts have different number of benzimidazole moieties per molecule in order to achieve targeted metal-NHC complexes. For the first and third

series, the mono- **1-7** and bis-benzimidazolium **14-20** salts bearing different substituents at nitrogen atoms were synthesized. In general, these two series present the non-symmetrical mono- and bis-benzimidazolium salts as ligands to their respective silver(I)- and gold(I)-NHC complexes. Different to the first series, the second and fourth series present the symmetrical bis-, **8-13** and tetrakis-benzimidazolium, **21-28** salts and their respective silver(I)-NHC complexes. Additional to that, the precursors to synthesize **21-28** namely, 3-(2-bromoethyl)-1-alkylbenzimidazole bromide (where alkyl = ethyl, *n*-propyl, *n*-butyl, *n*-benzyl, respectively), **i-iv** were also prepared. Noteworthy, **iii** and **iv** are reported in the literature [103].

The primary interest of this study is the synthesis of silver(I)-NHC complexes due to the accessibility of their synthesis method and applications. Silver(I)-NHC complexes are well known for their potential as a carbene ligand transfer agent as well as an antibacterial agent. All silver(I)-NHC complexes were tested for their antibacterial activity through disc diffusion method and MIC and MBC level determinations. The present of silver(I) ions in the complexes become the main component to inhibit the bacteria growth [104]. On the other hand, gold(I)-NHC complexes are the additional compounds prepared in this work in order to evaluate the ability of silver(I)-NHC complexes application for ligand transfer. The interest in synthesizing gold(I)-NHC complexes lies on the optical properties despite numerous reports of other applications. The emissive nature of gold(I)-NHC complexes is mainly due to the presence of electron-rich groups in the carbene ring, the presence of chromophore ligand directly bonded to the gold center, the present of aurophilic interactions and appropriate energetic state

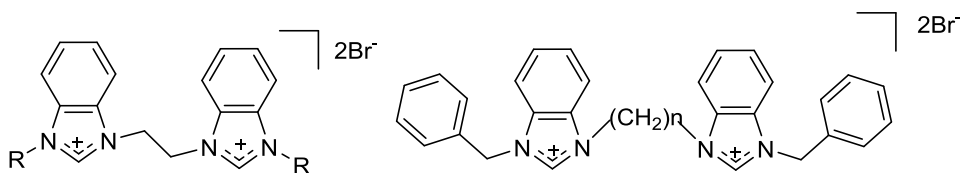
characteristic of cyclometallated or three-coordinate species [105]. Referring to above potential of both silver(I) and gold(I)-NHC complexes, all the benzimidazolium salts were used to produce silver(I)-NHC complexes, **Ag1-Ag28**. Meanwhile, due to the limited gold source, only the two series of silver(I)-NHC complexes with non-symmetrical benzimidazole-2-ylidene ligands, **Ag1-Ag7** and **Ag14-Ag20** were chosen to be used as ligand transfer agents in preparation of their respective gold(I)-NHC complexes, **Au1-Au7** and **Au14-Au28**.

All the prepared compounds were characterized using melting points analysis, elemental analysis data, IR and NMR spectroscopic techniques. The structural properties of the selected compounds were confirmed using single crystal X-ray diffraction techniques. Detailed discussions about the syntheses, characterization, structural analyses and applications of all compounds will be further discussed in Chapter 3 and 4. The structures of all targeted benzimidazolium salts are shown in Figure 1.6.



1-7

1, R = methyl; **2**, R = ethyl; **3**, R = *n*-propyl; **4**, R = *n*-pentyl;
5, R = *n*-hexyl; **6**, R = *n*-heptyl, **7**, R = *n*-benzyl

