UNIVERSITI
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Pejabat Pengurusan Dan Kreativiti Penyelidikan
Research Creativity and Management Office

Canselori,

Universiti Sains Malaysia
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11800 USM Pulau Pinang
T : (6)04-653 3108/3178/3988/5019
F : (6)04-656 6466/8470
: (6)04-653 2350
L : www.research.usm.my

Ruj. Kami : FPP 2009/092 (P3158)
Tarikh : 30 September 2011

Dr. Rosenani S. M. Anwarul Haque
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia

Puan,

LAPORAN AKHIR GERAN PENYELIDIKAN JANGKA PENDEK
Tajuk Projek : "Mercury-N-Heterocyclic Carbenes (NHC) Complexes as Carbene Transfer Agents"
No. Akaun : 304/PKIMIA/639001

Dengan hormatnya perkara di atas dirujuk.

2. Terlebih dahulu saya ucapkan terima kasih di atas satu salinan laporan akhir untuk Geran Penyelidikan Jangka Pendek seperti tajuk di atas. Bersama ini dilampirkan komen penilaian daripada Dekan Penyelidikan Pelantar Sains Fundamental untuk perhatian puan.

3. Seterusnya walaupun projek ini telah selesai, Jabatan Bendahari telah dinasihatkan untuk menangguhkan penutupan akaun projek kepada **31 Oktober 2011.** Tempoh ini diberi untuk membolehkan penjelasan semua urusan tuntutan dan bayaran yang telah dibelanjakan di dalam tempoh projek. Walau bagaimanapun, puan dinasihatkan supaya tidak mengeluarkan borang-borang pesanan baru di dalam tempoh ini.

4. Selanjutnya sila ambil perhatian terhadap perkara-perkara berikut sekiranya berkaitan :

(i) semua penerbitan harus merakamkan penghargaan kepada Geran Penyelidikan Jangka Pendek dan puan dipohon mengemukakan satu salinan ke Pejabat ini; dan

(ii) pihak kami akan mengagihkan semula peralatan yang telah dibeli menggunakan peruntukan geran ini seandainya terdapat penyelidik lain yang memerlukan peralatan tersebut.

5. Harap maklum, projek ini dianggap telah selesai dengan jayanya.

Sekian, terima kasih.

"BERKHIDMAT UNTUK NEGARA"
'Memastikan Kelestarian Hari Esok'

Yang menjalankan tugas,

(NOOR ADNIE BAJURI)
Penolong Pegawai Tadbir
Unit Pengurusan Geran & Pembangunan Penyelidikan

UNIVERSITI SAINS MALAYSIA
DITERIMA
26 SEP 2011
Pejabat Ketua Pustakawan

HAH, SM, HAR

LAPORAN AKHIR GERAN PENYELIDIKAN JANGKA PENDEK
Tajuk Projek : "Mercury-N-Heterocyclic Carbenes (NHC) Complexes as Carbene Transfer Agents"
No. Akaun : 304/PKIMIA/639001

s.k.
Dekan Penyelidikan
Pelantar Sains Fundamental
Pejabat Pelantar Penyelidikan
Universiti Sains Malaysia

Dekan
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia

Timbalan Dekan (Pengajian Siswazah & Penyelidikan)
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia

Ketua Pustakawan
Perpustakaan Hamzah Sendut 1
Universiti Sains Malaysia

} Disampaikan satu salinan laporan akhir projek untuk simpanan Perpustakaan

Penolong Bendahari Kanan
Unit Pembayaran Kewangan Penyelidikan
Jabatan Bendahari
Universiti Sains Malaysia

} Sila ambil tindakan menutup akaun projek pada **31 Oktober 2011** dan sila kemukakan satu salinan penyata kewangan terakhir ke Pejabat ini

Pegawai Sains
Pelantar Sains Fundamental
Pejabat Pelantar Penyelidikan
Universiti Sains Malaysia

NAB/yu...laporan akhir induk (19 Sept. 2011)

P 3158

UNIVERSITI SAINS MALAYSIA

SHORT TERM GRANT
FINAL REPORT ASSESSMENT FORM

A
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9 SEP 2011
UNIVERSITI SAINS MALAYSIA
RCMO

A. Project title: **Mercury-N-Heterocyclic Carbenes (NHC) Complexes As Carbene Transfer Agents**

Project leader: **Dr Rosenani S.M Anwarul Haque [School of Chemical Sciences]**

Tel:

Fax:

B. Name of Chairperson: **Prof Abdul Latif Ahmad**

Contacts of Chairperson: Tel: **04-653 3090** Fax: **04-658 4149**

Date of this review:

C. **Summary of assessment** (Tick the appropriate boxes. Also, provide additional comments in Section F)

		Inadequate		Acceptable	Very Good	
		1	2	3	4	5
1.	Achievement of project objectives	☐	☐	☐	■	☐
2.	Quality of output	☐	☐	☐	☐	■
3.	Quality of impacts	☐	☐	■	☐	☐
4.	Technology transfer/commercialization potential	☐	☐	■	☐	☐
5.	Quality and Intensity of collaboration	☐	☐	☐	■	☐
6.	Overall assessment of benefits	☐	☐	☐	■	☐

D. **Action to take** [Tick the appropriate boxes]

■ Project file to be closed

☐ Project to be reviewed once additional information has been obtained by the Project Leader [Please see section E]

☐ Forward to Innovation Office for consideration

☐ Other:

E. **Additional information to be provided by the project leader**

F. **Additional Comments**

This assessment has been done by Prof Bahruddin Saad and he has this to say :

Excellent output for a Short Term Grant.

PROFESSOR ABDUL LATIF AHMAD CEng FIChemE
Research Dean
Fundamental Science Platform
Research & Innovation Division
Universiti Sains Malaysia
11800 Pulau Pinang

Chairperson's Signature

8/9/11

Date

UNIVERSITI SAINS MALAYSIA

PEJABAT PELANTAR PENYELIDIKAN
OFFICE OF RESEARCH PLATFORM

RECEIVED
23 AUG 2011
SFM
USM

Kepada:

Prof. Bahruddin Saad
Pusat Pengajian Sains Kimia

Daripada:

Pegawai Sains
Pelantar Penyelidikan Sains Fundamental

Tarikh:

18 Ogos 2011

Tuan,

PENILAIAN LAPORAN AKHIR GERAN PENYELIDIKAN JANGKA PENDEK USM

Disertakan laporan akhir projek penyelidikan geran penyelidikan jangka pendek USM yang bertajuk :

Mercury-N-Heterocyclic Carbenes (NHC) Complexes as Carbene Transfer Agents.

Dr Rosenani S.M Anwarul Haque [Pusat Pengajian Sains Kimia]

Oleh itu, kerjasama tuan diperlukan untuk membuat penilaian dengan menggunakan `Final Report Assessment Form` yang disediakan dan kembalikan ke Pejabat Pelantar Penyelidikan sebelum atau pada **6 September 2011.**

Sekian, saya ucapkan terima kasih di atas perhatian dan kerjasama tuan.

"BERKHIDMAT UNTUK NEGARA"
"Memastikan Kelestarian Hari Esok"

Nursyatina

Sukacita dikembalikan borang penilaian saya.

22/8/2011

(NURSYATINA BT ABDUL RAOF)
emel : nursyatina@usm.my
samb : 3092

s.k Prof. Abdul Latif Ahmad
Dekan Penyelidikan
Pelantar Penyelidikan Sains Fundamental

Universiti Sains Malaysia, 11800, Pulau Pinang, Malaysia
Tel: 604-653 3888 ext. 3086, 3087, 3088, 3092, 3093, 3095, 3096, 3037; Fax : 604-658 4149; Website : www.usm.my

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SHORT TERM GRANT
FINAL REPORT ASSESSMENT FORM

A. Project title: **Mercury-N-heterocyclic Carbenes (NHC) Complexes as Carbene Transfer Agents.**

Project leader: **Dr Rosenani S. M. Anwarul Haque [School of Chemical Sciences]**

Tel:
Fax:

B. Name of reviewer: **Prof Bahruddin Saad [School of Chemical Sciences]**

Contacts of reviewer:
Tel:
Fax:

Date of this review:

C. **Summary of assessment** (Tick the appropriate boxes. Also, provide additional comments in Section F)

		Inadequate		Acceptable	Very Good	
		1	2	3	4	5
1.	Achievement of project objectives	☐	☐	☐	☑	☐
2.	Quality of output	☐	☐	☐	☐	☑
3.	Quality of impacts	☐	☐	☑	☐	☐
4.	Technology transfer/commercialization potential	☐	☐	☑	☐	☐
5.	Quality and Intensity of collaboration	☐	☐	☐	☑	☐
6.	Overall assessment of benefits	☐	☐	☐	☑	☒

D. **Action to take** [Tick the appropriate boxes]

☑ Project file to be closed

☐ Project to be reviewed once additional information has been obtained by the Project Leader [Please see section E]

☐ Forward to Innovation Office for consideration

☐ Other:

E. **Additional information to be provided by the project leader**

F. **Additional Comments**

Excellent output for a Short Term Grant.

Reviewer's Signature

22/8/2011

Date

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Pejabat Pengurusan Dan Kreativiti Penyelidikan
Research Creativity and Management Office

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11800, USM Pulau Pinang
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Ruj. Fail : FPP 2009/092 (P3158)
Tarikh : 9 Ogos 2011

R[illegible]ED
11 AUG 2011
USM

Profesor Abdul Latif Ahmad
Dekan Penyelidikan
Pelantar Sains Fundamental
Pejabat Pelantar Penyelidikan
Universiti Sains Malaysia

Tuan,

PENILAIAN LAPORAN AKHIR GERAN PENYELIDIKAN JANGKA PENDEK
Tajuk Projek : "Mercury-N-Heterocyclic Carbenes (NHC) Complexes as Carbene Transfer Agents"
No. Akaun : 304/PKIMIA/639001

Dengan hormatnya perkara di atas dirujuk.

2. Pejabat Pengurusan dan Kreativiti Penyelidikan (RCMO) telah menerima laporan akhir daripada **Dr. Rosenani S. M. Anwarul Haque dari Pusat Pengajian Sains Kimia.**

3. Disampaikan laporan tersebut untuk tindakan tuan seperti berikut :-

(a) Penilaian untuk penutupan akaun projek ☑

(b) Lain-Lain ☐

Sekian, terima kasih.

"BERKHIDMAT UNTUK NEGARA"
'Memastikan Kelestarian Hari Esok'

Yang menjalankan tugas,

(NOOR ADNIE BAJURI)
Penolong Pegawai Tadbir
Unit Pengurusan Geran & Pembangunan Penyelidikan

s.k. Dr. Rosenani S. M. Anwarul Haque
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia

Pegawai Sains
Pelantar Sains Fundamental
Pejabat Pelantar Penyelidikan
Universiti Sains Malaysia

NAB/yu...penilaian laporan akhir (09 Ogos 2011)

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3 AUG 2011
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Prof Asma Ismail
Timbalan Naib Canselor Penyelidikan dan Inovasi
Universiti Sains Malaysia
11800 Pulau Pinang

1 Ogos 2011

di perakukan

Melalui:

Prof Wan Ahmad Kamil Che Mahmod
Dekan, Pusat Pengajian Sains Kimia

Prof. Dr. Wan Ahmad Kamil Mahmood
Dekan
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia

Prof Norita Mohamed
Timbalan dekan Penyelidikan
Pusat Pengajian Sains Kimia

Professor Norita Mohamed
Deputy Dean
(Research & Postgraduate Studies)
School of Chemical Sciences
Universiti Sains Malaysia

Yang berbahagia Prof

Laporan Akhir Geran Jangka Pendek.

