CrossMark
click for updates

View Article Online
View Journal

Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. Monticelli, C. Tubaro, M. Baron, M. Basato, P. Sgarbossa, C. Graiff, G. Accorsi, T. P. Pell, D. J. Wilson and P. Barnard, *Dalton Trans.*, 2016, DOI: 10.1039/C6DT01129B.

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Please do not adjust margins

ROYAL SOCIETY OF CHEMISTRY View Article Online
DOI: 10.1039/C6DT01129B

Journal Name

ARTICLE

Metal complexes with di(N-heterocyclic carbene) ligands bearing a rigid *ortho*-, *meta* or *para*-phenylene bridge

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Marco Monticelli,[a] Cristina Tubaro,*[,a] Marco Baron,[a] Marino Basato,[a] Paolo Sgarbossa,[b] Claudia Graiff,[c] Gianluca Accorsi,[d] Thomas P. Pell,[e] David J. D. Wilson[e] and Peter J. Barnard*[,e]

Three novel dinuclear bis-dicarbene silver(I) complexes of general formula $[Ag_2(MeIm\text{-}phenylene\text{-}MeIm)_2](PF_6)_2$ (Im = imidazol-2-ylidene) were synthesized. The corresponding copper(I) and gold(I) complexes were obtained by transmetalation of the di(N-heterocyclic carbene) ligand from the silver(I) species, and both coordination geometry and stoichiometry are maintained for all three group 11 metals as expected. The photophysical properties of the Ag(I) and Au(I) complexes were also investigated and discussed; in particular the most strongly emitting complex was also studied via DFT calculations. In addition, the ruthenium(II) and iridium(III) complexes [RuCl(MeIm-(*o*-phenylene)-MeIm)(*p*-cym)](PF_6) and [IrClCp*(MeIm-(*o*-phenylene)-MeIm)](PF_6) were prepared and shown to present in these cases a chelating coordination of the di(N-heterocyclic carbene) ligand.

Introduction

Late transition metal complexes of N-heterocyclic carbene (NHC) ligands[1] have been intensively investigated over the last twenty years.[2] This attention results from the wide range of possible applications of complexes of this type in catalysis,[3] material science[4] and bioinorganic chemistry.[5] Recently there has been much interest in the preparation and study of luminescent NHC complexes of late transition metals[6] e.g. Cu(I),[7] Ag(I),[8] Au(I,III),[9] Ni(II),[10] Pd(II),[10,11] Pt(II),[10-12] Ir(III),[13] Ru(II).[14] Due to the planar nature of NHCs, these donors are well suited to the synthesis of luminescent dinuclear Au(I) complexes that support short aurophilic Au···Au interactions. A number of complexes of this type with di(N-heterocyclic carbene) ligands (diNHC)[15] and a variety of linker groups have been reported and some of them display fascinating luminescent properties.[16-21] Generally the di(N-heterocyclic carbene) ligands (diNHC) have either an alkyl chain, $(CH_2)_n$ (n = 1 - 4), or a *ortho*-, *meta*- or *para*-xylylene as bridging group between the two carbene moieties.

In this work, we extend our studies to rigid *ortho*-, *meta*- and *para*-phenylene bridging groups. The different substitution patterns on the phenylene ring were found to influence the bridging versus chelating coordination properties of the dicarbene ligands. A limited number of examples have been previously reported in the literature with this class of ligands[22-35] and, in most cases they involve diNHC groups with the *meta*-phenylene bridge. This choice is justified by the fact that these ligands commonly behave as *CCC*-pincers, as a consequence of metalation of the carbon in position 2 of the phenylene bridge (mainly to Ir(III),[22,24] Ru(II)[26,30] or Pt(II)[19]).

In the present study, a series of dinuclear silver(I) complexes of the phenylene bridged NHC ligands were prepared from the imidazolium salt precursors and Ag_2O. The synthesis of the corresponding gold(I) and copper(I) complexes was readily achieved through transmetalation of the carbene ligand from the corresponding silver(I) complexes. Finally, transmetalation of the dicarbene ligand to iridium(III) and ruthenium(II) was successful with the *ortho*-phenylene ligand only.