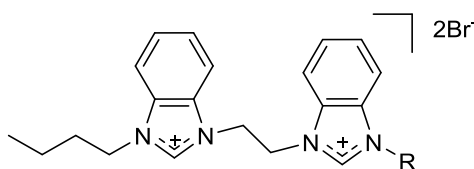


8-10

8, R = ethyl; **9**, R = *n*-propyl; **10**, R = *n*-butyl

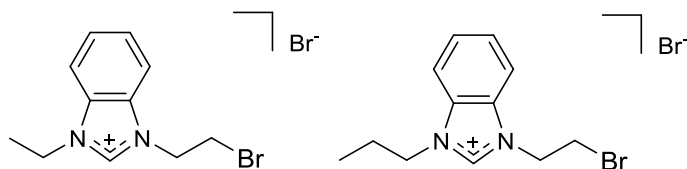
11-13

11, *n* = 2; **12**, *n* = 3; **13**, *n* = 4



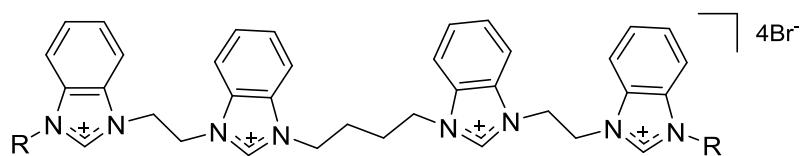
14-20

14, R = methyl; **15**, R = ethyl; **16**, R = *n*-propyl; **17**, R = *n*-pentyl;
18, R = *n*-hexyl; **19**, R = *n*-heptyl, **20**, R = *n*-benzyl



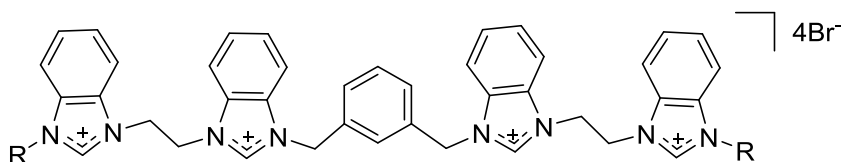
i

ii



21-24

21, R = ethyl; **22**, R = *n*-propyl; **23**, R = *n*-butyl; **24**, R = *n*-benzyl



25-28

25, R = ethyl; **26**, R = *n*-propyl; **27**, R = *n*-butyl; **28**, R = *n*-benzyl

Figure 1.6: The targeted benzimidazolium salts **1-28** and precursors **i** and **ii**.

CHAPTER 2

LITERATURE REVIEWS

2.1 Carbene and *N*-heterocyclic carbenes

The formation of dichloro carbene as an intermediate in cyclopropanation reaction was the first evidence of discovery of the carbene, reported in 1954 [106]. During this time, carbene was only known as highly reactive and short-lived intermediates in organic reaction. A decade later, Fischer carbene, a singlet carbene with electrophilic character was the first type of carbene introduced by E. Fischer and A. Massböl. Starting from there, carbenes were divided based on their reactivity toward metal ions. The bonding in the Fischer carbenes formed when the sp^2 orbital of the carbene donated the electron pair in σ type and the empty p -orbital accept back the donation from the metal but in π mode (Figure 2.1(a)) [107]. The second type of carbene is the Schröck carbene, a triplet carbenes with nucleophilic character. Found by Schröck a decade after the discovery of Fischer carbenes, this carbene formed by the covalent bonds between the two unpaired electrons of carbene with the two electrons of the metal (Figure 2.1(b)) [108].

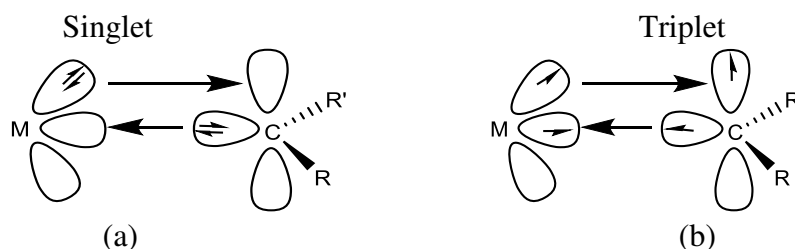
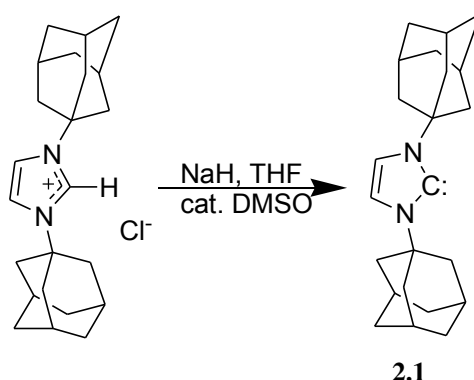


Figure 2.1: Bonding in (a) Fischer carbene complexes [6] and; (b) Schröck carbene complexes [108].