Dengan segala hormatnya perkara di atas adalah di rujuk. Di sertakan di sini laporan akhir untuk geran penyelidikan jangka pendek seperti butir berikut:

Project Title	:	Mercury-N-heterocyclic carbenes (NHC) complexes as carbene transfer agents.
Grant Number	:	304/PKIMIA/639001
Project Coordinator	:	Dr. Rosenani SMA Haque
Date of Commencement	:	1st February 2009
Date of Expiry	:	31st January 2011
Amount	:	RM34,600

2. Sebanyak 11 penerbitan telah di hasilkan untuk projek ini, Sila lihat lampiran.

Sekian, harap maklum dan saya harap pihak Prof dapat mempertimbangkan permohonan geran penyelidikan jangka pendek saya yang akan menyusul dalam masa terdekat.

Salam hormat.

Yang benar

Rosenani

Dr Rosenani S.M. Anwarul Haque
Pensyarah Kanan
Pusat Pengajian Sains Kimia

Dr. Rosenani S.M. Anwarul Haque
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia
11800 Pulau Pinang

UNIVERSITI SAINS MALAYSIA

LAPORAN AKHIR PROJEK PENYELIDIKAN JANGKA *PENDEK*

FINAL REPORT OF SHORT TERM RESEARCH PROJECT

Sila kemukakan laporan akhir ini melalui Jawatankuasa Penyelidikan di Pusat Pengajian dan Dekan/Pengarah/Ketua Jabatan kepada Pejabat Pelantar Penyelidikan

1. Nama Ketua Penyelidik:
Name of Research Leader: **Rosenani SM Anwarul Haque**

☐ Profesor Madya/ *Assoc. Prof.* ☑ Dr./ *Dr.* ☐ Encik/Puan/Cik *Mr/Mrs/Ms*

2. Pusat Tanggungjawab (PTJ):
School/Department: **School of Chemical Sciences**

3. Nama Penyelidik Bersama:
Name of Co-Researcher

4. Tajuk Projek:
Title of Project: **Mercury-N-heterocyclic carbenes (NHC) complexes as carbene transfer agents.**

5. Ringkasan Penilaian/*Summary of Assessment:*	Tidak Mencukupi *Inadequate*		Boleh Diterima *Acceptable*	Sangat Baik *Very Good*	
	1	2	3	4	5
i) Pencapaian objektif projek: *Achievement of project objectives*	☐	☐	☐	☐	☑
ii) Kualiti output: *Quality of outputs*	☐	☐	☐	☐	☑
iii) Kualiti impak: *Quality of impacts*	☐	☐	☐	☐	☑
iv) Pemindahan teknologi/potensi pengkomersialan: *Technology transfer/commercialization potential*	☐	☐	☐	☑	☐
v) Kualiti dan usahasama : *Quality and intensity of collaboration*	☐	☐	☐	☐	☑
vi) Penilaian kepentingan secara keseluruhan: *Overall assessment of benefits*	☐	☐	☐	☐	☑

6. **Abstrak Penyelidikan**
(Perlu disediakan di antara 100 - 200 perkataan di dalam **Bahasa Malaysia dan juga Bahasa Inggeris**. Abstrak ini akan dimuatkan dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & masyarakat luar).

Abstract of Research
(An abstract of between 100 and 200 words must be prepared in Bahasa Malaysia and in English). This abstract will be included in the Annual Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large)

A Separate Sheet is Attached (Appendix 1)

7. **Sila sediakan laporan teknikal lengkap yang menerangkan keseluruhan projek ini. [Sila gunakan kertas berasingan]**
Applicant are required to prepare a Comprehensive Technical Report explaning the project. (This report must be appended separately)

A Separate Sheet is Attached (Appendix 2)

Senaraikan kata kunci yang mencerminkan penyelidikan anda:
List the key words that reflects your research:

Bahasa Malaysia	*Bahasa Inggeris*
Kompleks merkuri	Mercury complexes
Agen pemindahan karben	Carbene transfer agents
N-heterosiklik karben	N-heterocyclic carbenes

8. **Output dan Faedah Projek**
Output and Benefits of Project

(a) * **Penerbitan Jurnal**
Publication of Journals
(Sila nyatakan jenis, tajuk, pengarang/editor, tahun terbitan dan di mana telah diterbit/diserahkan)
(State type, title, author/editor, publication year and where it has been published/submitted)

A total of 11 publications in ISI indexed journals (A Separate Sheet is Attached-Appendix 3)

(b) **Faedah-faedah lain seperti perkembangan produk, pengkomersialan produk/pendaftaran paten atau impak kepada dasar dan masyarakat.**
State other benefits such as product development, product commercialisation/patent registration or impact on source and society.

This project helped us in many ways in the last couple of years, to quote important ones, the collaboration with different research unit (theoretical groups) which assisted us to get more insight into our research. In terms of output, we published eleven papers and one more is communicated in international repute peer-reviewed journals. Now we are inspired by the aid drawn from this project and in future we will go with the deeper and accurate research entities particularly exploring complexes that possess bioactivity; results of which will help the mankind and budding scientists working particularly in this domain of research.

* Sila berikan salinan/*Kindly provide copies*

(See appendix 3 for papers published)

(c) **Latihan Sumber Manusia**
Training in Human Resources

i) Pelajar Sarjana:
Graduates Students
(Perincikan nama, ijazah dan status)
(Provide names, degrees and status)

A Separate Sheet is Attached (Appendix 4)

ii) Lain-lain:
Others

9. Peralatan yang Telah Dibeli:
Equipment that has been purchased

Rosenani

Tandatangan Penyelidik
Signature of Researcher

Dr. Rosenani S.M. Anwarul Haque
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia
11800 Pulau Pinang

1/8/2011
Tarikh
Date

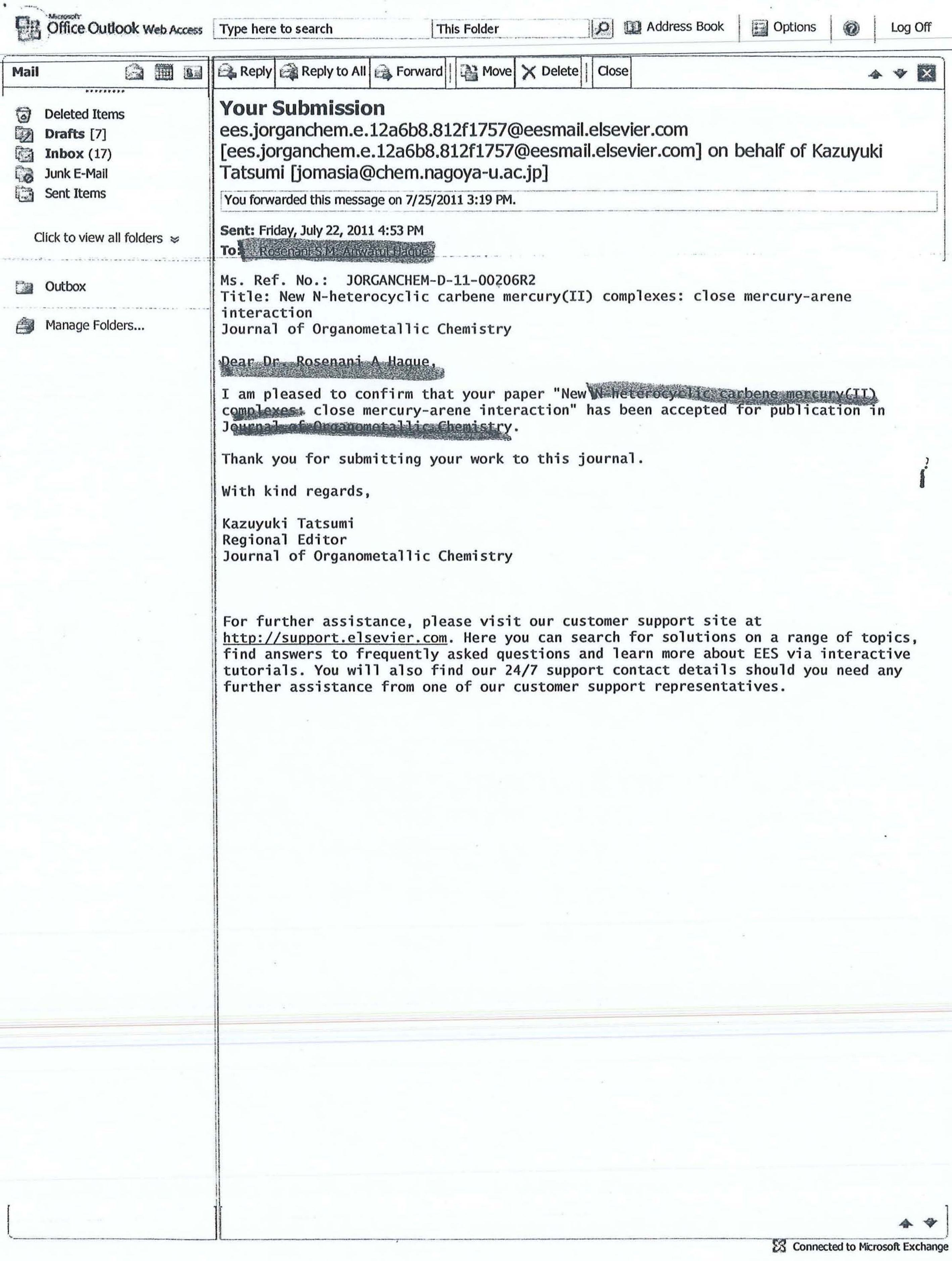
Komen Jawatankuasa Penyelidikan Pusat Pengajian/Pusat
Comments by the Research Committees of Schools/Centres

Project objectives have been met with numerous publications.

Professor Norita Mohamed
Deputy Dean
(Research & Postgraduate Studies)
School of Chemical Sciences
Universiti Sains Malaysia

TANDATANGAN PENGERUSI
JAWATANKUASA PENYELIDIKAN
PUSAT PENGAJIAN/PUSAT
Signature of Chairman
[Research Committee of School/Centre]

2/8/11
Tarikh
Date



Your Submission

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Ms. Ref. No.: JORGANCHEM-D-11-00206R2
Title: New N-heterocyclic carbene mercury(II) complexes: close mercury-arene interaction
Journal of Organometallic Chemistry

[redacted]

I am pleased to confirm that your paper "New [redacted] close mercury-arene interaction" has been accepted for publication in J[redacted].

Thank you for submitting your work to this journal.

With kind regards,

Kazuyuki Tatsumi
Regional Editor
Journal of Organometallic Chemistry

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Synthesis, characterization, and theoretical studies of xylyl linked bis-imidazolium and bis-benzimidazolium salts

*Muhammad Adnan Iqbal[a] [redacted], Shukri Sulaiman[b] Titia Izzati[b]

[a]*School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM Penang, Malaysia*

[b]*School of Distance Education, Universiti Sains Malaysia, 11800 USM Penang, Malaysia*

(*mai10_che022p@student.usm.my, *adnan_chem38@yahoo.com)

RECEIVED DATE (2011-6-1)

Abstract: Xylyl linked bis-imidazolium and bis-benzimidazolium salts were synthesized and characterized by spectroscopic techniques (NMR & FT-IR) and microanalysis. Density functional theory was used to calculate the binding free energies for acidic protons of both types of ligands and compared with the NMR results. The findings of this study provides a better understanding for the formation of free carbenes and therefore have potential applications to predict the complex formation reactions as well as to assess strength of coordination bonds with metals for imidazole and benzimidazole based ligands.

Key Words: Imidazolium salts, Benzimidazolium salts, Density functional theory

1. Introduction:

The use of *N*-heterocyclic carbene (NHC) ligands is increasing rapidly in the organometallic and inorganic coordination chemistry [1]. This increase in popularity of these complexes is due to their potential catalytical ability, as evidenced by growing research in this area [2]. Every year, a number of new NHC ligands are reported all around the world in which the main body of information is accumulated on imidazole based NHCs whereas their benzannulated counterparts are relatively unexplored [1, 3-6]. Benzimidazole compounds are of chemical and biological interest [7]. The activity associated with benzimidazole containing compounds has widely been studied which proves them as good Analgesic and anti-inflammatory agents [8], Antimicrobial and Anthelmentic agents [9], Anti-Ulcer agents [10], Gastric [H^+-K^+] AT phase inhibitory agents [11], and Anti-hypertension Agents [12]. In view of above, we synthesized imidazole and benzimidazole-based NHC ligands (**III** and **IV**, *Scheme 1*) and a theoretical study was performed to predict the formation and stability of their respective complexes.

The salts were synthesized by dual step synthesis. In the 1st step, respective alkyl halides (*i*-Pr & *n*-Pr bromides) were attached either to imidazole or benzimidazole according to modified method developed by Starikova *et al.* [13]. In the 2nd step *N*-substituted imidazole and benzimidazoles were linked to *ortho*-xylene dibromide and *meta*-xylene dibromide respectively using dioxane as a reaction medium (*Scheme 1*).

The structures of respective ligands (**III** and **IV**) were constructed by ChemBioDraw Ultra 12.0 and theoretical calculations were performed using the Gaussain 03 softwear package [14]. The ligands

Australian Journal of Basic and Applied Sciences

P-112, St. # 10, Haseeb Shaheed Colony, Faisalabad, Punjab, Pakistan. Tel: +92(0)3332227333, editor@insipub.com, www.insipub.com

Manuscript No. 4743-AJBAS Name: Rosenani A. Haque

Address: School of Chemical Sciences, Universiti Sains Malaysia, Minden 11800, Penang, Malaysia Tel: +604-653-3578, E-mail: rosenani@usm.my

Manuscript Title: Synthesis and characterization of new silver(I)- and mercury(II)-N-heterocyclic carbene complexes

Manuscript Review
Blind review policy)

Manuscript Type: Research ☑ Review ☐ Case Study ☐ Short Communication ☐

Does title reflect the content?	Yes ☑	No ☐	Average ☐
Does abstract provide a brief summary of the research?	Yes ☑	No ☐	Average ☐
s materials and methods appropriate for the aims of the study?	Yes ☐	No ☐	Average ☑
Does findings add new information to the literature?	Yes ☐	No ☐	Average ☑
Are the findings discussed properly?	Yes ☐	No ☐	Average ☑
Are the references related and up-to-date?	Yes ☐	No ☐	Average ☑
Does figures and tables reflect the content of the of the article?	Yes ☐	No ☐	Average ☑
s the use of English language appropriate?	Yes ☐	No ☐	Average ☑
Should the manuscript be shortened?	Yes ☐	No ☑	

te: ☑ shows selected option.

her comments (If any):

nclusion:_ ☐ 1- Publish as it is ☑ 2- Publish with minor corrections ☐ 3- Send for corrections ☐ 4- Reject

te: 17-05-2011

nvoice for Processing Cost

r. No.	Details		Amount (USD)
	Processing cost of manuscript		180.00/-
		Amount Received	0.00/-
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2,4-Bis(3-allylimidazolium-1-ylmethyl)mesitylene bis(hexafluorophosphate)

Rosenani A. Haque, Mohammed Z. Ghdhayeb, Madhukar Hemamalini and Hoong-Kun Fun

Comment

Since Arduengo's report of stable imidazol-2-ylidenes (Arduengo *et al.*, 1991), there has been growing interest in the use of *N*-heterocyclic carbene (NHC) species (Scott & Nolan, 2005). NHC ligands act as σ-donor ligands with minimal π-accepting. NHC ligands have proved to be particularly useful in olefin metathesis and palladium-catalyzed cross-coupling reactions. Imidazol-2-ylidene and imidazolin-2-ylidene-based ruthenium alkylidenes are more active and thermally stable than the original tricyclohexylphosphine-based systems developed by Scholl *et al.*, (1999). The title compound, (I), which possesses an imidazolidine ring, is a member of this NHC family.

The asymmetric unit of the title compound, (Fig. 1), consists of one 2,4-Bis(3-allylimidazolium-1-ylmethyl)mesityleninium dication and two hexafluorophosphate anions. The central benzene (C8–C13) ring makes dihedral angles of 89.80 (8)° and 85.23 (7)° with the terminal imidazole (N1/N2/C4–C6)/(N3/N4/C15–C17) rings. The P–F distances in the anion are in the range 1.5906 (9)–1.6161 (9) Å. This values agree with a previously reported crystal structure (Villegas *et al.*, 2005).

In the crystal (Fig. 2) of (I), the cations and anions are linked *via* intermolecular C—H···F (Table 1) hydrogen bonds forming a three-dimensional network.

Experimental

A mixture of imidazole (0.9 g, 13.2 mmol) and sodium hydroxide (0.5 g, 12 mmol) in DMSO (5 ml) was heated to 90°C for 2 hr. The mixture was cooled to room temperature using a water bath. To this mixture, a solution of 2,4-bis(bromomethyl) mesitylene (2 g, 6.5 mmol) in DMSO (10 ml) was added. The mixture was then heated to 40°C for 1 hr, then poured into water (40 ml) followed by cooling in ice. The precipitate formed was collected, washed with water, and recrystallized from methanol/water to give product A (1,3 - bis(N-imidazole -1- yl methyl) benzene) as a white solid (1.39 g, 56 %). Furthermore, a mixture of A (0.5 g, 1.3 mmol) and allyl bromide (0.4 g, 3.3 mmol) in acetonitrile (30 ml) was refluxed at 90°C for 24 hr. The solvent was removed under reduced pressure to give a pale-brown oil. The resulted bromide salt was converted to its hexafluorophosphate salt by metathesis reaction using KPF_6 (0.2g, 1.1 mmol) in 20 ml of methanol. The precipitate formed was collected and washed with distilled water (2 × 5 ml) and then recrystallized from acetonitrile to give colorless solid (0.41g, 87%). Colourless blocks of (I) were obtained by slow evaporation of the salt solution in acetonitrile at room temperature.

Refinement

Atoms H1A, H2A, H2B, H19A, H20A and H20B were located from a difference Fourier maps and refined freely [C–H = 0.96 (2)–1.01 (2) Å]. The remaining H atoms were positioned geometrically [C–H = 0.93–0.97 Å] and were refined using a

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1,3-Bis[(3-allylimidazol-3-ium-1-yl)-methyl]benzene bis(hexafluoridophosphate)

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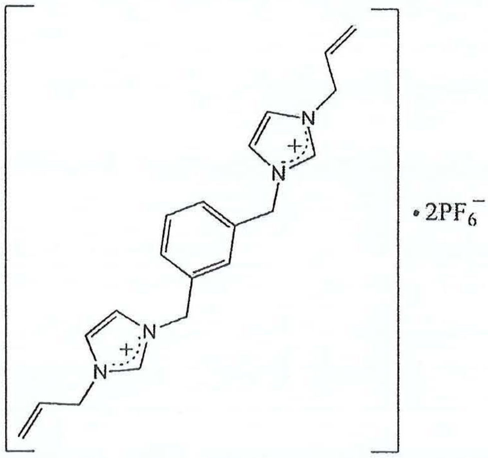
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.007 Å; disorder in main residue; R factor = 0.108; wR factor = 0.201; data-to-parameter ratio = 12.1.

In the title compound, $C_{20}H_{24}N_4^{2+}\cdot 2PF_6^-$, the ethene and 3-allylimidazolium moieties of the cation are disordered over two positions with refined site occupancies of 0.664 (19): 0.336 (19) and 0.784 (7):0.216 (7), respectively, whereas four F atoms of one hexafluoridophosphate anion and all atoms in the other hexafluoridophosphate anion are disordered over two positions with refined site occupancies of 0.764 (5):0.2365) and 0.847 (9):0.153 (9), respectively. The benzene ring is inclined at angles of 78.2 (3), 81.3 (4) and 73.9 (12)° with the 1*H*-imidazol-3-ium ring and the major and minor components of the disordered 1*H*-imidazol-3-ium ring, respectively. In the crystal, the hexafluoridophosphate anions link the cations into two-dimensional networks parallel to (001) *via* intermolecular C—H···F hydrogen bonds. The crystal structure is further consolidated by π–π [centroid–centroid distance = 3.672 (3) Å] and C—H···π interactions.

Related literature

For general background to and the biological activity of carbene derivatives, see: Yang & Nolan (2001); Böhm *et al.* (2000); Jafarpour & Nolan (2001); Bourissou *et al.* (2000); Herrmann *et al.* (1996, 1997); Arduengo *et al.* (1991); Danopoulos *et al.* (2002); Dias & Jin (1994); Caballero *et al.* (2001); Thompson *et al.* (1999); Melaiye *et al.* (2005). For bond-length data, see: Allen *et al.* (1987). For a related structure, see: Haque *et al.* (2010).



Experimental

Crystal data

$C_{20}H_{24}N_4^{2+}\cdot 2PF_6^-$
M_r = 610.37
Monoclinic, $P2_1/c$
a = 9.8748 (4) Å
b = 9.9098 (3) Å
c = 26.124 (1) Å
β = 101.138 (2)°
V = 2508.27 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.28 mm^{-1}
T = 296 K
0.25 × 0.20 × 0.20 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.921, T_{max} = 0.924
35601 measured reflections
5217 independent reflections
4324 reflections with $I > 2\sigma(I)$
R_{int} = 0.059

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.108
$wR(F^2)$ = 0.201
S = 1.14
5217 reflections
431 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*2 and *Cg*3 are the centroids of the N3*A*/N4*A*/C15*A*–C17*A* and N3*B*/N4*B*/C15*B*–C17*B* rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3*A*···F7*A*^{i}	0.93	2.40	3.276 (6)	156
C5—H5*A*···F5^{ii}	0.93	2.51	3.320 (6)	146
C8—H8*A*···F11*A*^{iii}	0.93	2.27	3.107 (8)	150
C10—H10*A*···F7*A*	0.93	2.25	3.130 (6)	158
C16*A*—H16*A*···F6^{iii}	0.93	2.48	3.407 (9)	172
C20*A*—H20*A*···*Cg*2	0.93	2.89	3.489 (11)	123
C20*B*—H20*C*···*Cg*3	0.93	2.84	3.44 (5)	124

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x, y-1, z$; (iii) $x+1, y, z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Potassium bis[bis(1-benzyl-3-methylimidazolium)silver(I)] tris(hexafluoridophosphate)

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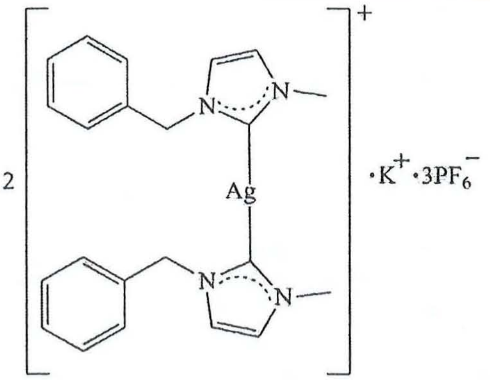
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.035; wR factor = 0.124; data-to-parameter ratio = 20.2.

In the title compound, $K[Ag(C_{11}H_{12}N_2)_2]_2(PF_6)_3$, the 12-coordinate potassium cation lies on a crystallographic twofold axis and one of the hexafluorophosphate anions is generated by $\bar{1}$ symmetry. In the complex cation, the Ag^I ion is coordinated by two C atoms; the two imidazolium rings are orientated at a dihedral angle of 8.14 (14)°. In the 1-benzyl-3-methylimidazolium units, the dihedral angles between imidazolium and phenyl rings are 80.47 (15) and 76.53 (14)°. The F atoms of the general-position hexafluorophosphate anion are disordered over two sets of sites in a 0.767 (17):0.233 (17) ratio. In the crystal, the hexafluorophosphate anions link the cations into three-dimensional networks *via* intermolecular C—H···F hydrogen bonds and are further consolidated by π–π stacking [centroid–centroid distances = 3.5518 (15) Å] interactions.