The NHCs chemistry was firstly introduced by Wanzlick, Schonherr and Öfele in 1960s [109,110]. However, the interest in this area rapidly increased after the isolation of the first stable crystalline NHC, namely 1,3-di-(1-adamantyl)imidazol-2-ylidene, **2.1** by Arduengo in 1991 (Scheme 2.1) [13]. Initially, the bulky substituent and the aromaticity properties of imidazolium core of this compound were believed to provide the steric effect for successful isolation. However, after several successful attempts to isolate other carbenes using just a simple methyl group as substituent and non-aromatic heterocycle as carbene core, Arduengo negated the hypothesis [13].



Scheme 2.1: The synthesis of 1,3-di-(1-adamantyl)imidazol-2-ylidene, **2.1** from 1,3-di(adamantly)imidazolium chloride [13].

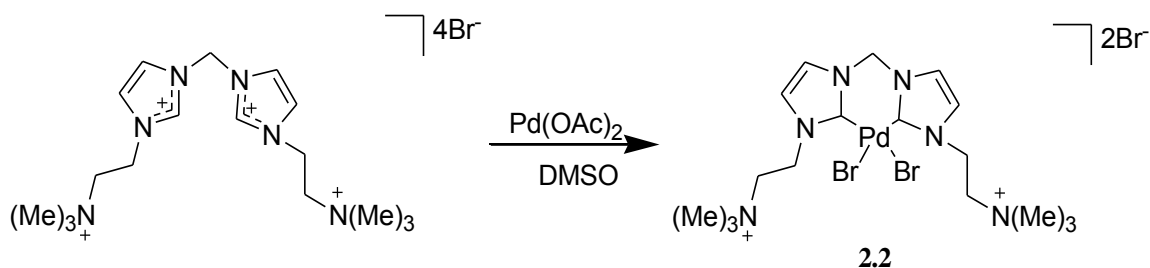
2.2 Metal-NHC complexes

2.2.1 General synthetic methods

(a) *In-situ* deprotonation

Before the successful isolation of free NHC **2.1** by Arduengo in 1991 [13], the first metal complex by Wanzlick and co-workers [109] and Öfele [110] in 1968 opens the avenue of metal-NHC history. Their works were the first *in-situ* deprotonation one pot reaction of imidazolium salts with basic metal sources such

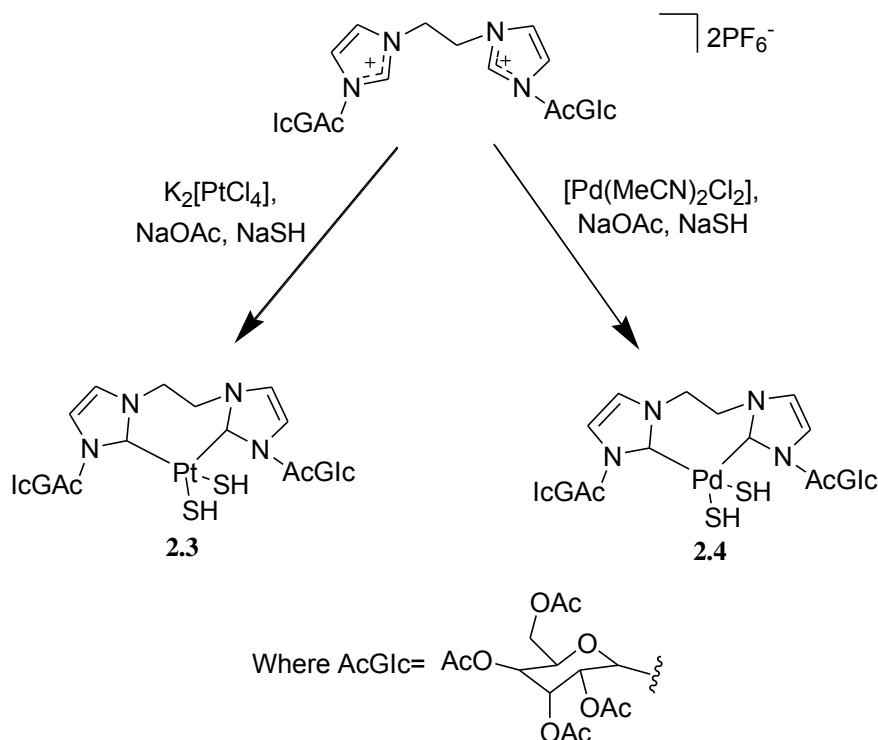
as pentacarbonylhydrido chromium and mercuric acetate to produce chromium(0)- and mercury(I)-NHC complexes, respectively [110,111]. This is an economical method where the azolium salts are treated only with one metal compound that can act as a base to extract the acidic carbene proton as well as a metal source that subsequently trap the NHC ligand to produce the desired complexes. Other than this basic metal, the other examples of the basic metal salt used in this type of reaction are palladium(II) acetate [112], silver(I) oxide [25] and mercury(II) acetate [113]. This efficient and direct method become significant as the NHC is not required to be isolated, and even the unstable or difficult to handle NHCs can produce their respective metal complexes through this method. As example, Scheme 1.3 shows the synthesis of palladium(II)-NHC complex, **2.2** from the reaction of respective imidazolium salt with palladium(II) acetate, reported by Asensio and co-workers.