Related literature

For general background to and the biological activity of carbene derivatives, see: Lee *et al.* (2001); Bourissou *et al.* (2000); Herrmann & Köcher (1997); Hermann *et al.* (1996); Zhou *et al.* (2008); Wang & Lin (1998); Lin & Vasam (2007); Ray *et al.* (2007); Özdemir *et al.* (2010); Medvetz *et al.* (2008). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986). For related structures, see: Haque *et al.* (2010*a*,*b*). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$K[Ag(C_{11}H_{12}N_2)_2]_2(PF_6)_3$
M_r = 1378.65
Monoclinic, $C2/c$
a = 19.917 (2) Å
b = 23.047 (2) Å
c = 11.5787 (12) Å
β = 103.108 (3)°
V = 5176.4 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.04 mm^{-1}
T = 100 K
0.49 × 0.42 × 0.17 mm

Data collection

Bruker SMART APEXII DUO CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.632, T_{max} = 0.847
66454 measured reflections
7528 independent reflections
7058 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.124
S = 1.11
7528 reflections
372 parameters
51 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.91 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ag1—C12	2.092 (2)	Ag1—C1	2.093 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14A···F1^i	0.93	2.45	3.285 (5)	149
C15—H15A···F6	0.97	2.51	3.204 (5)	129
C15—H15B···F4^i	0.97	2.51	3.415 (7)	156
C22—H22A···F6^{ii}	0.96	2.42	3.171 (5)	135

Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (ii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Bis{1,4-bis[(3-butylimidazolium-1-yl)methyl]benzene}silver(I) bis(hexafluoridophosphate)

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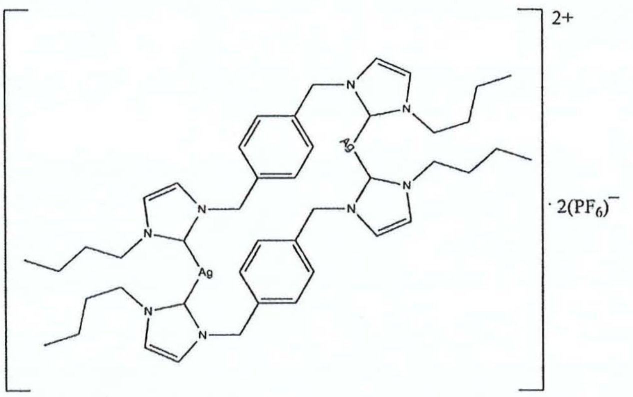
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.007 Å; R factor = 0.051; wR factor = 0.161; data-to-parameter ratio = 23.1.

The asymmetric unit of the title complex, $[Ag_2(C_{22}H_{30}N_4)_2](PF_6)_2$, consists of one Ag^I ion, one 1,4-bis[(3-butylimidazolium-1-yl)methyl]benzene ligand and one discrete hexafluoridophosphate anion. The formula unit is generated by an inversion center. The unique Ag^I ion is coordinated by two C atoms of two heterocyclic carbene ligands in an essentially linear geometry. In the crystal structure, cations and anions are linked through weak C—H⋯F hydrogen bonds, forming a three-dimensional network.

Related literature

For applications of *N*-heterocyclic carbenes, see: Tryg *et al.* (2005); Herrmann (2002); Herrmann *et al.* (1998); McGuinness *et al.* (1999); Tominaga *et al.* (2004); Magill *et al.* (2001); Yongbo *et al.* (2008); Garrison & Youngs (2005); Kascatan-Nebioglu *et al.* (2007); Özdemir *et al.* (2010); Medvetz *et al.* (2008); Catalano & Malwitz (2003). For a related structure, see: Chen & Liu (2003). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$[Ag_2(C_{22}H_{30}N_4)_2](PF_6)_2$
M_r = 1206.68
Triclinic, $P\bar{1}$
a = 11.3636 (15) Å
b = 11.4119 (15) Å
c = 11.9918 (15) Å
α = 63.528 (2)°
β = 89.335 (2)°
γ = 65.811 (2)°
V = 1241.7 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.94 mm^{-1}
T = 100 K
0.24 × 0.14 × 0.08 mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.806, T_{max} = 0.930
25433 measured reflections
7142 independent reflections
6512 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.161
S = 1.16
7142 reflections
309 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 3.16 e Å^{-3}
$\Delta\rho_{min}$ = −1.23 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C2—H2A⋯F3^{i}	0.93	2.42	3.251 (6)	149
C5—H5A⋯F1^{ii}	0.93	2.52	3.392 (6)	157
C7—H7B⋯F5^{ii}	0.97	2.44	3.367 (6)	160
C11—H11A⋯F6^{iii}	0.97	2.44	3.364 (7)	159
C11—H11B⋯F2^{iv}	0.97	2.38	3.129 (7)	134

Symmetry codes: (i) $-x+1. -y+1, -z$; (ii) $-x+1, -y+1, -z+1$; (iii) $x-1, y, z$; (iv) $-x+1, -y. -z+1$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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3,5-Bis(3-butylimidazolium-1-ylmethyl)-toluene bis(hexafluorophosphate)

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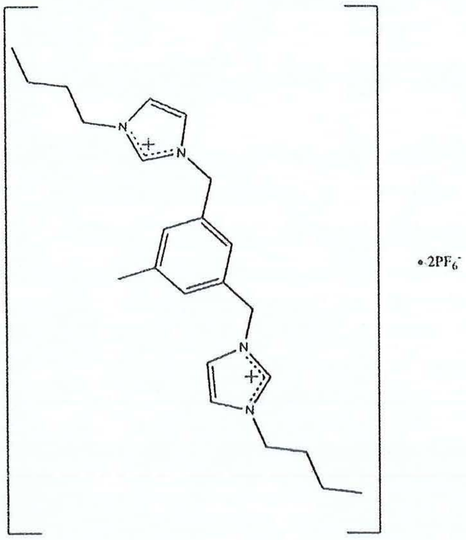
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; disorder in main residue; R factor = 0.046; wR factor = 0.122; data-to-parameter ratio = 23.2.

In the title compound [systematic name: 3,3′-Dibutyl-1,1′-(5-methyl-*m*-phenylenedimethylene)diimidazol-1-ium bis(hexafluoridophosphate)], $C_{23}H_{34}N_4^{2+}\cdot 2PF_6^-$, the imidazole rings are inclined at angles of 68.06 (7) and 75.05 (8)° with respect to the central benzene ring. In the crystal, molecules are linked into one-dimensional columns along [010] *via* weak intermolecular C—H···F hydrogen bonds. The crystal structure is further consolidated by weak C—H···π(arene) interactions. One of the *n*-butyl groups is disordered over two sites with refined occupancies of 0.694 (5) and 0.306 (5). In addition, four of the F atoms of one of the PF_6^- cations are disordered over two sites with occupancies of 0.64 (3) and 0.36 (3).

Related literature

For general background to imidazoline-2-ylidenes, see: Arduengo *et al.* (1991). For the organometallic and coordination chemistry of *N*-heterocyclic carbene ligands, see: Chen *et al.* (2002); Zhou *et al.* (2008); Hahn & Jahnke (2008); Danopoulos *et al.* (2007); Bourissou *et al.* (2000); McGuinness & Cavell (2000); Garrison *et al.* (2001). For catalytic studies related to organic synthesis, see: Cavell & McGuinness (2004); Liu *et al.* (2007). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986). For standard bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{23}H_{34}N_4^{2+}\cdot 2PF_6^-$
M_r = 656.48
Monoclinic, $P2_1/c$
a = 9.6207 (1) Å
b = 11.1801 (1) Å
c = 27.9277 (3) Å
β = 102.416 (1)°
V = 2933.66 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.25 mm^{-1}
T = 100 K
0.49 × 0.20 × 0.14 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{\min}$ = 0.890, $T_{\max}$ = 0.967
45569 measured reflections
10399 independent reflections
7294 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.122
S = 1.03
10399 reflections
448 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.39 e Å^{-3}
$\Delta\rho_{\min}$ = −0.26 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C1–C6 phenyl ring.

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8A···F4	0.93	2.42	3.0154 (16)	121
C8—H8A···F5	0.93	2.39	3.2700 (16)	157
C16—H16A···F3	0.93	2.31	3.1941 (16)	160
C16—H16A···F4	0.93	2.45	3.1677 (16)	134
C21A—H21B···F4	0.97	2.49	3.196 (2)	130
C3—H3A···F12$^{\rm i}$	0.93	2.44	3.3147 (16)	157
C5—H5A···F9$A^{\rm ii}$	0.93	2.55	3.420 (8)	156
C7—H7A···F10$A^{\rm ii}$	0.97	2.51	3.427 (6)	158
C9—H9A···F12$^{\rm iii}$	0.93	2.48	3.2805 (17)	144
C12—H12A···F3$^{\rm iv}$	0.97	2.53	3.3358 (18)	140
C18—H18A···F8$A^{\rm v}$	0.93	2.38	3.148 (11)	140
C22A—H22C···$Cg1^{\rm vi}$	0.96	2.76	3.535 (3)	138
C23—H23B···$Cg1^{\rm vii}$	0.96	2.59	3.487 (2)	155
C22B—H22E···$Cg1^{\rm vi}$	0.96	2.86	3.637 (8)	139

Symmetry codes: (i) $x-1, y+1, z$; (ii) $x-1, y, z$; (iii) $-x+1, -y+1, -z+2$; (iv) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (v) $-x+1, -y+2, -z+2$; (vi) $x+1, y, z$; (vii) $-x, -y+2, -z+2$.

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3,3′-Dibenzyl-1,1′-(2,4,6-trimethyl-*m*-phenylenedimethylene)diimidazol-3-ium dibromide

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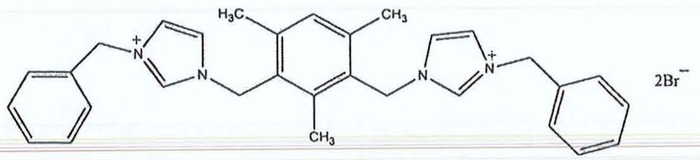
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; R factor = 0.040; wR factor = 0.101; data-to-parameter ratio = 25.2.

In the title molecular salt, $C_{31}H_{34}N_4^{2+}\cdot 2Br^-$, the central benzene ring makes dihedral angles of 80.47 (12) and 82.78 (12)° with the adjacent imidazole rings. The dihedral angle between the two terminal phenyl rings is 79.16 (13)°. In the crystal, the cations and anions are linked *via* C—H···Br hydrogen bonds, forming supramolecular chains along the c axis.

Related literature

For applications of *N*-heterocyclic carbenes (NHCs), see: Winkelmann & Navarro (2010); Papini *et al.* (2008); Marion *et al.* (2007); Burstein & Glorius (2004); Sohn *et al.* (2004); Grasa *et al.* (2002); Singh & Nolan (2005). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{31}H_{34}N_4^{2+}\cdot 2Br^-$
M_r = 622.44
Monoclinic, $P2_1/c$
a = 8.9851 (2) Å
b = 12.8044 (2) Å
c = 25.6419 (5) Å
β = 102.611 (1)°
V = 2878.90 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.84 mm^{-1}
T = 100 K
0.49 × 0.43 × 0.21 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.337, T_{max} = 0.585
32884 measured reflections
8490 independent reflections
6550 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.101
S = 1.04
8490 reflections
337 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7A···Br2	0.97	2.90	3.754 (2)	147
C7—H7B···Br1^{i}	0.97	2.92	3.787 (2)	149
C8—H8A···Br2	0.93	2.81	3.496 (3)	132
C10—H10A···Br1^{i}	0.93	2.74	3.565 (2)	148
C18—H18B···Br2^{ii}	0.97	2.74	3.702 (2)	172
C19—H19A···Br1^{i}	0.93	2.74	3.553 (2)	147
C21—H21A···Br2^{iii}	0.93	2.83	3.603 (3)	141

Symmetry codes: (i) $x+1, y, z$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $x+1, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2422).

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Structure Reports Online
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2,4-Bis[(3-butylimidazol-3-ium-1-yl)methyl]-1,3,5-trimethylbenzene bis(hexafluorophosphate)

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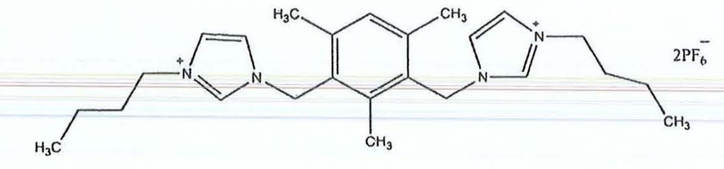
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; disorder in main residue; R factor = 0.055; wR factor = 0.135; data-to-parameter ratio = 19.4.

In the title molecular salt, $C_{25}H_{38}N_4^{2+}\cdot 2PF_6^-$, one of the butyl groups and four F atoms in the basal plane of one of the PF_6^- octahedra are disordered over two sets of sites, with occupancy ratios of 0.704 (5):0.296 (5) and 0.71 (3):0.296 (5), respectively. The central benzene ring makes dihedral angles of 85.17 (12) and 81.97 (12)° with the terminal imidazole rings. In the crystal, cations and anions are linked together *via* intermolecular C—H···F hydrogen bonds forming a three-dimensional network.

Related literature

For applications of *N*-heterocyclic carbenes, see: Tryg *et al.* (2005); Herrmann (2002); Tominaga *et al.* (2004); Magill *et al.* (2001); Arduengo *et al.* (1991); Herrmann & Kocher (1997); Herrmann *et al.* (1998); McGuinness *et al.* (1999). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{25}H_{38}N_4^{2+}\cdot 2PF_6^-$
M_r = 684.53
Monoclinic, $P2_1/n$
a = 12.3851 (2) Å
b = 19.6516 (3) Å
c = 12.7586 (2) Å
β = 104.698 (1)°
V = 3003.66 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 100 K
0.39 × 0.17 × 0.12 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.911, T_{max} = 0.971
34854 measured reflections
8766 independent reflections
5113 reflections with $I > 2\sigma(I)$
R_{int} = 0.064

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.135
S = 1.03
8766 reflections
453 parameters
177 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···F5^{i}	0.97	2.45	3.312 (3)	149
C5—H5*A*···F9*A*^{ii}	0.93	2.35	3.235 (9)	159
C6—H6*A*···F6^{ii}	0.93	2.51	3.248 (3)	136
C6—H6*A*···F12^{ii}	0.93	2.54	3.145 (3)	123
C7—H7*A*···F4^{iii}	0.93	2.32	3.140 (3)	146
C15—H15*A*···F10*A*^{iv}	0.97	2.54	3.103 (9)	117
C15—H15*A*···F11^{iv}	0.97	2.50	3.353 (3)	147
C19—H19*B*···F6^{iii}	0.97	2.54	3.327 (3)	138

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, -y, -z+1$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x+1, -y, -z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

RAH thanks Universiti Sains Malaysia for the FRGS fund (203/PKIMIA/671115), short-term grant (304/PKIMIA/639001) and RU grants (1001/PKIMIA/813023 and 1001/PKIMIA/811157). AWS thanks Universiti Sains Malaysia for the RU grant (1001/PKIMIA/843090). HKF and MH thank the Malaysian Government and Universiti Sains Malaysia for the Research University grant No. 1001/PFIZIK/811160. MH also thanks Universiti Sains Malaysia for a post-doctoral research fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ5098).

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3,3′-[1,2-Phenylenebis(methylene)]bis(1-heptylbenzimidazolium) dibromide monohydrate

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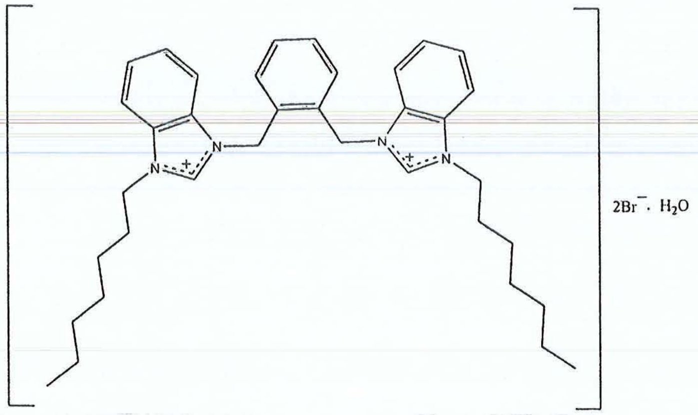
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; disorder in main residue; R factor = 0.032; wR factor = 0.077; data-to-parameter ratio = 29.3.

In the title salt, $C_{36}H_{48}N_4^{2+}\cdot 2Br^-\cdot H_2O$, the central benzene ring makes dihedral angles of 84.77 (9) and 69.92 (7)° with the adjacent imidazole rings. In the crystal, one of the heptyl groups is disordered over two sets of sites with an occupancy ratio of 0.474 (5):0.526 (5). In the crystal, the cations, anions and water molecules are connected *via* intermolecular O—H···Br, C—H···Br and C—H···O hydrogen bonds, forming a three-dimensional network.

Related literature

For details and applications of *N*-heterocyclic carbenes (NHCs), see: Winkelmann & Navarro (2010); Kascatan-Nebioglu *et al.* (2007); Teyssot *et al.* (2009); Herrmann *et al.* (1995); Choi *et al.* (2001); Kumar & Kumar (2009). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{36}H_{48}N_4^{2+}\cdot 2Br^-\cdot H_2O$
M_r = 714.62
Triclinic, $P\bar{1}$
a = 8.8494 (1) Å
b = 14.7170 (3) Å
c = 16.0838 (2) Å
α = 115.705 (1)°
β = 105.380 (1)°
γ = 91.946 (1)°
V = 1792.83 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.29 mm^{-1}
T = 100 K
0.39 × 0.18 × 0.16 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.469, T_{max} = 0.715
50860 measured reflections
12945 independent reflections
10091 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.077
S = 1.02
12945 reflections
442 parameters
9 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.84 e Å^{-3}
$\Delta\rho_{min}$ = −0.75 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W1···Br1	0.84 (3)	2.50 (3)	3.3271 (17)	169 (2)
O1W—H2W1···Br2	0.79 (3)	2.54 (3)	3.3280 (14)	177 (3)
C1—H1A···Br1^{i}	0.95	2.80	3.6093 (15)	144
C3—H3A···Br2^{ii}	0.95	2.92	3.7866 (16)	153
C5—H5A···Br2^{iii}	0.95	2.89	3.8162 (17)	167
C8—H8A···Br2^{iv}	0.99	2.93	3.9117 (16)	172
C15—H15A···Br2^{iv}	0.99	2.72	3.6809 (19)	165
C15—H15B···Br1^{iv}	0.99	2.80	3.7842 (15)	170
C18—H18A···O1W^{v}	0.95	2.46	3.187 (2)	133
C20—H20A···Br2	0.95	2.76	3.6602 (16)	158
C22—H22A···Br1^{i}	0.95	2.70	3.5577 (15)	150
C23—H23A···Br2^{i}	0.99	2.89	3.7836 (14)	151
C23—H23B···Br2^{ii}	0.99	2.81	3.7285 (17)	154

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1, y, z+1$; (iii) $x, y, z+1$; (iv) $-x, -y+1, -z+1$; (v) $x-1, y, z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2732).

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1,2–bis(allylimidazole-1-ylmethyl)benzene-bis(hexafluorophosphate)

(Oallyl)

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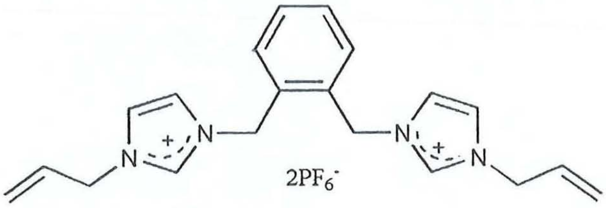


Comment

N-heterocyclic carbene (NHC) ligands have long been at the forefront of catalytic research and are studied extensively for the preparation of various transition metal catalysts (Bielawski and Grubbs.,2000; Herrmann *et al.*,1998). NHCs, on account of their strong chelation, stability towards air and moisture, modest cost and their availability in ionic form, makes them versatile precursors in catalysis ranging from C-C coupling to olefin polymerizations (Yeung *et al.*,2011; Jokic *et al.*,2010;Yu *et al.*,2010). The main point of focus in the reported compound is the presence of ally and methylene groups, which rotate the molecule when treated with metal ion to form a cage-like-structure suitable for the polymerization of ethylene and other higher olefins (Esteruelas *et al.*,2003). Fortified by the highly active and interesting characteristics obtained from complexes ligated by bis-carbene NHC backbone, the present ligand system is designed and synthesized in view of getting stable and active olefin polymerization catalyst.

Abstrak Penyelidikan / Abstract of Research

Bahasa

Satu siri ligan nobel *N*-heterosiklik karben (NHC) dan kompleksnya iaitu kompleks merkuri(II) yang mengandungi teras imidazol/benzimidazol disintesis dalam kadar hasil yang baik pada kos rendah-sederhana. Semua sebatian ini dicirikan dengan bantuan pelbagai spektro-analisis dan teknik pembelauan X-ray kristal tunggal. Kesemua sebatian nobel ini adalah dalam keadaan pepejal yang stabil, tidak sensitif terhadap udara dan lembapan dan mempunyai struktur yang sepadan dengan system katalitik aktif yang sedia ada. Kompleks Hg(II) menunjukkan interaksi kuat dengan atom karbon aril yang telah berjaya diselesaikan dengan bantuan kajian DFT. Tujuan kajian ini adalah untuk mencari parameter fizikal dan kimia, dimana ia sukar diperolehi secara eksperimen untuk kompleks, dan untuk mengkaji sifat interaksi bukan-ikatan antara Hg dan cincin aril. Pengiraan DFT telah menunjukkan bahawa pemindahan ion kaunter tidak menjejaskan jarak ikatan dan sudut ikatan yang disambungkan ke atom Hg sahaja. Ini mungkin mencerminkan sumbangan ion kaunter dalam ciri-ciri pusat logam elektronik. Kompleks Hg(II) yang disediakan digunakan dalam mengkaji tindak balas pemindahan karben bagi menghasilkan kompleks palladium(II) dan ruthenium(II), di mana kompleks ini mendapat tempat yang amat penting dalam penyelidikan biologi dan katalitik.

English

A series of novel *N*-heterocyclic carbene (NHC) ligands and their respective mercury(II) complexes bearing imidazole/benzimidazole core are synthesized in good yields at low-to-moderate costs. The compounds are characterized with the help of various spetro-analytical and single crystal X-ray diffraction techniques. All novel compounds are stable solids, non-sensitive towards air and moisture and possessing structural relevance with the existing catalytically active systems. X-ray studies and DFT calculations shows Hg(II) complexes to exhibit a unique binding behavior. In addition to bonding at the carbene centers, the Hg also shows strong interaction with an aryl carbon in the vicinity of the structure. DFT calculations provide physical and chemical parameters, which are difficult to obtain experimentally for the complexes as well as the nature of non-bonding interaction between the Hg and the aryl ring. DFT calculations have shown that removing the counter ions does affect the bond distances and bond angles connected to the Hg atom only. This may reflect the contribution of the counter ion in the electronic characters of the center metal. Prepared Hg(II) complexes are studied for carbene transfer reactions to produce palladium(II) and ruthenium(II)-NHC complexes, which found great importance in biological and catalytic research.

Comprehensive Final Report

Contents

Project Details

Project Title : Mercury-N-heterocyclic carbenes (NHC) complexes as carbene transfer agents.