Scheme 2.2: Palladium(II) acetate as a base and metal source in the formation of palladium(II)-NHC complex, **2.2** by Asensio and co-workers [112].

The second type of *in-situ* deprotonation is using an external base in order to deprotonate NHC salts to facilitate the formation of NHC complexes. The uses of non-basic metal compound that unable to deprotonate the carbene proton was the main reason the strong bases such as potassium carbonate [114], lithium tert-butoxide [115] and sodium acetate were used [116]. As shown in Scheme 2.3,

Imanaka and co-workers used sodium acetate to synthesize the platinum(II)- and palladium(II)-NHC complexes **2.3** and **2.4**, respectively for catalysis study purpose [116]. Noteworthy, in the absence of strong base, neither precipitates nor crystals formed after a certain period of time, indicating that strong base is one of the important elements to ensure successful complexation.

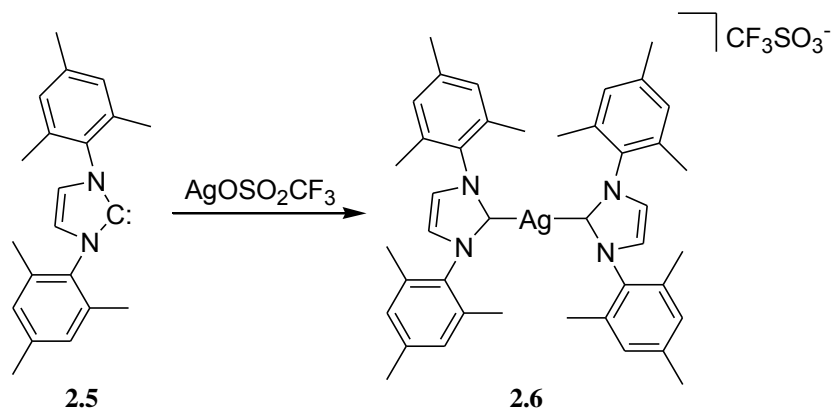


Scheme 2.3: The example of in-situ deprotonation using external base, sodium acetate to produce platinum(II)-NHC complex, **2.3** and palladium(II)-NHC complex, **2.4** by Imanaka and co-workers [116].

(b) *Free carbene*

The free carbene method is the method in which the azolium salts are reacted with a strong base such as potassium *tert*-butoxide, sodium hydride or lithium bis(trimethyl)amide and subsequently, the metal sources are added. This method is used extensively to synthesized silver(I)- and mercury(II)-NHC complexes where the free carbene is stable enough to be isolated. Following the isolation of free carbene **2.1**, in 1993, Arduengo produced another free carbene

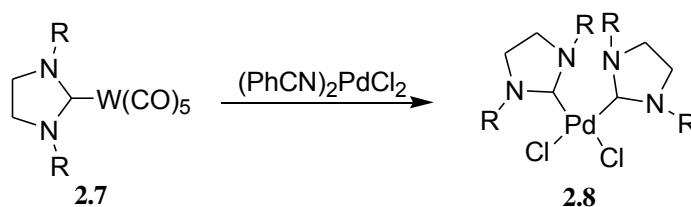
ligand namely, 1,3-dimesitylimidazol-2-ylidene, **2.5** which was used to synthesize the first silver(I)-NHC complex, **2.6** by direct reaction with silver(I) triflate [8] (Scheme 2.4). Since this method requires the initial generation of free carbene, it is limited to those azolium salts that can only produce stable carbenes.



Scheme 2.4: The reaction between a free carbene, **2.5** with silver(I) triflate to facilitate the formation of first silver(I)-NHC complex, **2.6** by Arduengo and co-workers [8].