Grant Number : 304/PKIMIA/639001

Project Coordinator : Dr. Rosenani SMA Haque

Date of Commencement : 1st February 2009

Date of Expiry : 31st January 2011

Researchers Employed : Students (PhD, masters and undergraduate)

Allotted Fund : RM34,600

Number of Publications : 11

% Utilization of Fund : 100 %

Remarks : Successfully completed

1. Project Overview

1.1. Consortium Description

The short term project (304/PKIMIA/639001) is solely a single consortium of Dr. Rosenani SMA Haque as a coordinator, followed by the assistance of a group of students to execute the project goals. This is the first project undertaken by Dr Rose after completion of her PhD in 2008. All researchers worked under this project share a common mission, which is to conduct research on the application of formal and new methods for the development of novel metal-based coordination compounds with *N*-heterocyclic carbene (NHC) ligands. Methods of preparation for NHC complexes have generated a lot of interests in the organometallic community for the past 2 decades due to the vast potential applications offered by these complexes. This project was inspired by Dr Rose's PhD preliminary results in NHC carbene transfer method using mercury complexes; a new and uncommon approach. This project has also generated interests of a couple of collaborators from USM and abroad. Our external collaborators in USM as well as in The University of Mauritius, are all prominent players in the entrenched related knowledge area, and contributed significantly in the structure analysis using single crystal X-ray diffraction technique and theoretical calculations. These collaborations helped us more to get insight into the structures of compounds which led to the decent achievements.

1.2. Main Achievements

In the project approach, the components of Hg-NHC complex systems are modeled as carbene transfer entities with well-defined dynamic parameters. Preparation of novel metal-NHC complexes have been at the forefront of many research areas. However, the stability, non-sensitiveness towards air and moisture, lower cost and particularly ease of preparation has been an issue. In this project, we have attempted to achieve confirmation, optimization, synthesis and design of NHC ligands and Hg(II) complexes so that the resulting behaviors of the complexes are correct, optimal and relevant. In this approach, we have successfully synthesized and characterized a series of NHC ligands and their Hg(II) complexes in good yields at low-to-moderate costs. Structures of many of the NHC-ligands and Hg(II) complexes have been determined by single crystal X-ray diffraction technique. All of the novel compounds are stable, and non-sensitive towards air and moisture and possessing structural relevance with the existing carbene transfer agents based on silver centered systems (a well-established system). The physical and chemical parameters of the Hg-NHC complexes that are difficult to obtain experimentally were obtained through the calculations using Density Function Theory (DFT). DFT calculations have shown that removing the counter ions does affect the bond distances and bond angles connected to the Hg atom only. This may reflect the contribution of the counter ion in the electronic characters of the center metal. On the other hand, few of the synthesized Hg(II)-NHC compounds showing fluorescence behavior, and the detailed investigations on the said activity will be conducted soon.

2. Project Objectives

The following description of the objectives of this project has been taken.

This project intends to contribute to the solutions for the growing synthetic inorganic chemistry needs to design reliable and efficient route for synthesis. In particular, it intends to provide novel methodologies and stable Hg(II)-NHC complexes for application as carbene transfer reagents. Its approach will be based on direct metallation of Hg source with NHC salts encompassing a heterocyclic core viz., imidazole or benzimidazole. The resulting Hg(II)-NHC complexes are used as carbene transfer agents to prepare Pd(II), Ru(II) and Sn(II)-NHC complexes. This academic research outcome, in the form of novel compounds, the methods and tools of which can be a basis for the next generation research practice of such systems. In addition to its technological contributions, this project invests actively in knowledge transfer to the many researchers working on analysis and design of metal-NHC compounds. The main objectives of this project are listed below.

1. To synthesize meta-cyclophanes and related bis-imidazolium salts as precursors to NHC.
2. To synthesize and characterize mercury complexes of NHC
3. To transfer the NHC from mercury complexes to Pd(II), Ru(II) and Sn(II) as an alternative method for the complex preparations.
4.

3. Project Methodologies, Results and Achievements

3.1. Hg(II) based system developments

The persistence of this segment of report is to summarize the developments that took place within this project and put them in a larger scientific and technological context. We start with a general overview of model Hg-NHC-based design and analysis of systems from which the approach advocated by this project has emerged. The principles underlying this approach are those underlying the design and synthesis of stable coordination compounds relevant to the carbene transfer systems with respect to the nature of metal ion, extent of chelation, type of ligand, nature of heterocyclic ring system and counter ions. We then move to the more specific goal of the project, viz., the design of ligand periphery with imidazole or benzimidazole core provides suitable topology for the non-typical transition metal center. Moreover, it is expected that the academic propagation of this research results will influence and advance the field of synthetic organometallic chemistry of non-typical transition metal-NHC complexes. Considerable further work on applications as carbene transfer agents, with alternative approaches, all in the context of case studies of greater orders of magnitude, is needed to develop this Hg-NHC series into readily applicable standards.

3.2. Methodologies

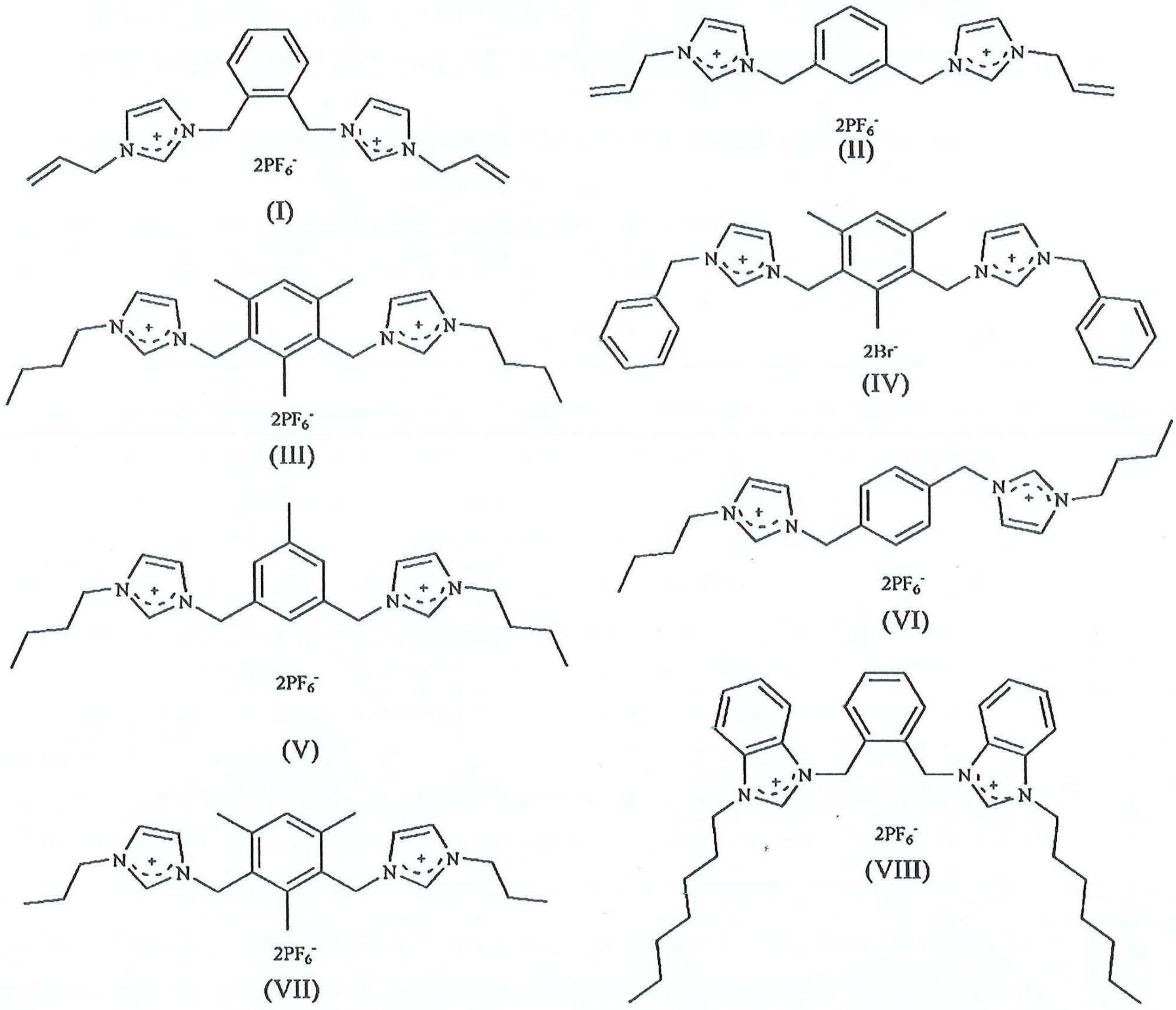
It is important to notice that the presence of sp^3 hybridized carbon and nitrogen atoms give more and more rigidity and robustness to the NHC-ligand systems which is the ease for the formation of stable metal-NHC complexes. Further, once the non-typical metal-NHC complex is formed, it is easy to proceed with the transition metal-NHC complexes using trans-metallation reactions which are like electrophilic inorganic substitution reactions. While working with the ligand systems, we found an easier and novel method for the preparation of NHC imidazolium salts, which save valuable time and expensive solvents. As an example, in the preparation of 1, 2–bis(allylimidazole-1-ylmethyl)benzene-bis(hexafluorophosphate) salt, we followed novel method of preparation as mentioned in the following way. A mixture of imidazole (0.9 g, 13.0 mmol) and sodium hydroxide (0.5 g, 12 mmol) in DMSO (5mL) was heated to 90 °C for 2 h, and then was cooled to room temperature. A solution of 1,2-bis(bromomethyl)benzene (1.5 g, 5.7 mmol) in DMSO (10 mL) was added to the mixture and heated slowly to 40 °C for 1 h with constant stirring. So obtained solution was poured into ice-cold water (40 mL). The precipitate was collected, washed with water, and recrystallized from methanol/water to give 1,2–bis(N-imidazole-1-ylmethyl)benzene [1] as a white solid (0.95 g, 79 %). Further, a mixture of [1] (0.5 g, 2.1 mmol) and allyl bromide (0.7 g, 6.1 mmol in acetonitrile (20 mL) was refluxed for 24 h. The solvent was removed under reduced pressure to result pale-brown oil, which was converted directly to its corresponding hexafluorophosphate salt by metathesis reaction using KPF6 (0.76g, 4.0 mmol) in 20 ml of methanol. The precipitate formed was collected and washed with distilled water (2 × 5 mL), and recrystallized from acetonitrile to give colorless solid. (1.1 g, 80 %). Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the salt solution in acetonitrile at room temperature.

3.3. Results and Discussion

In this section of the report, we are summarizing all the results which we got during last two years with the aid of this project. A large part of organometallic chemistry and catalysis is concerned with designing suitable models of metal-carbon frameworks. The class of models advocated in this project has its origins in the domain often called organometallics whose goal is to prove that, the separate array of compounds, especially, metal-NHCs, in which metal-to-carbon bonding is possible and such compounds are useful in biological and catalysis fields. We strongly believe that the phenomena of Hg(II)-NHCs relevant to the Ag(I)-NHC systems come first and that it is more useful to understand them and devise new novel models, whose semantics corresponds faithfully to these phenomena, rather than to rush and translate their study only on structural diversity factor. Both, Ag(I) and Hg(II) have the same number of outer electrons and expected to exhibit the similar properties. It is found in the literature that a large number of Ag(I)-NHCs are employed for the carbene transfer reactions and hence an attempt is made with Hg(II)-NHCs to get the similar results.

Under this headline, we have designed, synthesized and successfully characterized many series of Hg(II)-NHC compounds. There are numerous NHC ligands of bis-carbene imidazolium/benzimidazolium salts prepared and characterized (Figure-1) using various analytical techniques. On the other hand, 3-benzyl-1-alkylimidazolium salts act as mono- and bis-carbene chelates towards Ag(I) and Hg(II) are shown in Figure-2. Similarly, another set of bis-carbeneimidazolium salts with aryl-alkyl spacer ligands and their Ag(I) and Hg(II) complexes are shown in Figure-3. In case of compounds XI to XIV, X-ray studies reveal the mercury atom is coordinated to two carbene carbons of the imidazolium rings in linear arrangement. Apart from this, an interesting thing is observed in these cases that, there is a close interaction between the Hg centre and one of the carbon atoms of the aryl linker [Hg-C(arene) bond distances [2.742(2) for XI; 2.750(5) for XII; and 2.724(13) Å for XIII]. So it is thought to work for the theoretical studies viz., Density Function Theory (DFT) calculations, to go get more insight into the nature of bonding between Hg and carbon atoms of the aryl linker.

The aim of the DFT calculations is to find physical and chemical parameters, which are difficult to obtain experimentally for the Hg-NHC complexes, and to study the nature of non-bonding interaction between the Hg and the aryl ring. DFT calculations have shown that removing the counter ions does affect the bond distances and bond angles connected to the Hg atom only. This may reflect the contribution of the counter ion in the electronic characters of the metal center. Further, it is shown that the calculated distances between the Hg atom and the carbon atom of the aryl rings are in agreement with the crystal structure. However, the C-H out of plane bending is absent, indicating that this is a non-bonding interaction. In addition, these calculations are in the gas phase; thus, the molecule from any crystal effect that may cause such bending are released.



(I) (II) (III) (IV) (V) (VI) (VII) (VIII)

Figure-1. Bis-carbene imidazolium/benzimidazolium salts.

But the distance is not sufficiently short to be indicative of a significant bonding interaction. However the distances are much shorter than the sum of van der Waals radii of the respective elements. Therefore we feel that the C-arene bond distances in mercury complexes are best described as "close interactions" and since so far we only observe this in Hg-NHC complexes, we are inclined to regard it as quite unique for Hg-NHC.

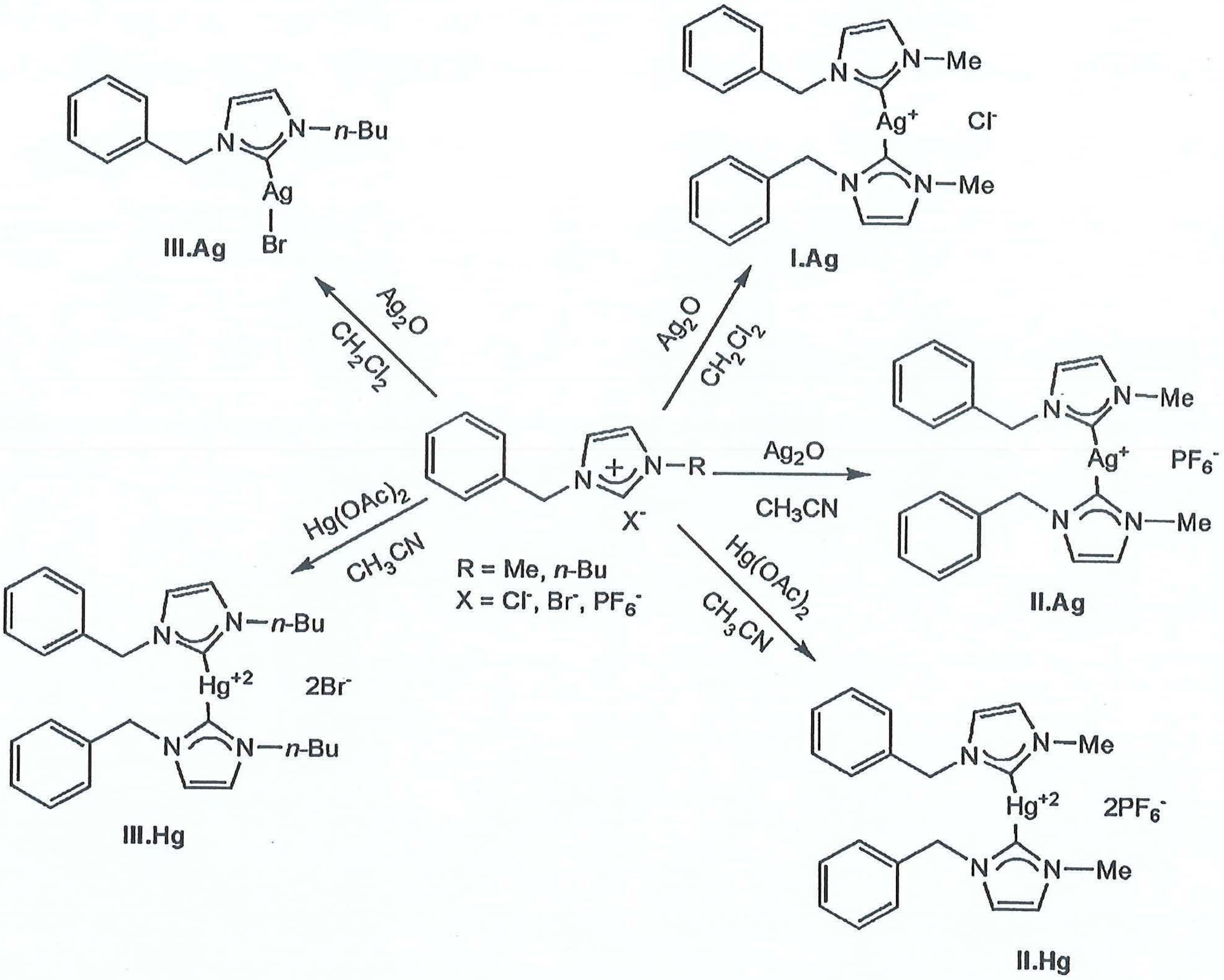
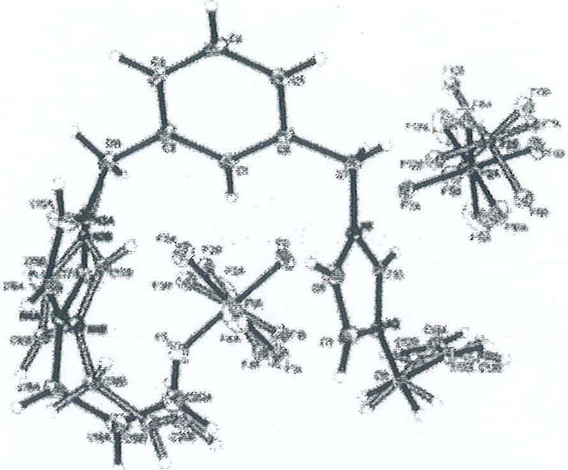
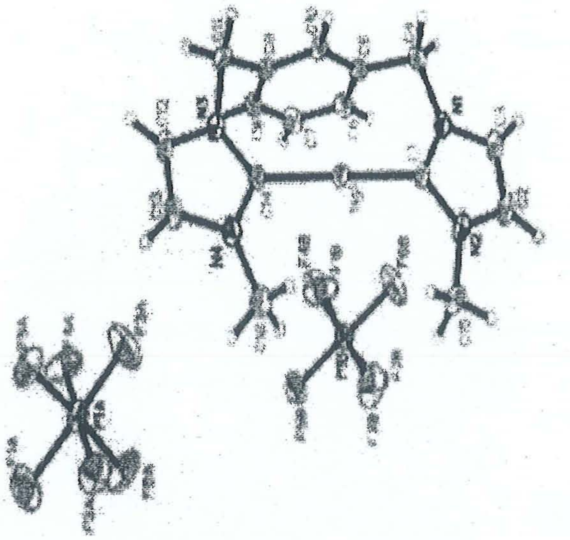
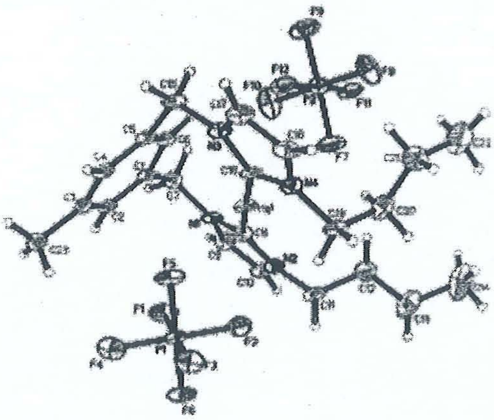


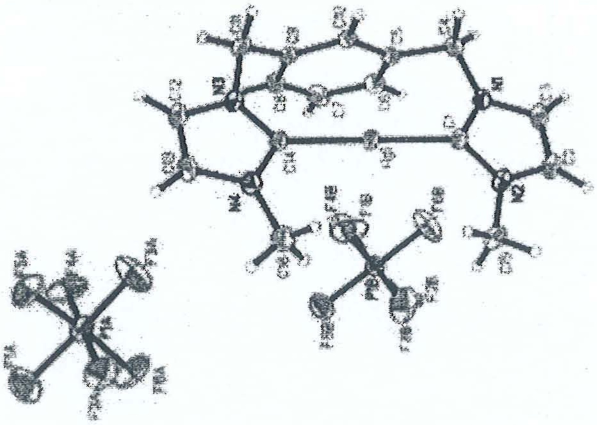
Figure-2. 3-Benzyl-1-alkylimidazolium salts act as mono-carbene chelates towards Ag(I) and Hg(II).

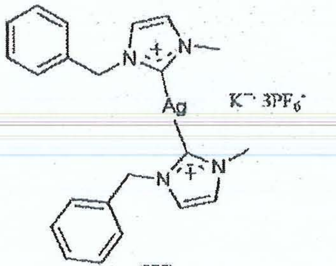
Followings are the pictures of structure determination using single crystal X-ray analysis.



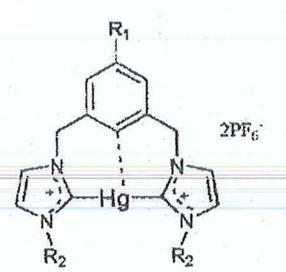




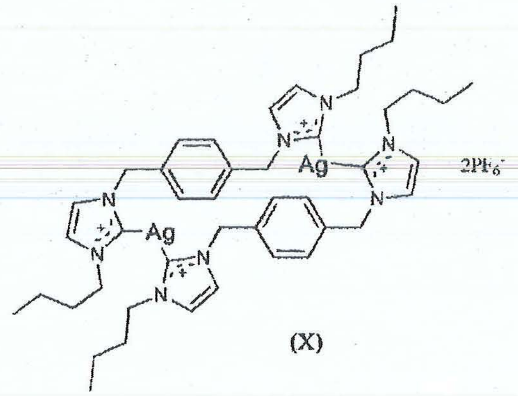




(IX)



(XI) - R_1: H, R_2: CH_3
(XII) - R_1: CH_3, R_2: CH_3
(XIII)- R_1: H, R_2: C_4H_9
(XIV)- R_1: CH_3, R_2: C_4H_9



(X)

Figure-3. Bis-carbeneimidazolium salts with aryl-alkyl spacer ligands and their Ag(I) and Hg(II) complexes.

Overall, the project moves towards this goal along several tracks that the more profound carbene transfer investigations are needed to call these as the compounds of choice in the future days. Indeed much of the project's resources are being spent on synthesis and their structural characterizations using single crystal X-ray analysis. A second direction aims to improve the situation regarding the 3-dimemtional structure-activity-relationship of the Hg complexes and their resemblance, both structural and functional with standard Ag-NHCs available in the literature.

Please see Appendix 5 for results of DFT calculation on the mercury complexes.

3.4. Achievement of the Objectives

All objectives which we have before getting this project were successfully achieved in the last couple of years with many interesting outcomes. The most important discovery was achieved in the last year, i.e. a very good abstraction on close interaction studies of aryl ring system to Hg atom which is now in press for publication in The Journal of Organometallic Chemistry. We hope to be successful in the design and synthesis of metal-arene close interaction studies which may take us to a fascinating world of molecular switches/devices.

In order to mention the done things, a series of NHC-ligands bearing imidazole or benzimidazole were prepared and successfully characterized. Using these ligand systems, a series of Hg(II) and Ag(I) complexes were prepared and characterized. Finally, by trans-metallation reactions of prepared Hg(II) complexes, the last objective of the preparation of Pd(II), Ru(II) and Sn(II) complexes was completed and yet few more research articles will be communicated in the nearest future gathering the results of this project.