(c) *Ligand transfer*

Transmetalation or ligand transfer is a method where a ligand is transferred between two different metal centres. Fisher and Bech were the first to introduce this method in their effort to prepare metal-carbene complex [117]. Besides, the uses of NHC in the same method was also repeated by Liu and co-workers in 1998, where the NHC was transferred from tungsten(0)-NHC complex **2.7** to palladium(II)- (**2.8**) and platinum(II)-NHC complexes (Scheme 2.5) [118].



Scheme 2.5: The first transmetalation reaction of NHC by Liu [118].

Following the formation of these complexes, rhodium(I)- and gold(I)-NHC complexes were then successfully synthesized *via* the same method with the use of tungsten(0)- and molybdenum(0)-NHC as a transfer agents [119]. The ability of mercury(II)-NHC to transmetalate the NHC ligand to other transition metals and main group elements such as sulphur, selenium and tellurium were also known [120]. Through this transmetalation method, the formation of free NHC can be avoided while the possibility of the decomposition of NHC is low. However, this method is only restricted to only several types of NHC ligand. The poor ligand transfer ability was shown by the NHC with saturated backbones compared to the NHC with unsaturated backbones which lead to the formation of product with low yield or even unsuccessful transmetalation [121]. Among all metal-NHC complexes, silver(I)-NHC complexes show potent ability to transmetalate. Further discussions on this topic are provided in Subchapters 1.5.4 and 1.6.1.

2.3 Silver(I)-NHC Complexes

2.3.1 Classes on NHC and respective silver(I)-NHC complexes

In this subchapter, the classification based on the number of NHC centers per ligand is discussed. The focused metal complexes are silver(I)-NHC complexes, but there are other metal-NHC complexes that may be included for the discussion on structural analysis.

(a) Mono-NHC

Mainly, the structure of mono-NHC silver(I) complexes can either be as neutral complexes which constitutes a singly NHC ligand coordinated to another type of ligand group in the form of [NHC-Ag-X] (where X = Cl, Br, I, acetate or

benzoate) [122-125] or as non-coordinated ionic [NHC-Ag-NHC]X (where X = PF₆⁻, BF₄⁻, Cl⁻, Br⁻ or I⁻), giving rise to a bis-NHC arrangement [126,127]. Figure 2.2 depicts the neutral complex **2.9** with chloride ligand [122], neutral complex **2.10** with acetate ligand [124] and the ionic silver(I)-NHC complex **2.11** with hexafluorophosphate ion in the lattice [127]. The preference in the formation of these complexes were largely depending on the reaction pathways, stoichiometric ratio of the reactants and the type of azolium salts used [33,46].

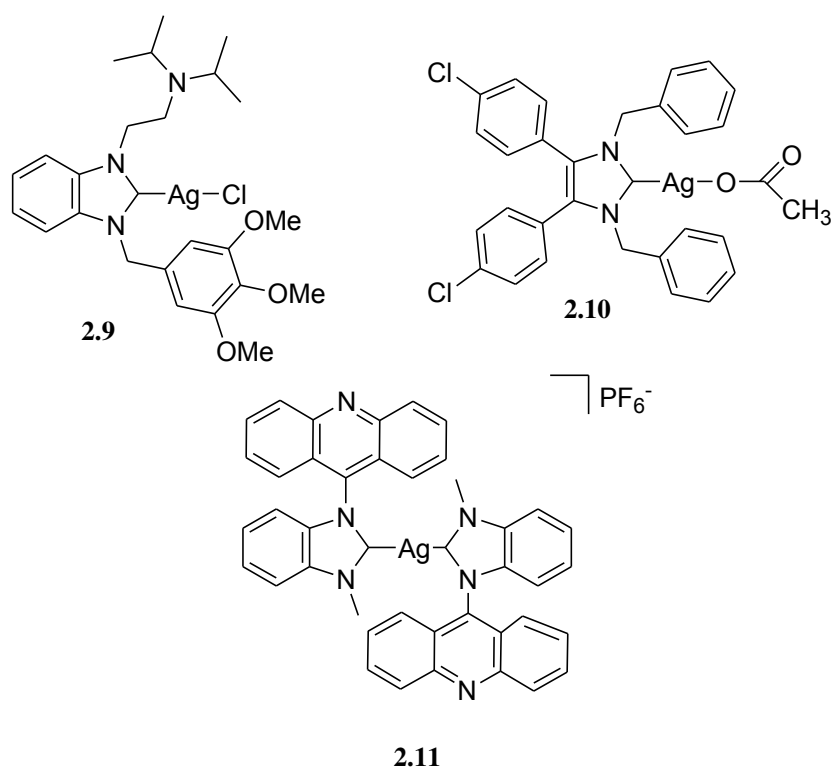
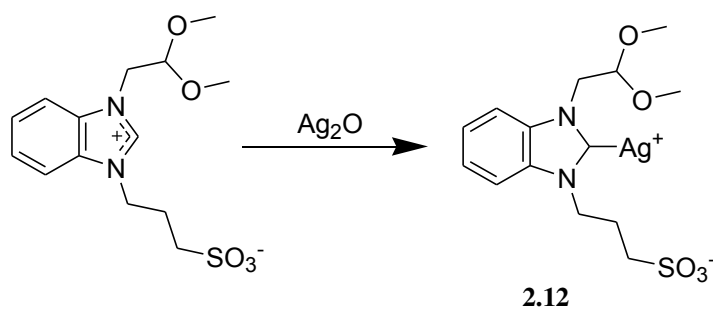


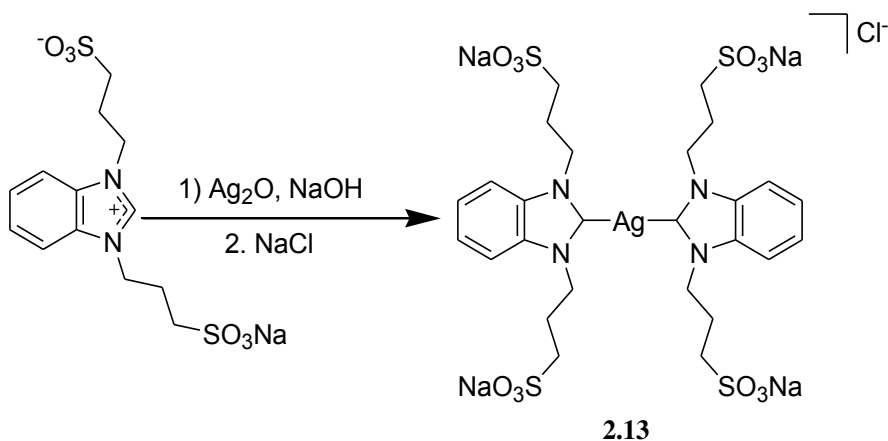
Figure 2.2: The mononuclear silver(I)-NHC complexes **2.9-2.11**, with different structures [122,124,127].

The new structural silver(I)-NHC complexes that are increasingly developed in the past few years are complexes with zwitterion substituted NHC. In this ligand, the positive charge of the NHC carbon can be neutralized by the sulfonated substituent. On the other hand, there are two possible structures of silver(I)-NHC complexes that may form by this ligand, depending on the type of materials used.

As shown in complex **2.12**, the charge of the silver ion is neutralized by sulfonated ion in the terminal substituent as recently reported by Özdemir (Scheme 2.6) [128]. This work is in contrast with the work reported by Marinelli, where the uses of sodium hydroxide and sodium chloride as part of the reaction mixture, lead to the formation of the cationic silver(I)-NHC complex **2.13**, with chloride ion in the lattice while sulfonated ions are coordinated to sodium ion (Scheme 2.7) [129].



Scheme 2.6: The silver(I)-NHC complex, **2.12** bearing zwitterion ligand [128].



Scheme 2.7: The silver(I)-NHC complex, **2.13** bearing zwitterion ligand [129].

(b) *Di-NHC*

Di-NHCs are the most abundant poly-NHC ligands, as these salts can coordinate readily with metals to form various metal NHC complexes with structural diversity depending on the ratio of metal to azolium salts and the type of spacer/bridge used to connect the two azolium groups [130]. Hitherto, reported bidentate dibenzimidazolium salts are limited to the symmetrical compound having

different types of linkers used to connect the two moieties, as shown in the dibenzimidazolium salts **2.14** and **2.15** (Figure 2.3) [131,132]. The ease in preparation of these salts thus has garnered interests from researchers to design the symmetrical homo-dibenzimidazolium salts [133].