4 Out Looks

The project enabled us to prepare and characterize a series of NHC ligands with mono and bis-imidazolium/benzimidazolium salts and their respective Ag(I), Hg(II), Pd(II), Ru(II) and Sn(II) complexes. All prepared Hg(II)-NHC complexes efficiently act as carbene transfer agents in order to prepare novel Pd(II), Ru(II) and Sn(II)-NHC complexes. It is scheduled to analyze further for catalytic activity of Pd(II) and Ru(II)-NHC complexes which shown remarkable structural relevance with the existing catalysts.

5 Conclusions

It is concluded that the close interaction studies of Hg and arenes carbon atoms was very inspiring to the project, in particular during the last half of the project. It exposed at the same time the catalysis study of the prepared Pd(II) and Ru(II)-NHC complexes was most notably concerning complexity issues. Perhaps, we defended the situation more clearly and still even more insights are needed for both studies. With exception of the new abstraction reported here, one can safely state that a full comprehension of the study on Hg(II)-NHC complexes was achieved after about 24 months and that, consequently, the interest of the consortium shifted to harder and unresolved challenges of other issues of the prepared compounds like close interaction studies, catalytic activities, etc., arise at the end. Concerning the original goals of this project, important parts were achieved already in the first half of the project. The impression that we did not have the right abstraction for conquering is the catalytic activity and that we will conduct in future. In summary, the project on Hg(II)-NHC complexes can be considered a success, a proof that the use of knowledge can lead to new insights into a complex problem.

Appendix 3 List of papers published

1. (Original research article)

   New N-heterocyclic carbene mercury(II) complexes: close mercury-arene interaction.

   Rosenani A. Haque, Abbas Washeel Salman, Teoh S. Guan, Hassan H. Abdllah.

   J. Organomet. Chem. (Accepted)

2. (Original research article)

   Synthesis and characterization of new silver(I)- and mercury(II)-N-heterocyclic carbene complexes.

   Rosenani A. Haque, Abbas Washeel Salman, Teoh Siang Guan

   Aust. J. Chem. (Accepted)

3 (Original research article)

2,4-Bis(3-allylimidazolium-1-ylmethyl)mesitylene-bis(hexafluorophosphate)

Rosenani A. Haque, Mohammed Z. Ghdhayeb, Madhukar Hemamalini and Hoong-Kun Fun.

Acta Cryst. (Accepted)

4 (Original research article)

2,4-Bis[(3-butylimidazol-3-ium-1-yl)-methyl]-1,3,5-trimethylbenzene-bis(hexafluorophosphate)

Rosenani A. Haque, Abbas Washeel Salman, Madhukar Hemamalini and Hoong-Kun Fun.

Acta Cryst. (2011). E67, o562.

5 (Original research article)

3,3'-Dibenzyl-1,1'-(2,4,6-trimethyl-m-phenylenedimethylene)diimidazol-3-iumdibromide.

Rosenani A. Haque, Abbas Washeel Salman, Paremala Nadarajan, Madhukar Hemamalini and Hoong-Kun Fun.

Acta Cryst. (2011). E67, o643.

6 (Original research article)

Potassium-bis[bis(1-benzyl-3-methylimidazolium)silver(I)] tris(hexafluoridophosphate)

Rosenani A. Haque, Abbas Washeel Salman, Choong Kah Whai, Ching Kheng Quah and Hoong-Kun Fun.

Acta Cryst. (2011). E67, m97.

7 (Original research article)

1,3-Bis[(3-allylimidazol-3-ium-1-yl)-methyl]benzene bis(hexafluoridophosphate)

Rosenani A. Haque, Mohammed Z. Ghdhayeb, Hassan H. Abdallah, Ching Kheng Quah and Hoong-Kun Fun. *Acta Cryst.* (2011). E67, o80.

8 (Original research article)

3,3'-[1,2-Phenylenebis(methylene)]bis(1-heptylbenzimidazolium)dibromide monohydrate

Rosenani A. Haque, Muhammad Adnan Iqbal, Madhukar Hemamalini and Hoong-Kun Fun
Acta Cryst. (2011). E67, o1814.

9 (Original research article)

Synthesis, characterization, and theoretical studies of xylyl linked bisimidazolium and bisbenzimidazolium salts

Muhammad Adnan Iqbal , Rosenani A. Haque, Shukri Sulaiman and Titia Izzati.
J. Chem. (2011), 2, 17.

10 (Original research article)

3,5-Bis(3-butylimidazolium-1-ylmethyl)-toluene-bis(hexafluorophosphate)

Rosenani A. Haque, Abbas Washeel, Siang Guan Teoh, Ching Kheng Quah and Hoong-Kun Fun.

Acta Cryst. (2010). E66, o2797.

11 (Original research article)

Bis{1,4-bis[(3-butylimidazolium-1-yl)-methyl]benzene}silver(I) bis(hexafluoridophosphate)

Rosenani A. Haque, Abbas Washeel, Siang Guan Teoh, Madhukar Hemamalini and Hoong-Kun Fun.

Acta Cryst. (2010). E66, m1286.

Communicated article

12 (Original research article)

1,2–bis(allylimidazole-1-ylmethyl)benzene-bis(hexafluorophosphate)
Rosenani A. Haque and Mohammed Z. Ghdhayeb.
Acta Cryst.

Appendix 4: List of Students

1. Abbas W. Salman April 2009, PhD student title of research: Carbene Transfer Reactions from Silver and Mercury *N*-heterocyclic carbenes (NHC) complexes to Tin as Anti-tumor and Anti-microbials Agents.
2. Nurdiyana Abdul Rashid March 2009 Final year project; Transmetallation of Silver Complex of *N*-heterocyclic Carbene to Tin.
3. Trinna Leong March 2009 Final year project; Synthesis, Characterization and Transmetallation of Silver and Tin *N*-Heterocyclic Carbene Complexes.
4. Lim Chin Teik March 2009 Final year project; Synthesis and Characterization of Silver and Mercury Complexes of Imidazolium-linked *Meta*-cyclophane.
5. Zetty Zulikha Hafiz March 2010 Final year Project: Mercury, Silver and Ruthenium complexes of *N*-heterocyclic carbene: synthesis, characterization and transfer reaction.
6. Mohd Zulhasnan Zurani March 2010 Final year Project: Synthesis and Structural Determination of Mercury *N*-heterocyclic carbene complex.
7. Siti Fatimah Nasri March 2010 Final year Project: Synthesis and Characterization of Silver and Mercury *N*-heterocyclic carbene complexes
8. Mohamad Z. Ghdhayeb March 2010, full time PhD student project title: Silver and Vanadium Complexes of New *N*-Heterocyclic Carbenes as Anti-diabetic Agents.
9. Name : Choong Kah Whai Final year Project 2010 Title : Synthesis and Characterization of N-heterocyclic carbene compounds of Zinc via transmetallation.
10. Name : Paremala a/p Nadarajan Final year Project 2010 Title : Carbene transfer from NHC - Ag to Ni^{+2}.
11. Name : Zetty Zulikha binti Hafiz Masters project Research title : Synthesis, characterization and computational studies of ruthenium-NHC complexes.
12. Siti Fatimah Bt Nasri Masters project Title: Syntheses, Characterization and computational studies of ruthenium-, silver and gold- N-Heterocyclic carbenes (NHC) complexes.
13. Noorhafizah Bt Hasanudin Title: Synthesis, characterisation and computational studies of cobalt- N-Heterocyclic carbenes (NHC) complexes.
14. Muhammad Adnan Iqbal Title: The synthesis of Imidazole linked Salophenes (NHC) and derivatives, a new class of NHC ligands , their Ag and Hg complexes for the transmetallation to Ln-NHC complexes using redox transmetallation method, structure, characterization and biological applications.
15. Damien Khoo Yiyuan Title: Synthesis and Characterisation of Neodymium-NHC Complexes via Transmetallation Period: Final Year Project, Sem 1 2010/2011 until Sem 2 2010/2011

Appendix 5

Results of theoretical calculations

The aim of the DFT calculations is to find physical and chemical parameters, which are difficult to obtain experimentally for the mercury complexes, and to study the nature of non-bonding interaction between the Hg and the aryl ring. Two types of starting structures have been subjected to the DFT calculations, with and without the two PF_6^- counter ions, in an attempt determine the effect of the counter ions on the energy and the geometry of the three complexes.

DFT calculations have shown that removing the counter ions does affect the bond distances and bond angles connected to the Hg atom only. This may reflect the contribution of the counter ion in the electronic characters of the center metal. Figure 6 shows the numbering of the common atoms between the three crystal structures, which can be considered as the active site for the theoretical study.

Table 1 shows the comparison between the bond distances and bond angles in the active site for the three complexes, theoretically and experimentally, in the presence of the counter ions. DFT calculations have shown that the calculated distances between the Hg atom and the carbon atom of the aryl rings are in agreement with the crystal structure. However, the C-H out of plane bending is absent, indicating that this is a non-bonding interaction. In addition, these calculations are in the gas phase; thus, the molecule from any crystal effect that may cause such bending are released.

Given that the NBO method provides more realistic charges than Mullikan, the charges for the active site of the title complexes were calculated and are tabulated in Table 2. In addition, the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy barrier, the dipole moment, and the thermodynamic parameters are reported.

Methods of calculations. Density functional theory (DFT) calculations were performed using Gaussian 03.[16] The crystal structures of the three mercury complexes were optimized in the gas phase in the ground state without any constraints. Use of DFT Becke's three-parameter Lee-Yang-Parr exchange-correlation functional (B3LYP) method with basis set 6-31G(d) for the atoms C, H, N, P, and F and the correlation-consistent pseudopotential cc-pVDZ-pp basis set developed by Dunning and coworkers for the Hg atom has been described in a previous study.[17] The optimized geometry of the three crystals was used to run the natural bond orbital (NBO), which is more robust than traditional Mullikan approach. In addition, NBO provides a localized depiction of the electron density over the molecule.

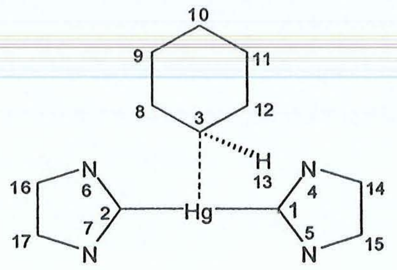


Table 2. Energy, charges, HOMO-LUMO barrier, and thermodynamic parameters for the active site of the three complexes with counter ions.

Structure	**Crystal 1** Methyl-comp	**Crystal 2** M-Butyl-comp	**Crystal 3** Butyl-complex
Energy /a.u.	-2874.1983	-3149.4088	-3100.0577
Charge			
Hg	0.951	0.929	0.990
C_3	-0.247	-0.260	-0.264
C_1	0.077	0.072	0.013
C_2	0.073	0.071	0.054
H_{13}	0.280	0.278	0.244
C_8	-0.074	-0.071	-0.093
C_9	-0.196	-0.191	-0.202
C_{10}	-0.198	0.012	-0.202
C_{11}	-0.190	-0.188	-0.180
C_{12}	-0.072	-0.071	-0.050
N_4	-0.360	-0.359	-0.356
N_5	-0.353	-0.356	-0.348
N_6	-0.360	-0.359	-0.364
N_7	-0.350	-0.350	-0.353
HOMO/a.u.	-0.2747	-0.2609	-0.2751
LUMO/a.u.	-0.0494	-0.0430	-0.0801
Difference (L-H)	0.2253	0.2180	0.1950
Dipole Moment/Debye	4.7719	2.9756	20.4534
Bond orbital btw Hg-C	s-sp^2	s-sp^2	s-sp^2
ΔS/kcal.mol^{-1}	0.21	0.27	0.25
ΔH/a.u.	-2873.80	-3148.80	-3109.48
ΔG/a.u.	-2873.90	-3148.93	-3109.60