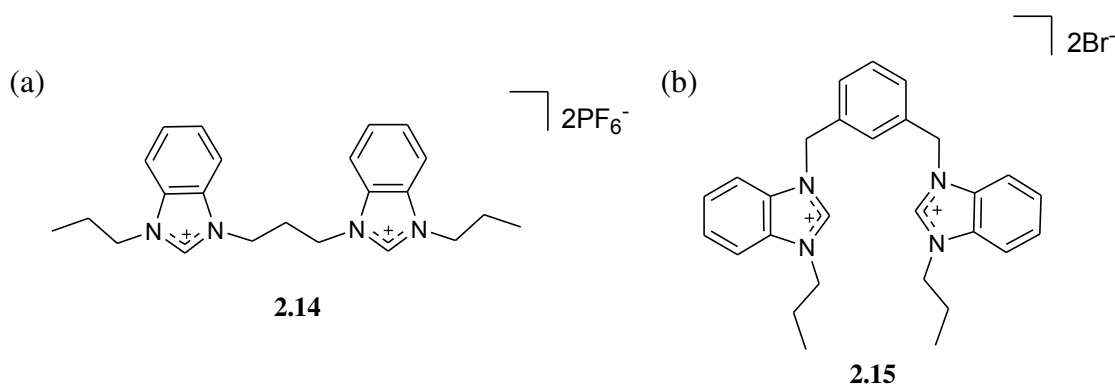


Figure 2.3: An example of symmetrical homo-di-NHC precursors, **2.14** [131] and **2.15** [132], respectively.

Furthermore, a series of di-NHC ligands can be classified to two groups; (a) homo-di-NHC ligand that contains only one type of azolium moiety; and (b) hetero-di-NHC ligand which is constructed by two different azolium moieties. For the latter [134,135], such examples being a mixture of triazolium and an imidazolium that was generated by transamination of *n,n*-dimethylformamide azine with the primary amine function of the *n*-aminoazoles [135].

Moreover, in 2011, Huynh and Jothibasud had reported the hetero-di-NHC palladium(II) complexes bearing a mixture of imidazolium and benzimidazolium moieties with propylene chain serving as a bridging group, as in complex **1.17** (Figure 2.4) [136]. The catalytic of these hetero-di-NHC complexes outperformed their homo-di-NHC analogues presumably due to the electronic asymmetry induced by hetero-di-NHC ligands.

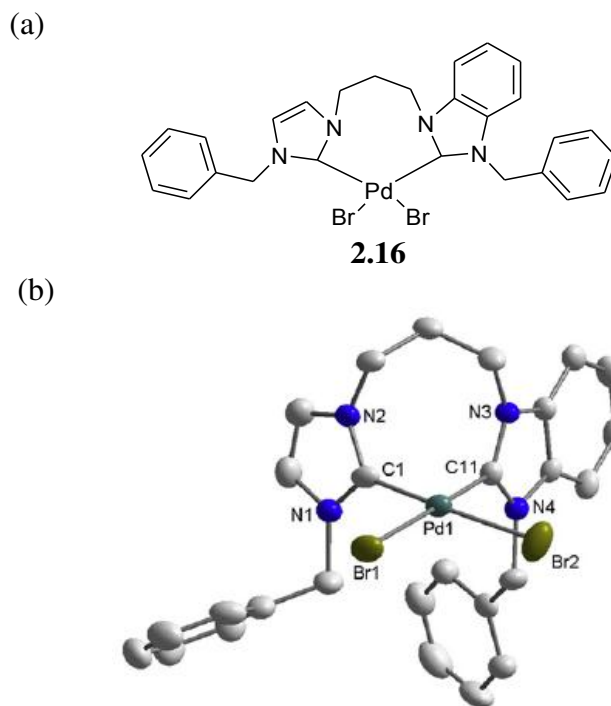


Figure 2.4: (a) Palladium(II)-NHC complex bearing di-hetero-carbene, **2.16** and; (b) the crystal structure of **2.16**. Hydrogen atoms were omitted for clarity [136].

(c) *Tri-NHC*

Tri-NHC systems are relatively scarce among all poly-NHC systems metal-complexes. Tri-NHC salt were first synthesized by Hu and co-workers in 2003, where the synthesis procedure involves one step reaction, in which an azole is left to react with a tripodal precursor [137]. Since then, a handful metal-NHC complexes were synthesized by the same group and others [138-142].

In 2007, Willans and co-workers reported a tris(imidazolium) hexasubstituted benzene cage compound as a precursor to synthesize silver(I)-NHC complex, **2.17**. As a consequence of insufficient free space within the respective tris(imidazolium) salt, only two out of three imidazolium NHC sites are activated, while the other remained protonated, as proved by single crystal X-ray crystallography study (Figure 2.5) [143].