Results and discussion

Synthesis of diiimidazolium salts

The *bis*(imidazol-1-yl)benzene precursors were prepared from *ortho*-, *meta*- or *para*-dibromobenzene and imidazole, using Cu(I) catalysed Ullmann-type coupling procedure (Scheme 1). The diimidazolium cations were prepared by alkylation of the *bis*(imidazole-1-yl)arenes with methyl iodide in dimethylsulfoxide at room temperature, to give the *bis*-imidazolium diiodide salts. The solubility of these compounds was improved via anion I^-/PF_6^- exchange, yielding the bis(hexafluorophosphate) salts. The same or analogous (with different nitrogen substituents) diimidazolium cationic compounds were already reported in the literature, and the synthesis involved a very similar two-step procedure.[22-35]

[a] *Dipartimento di Scienze Chimiche, Università degli Studi di Padova, via Marzolo 1, 35131 Padova (Italy).*
[b] *Dipartimento di Ingegneria Industriale, Università degli Studi di Padova, via Marzolo 9, 35131 Padova (Italy).*
[c] *Dipartimento di Chimica, Università degli Studi di Parma, Viale delle Scienze 17/A, 43100 Parma (Italy).*
[d] *CNR NANOTEC - Institute of Nanotechnology c/o Campus Ecotekne, University of Salento, Via Monteroni - 73100 Lecce (Italy).*
[e] *Department of Chemistry and Physics, La Trobe Institute for Molecular Science, La Trobe University, Victoria, 3086, Australia, Fax: (+)61 3 9479 1266.*

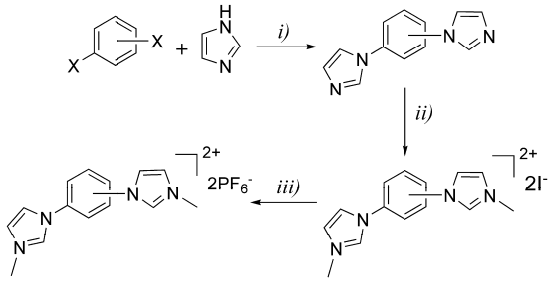
Electronic Supplementary Information (ESI) available: Crystal data for complexes **1a** (CCDC 1433307), **1a*** (CCDC 1433308), **1b** (CCDC 1433309), **2a** (CCDC 1433310), **2b** (CCDC 1433311) and **5a** (CCDC 1433312). See DOI: 10.1039/x0xx00000x

Published on 06 May 2016. Downloaded by University of California - Santa Barbara on 06/05/2016 11:22:19.

Dalton Transactions Accepted Manuscript

Please do not adjust margins

View Article Online
DOI: 10.1039/C6DT01120B

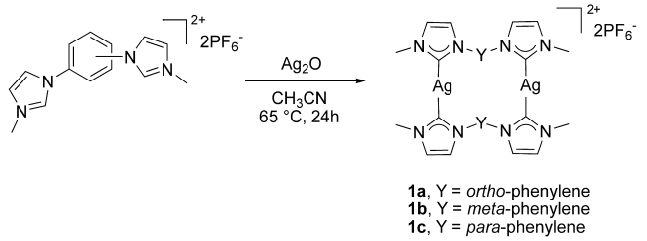


Scheme 1. Preparation of diimidazolium salts. Experimental details: i) imidazole, dibromobenzene, CuO, K_2CO_3, DMSO, 150 °C, 48 h. ii) MeI, DMSO, room temperature, 12 h. iii) NH_4PF_6 methanol.

Synthesis of group 11 metal complexes

The silver(I) di(N-heterocyclic carbene) complexes of general formula $[Ag_2(diNHC)_2](PF_6)_2$ were synthesized by reaction of the appropriate diimidazolium bis(hexafluorophosphate) salt with excess silver(I) oxide in acetonitrile at 65 °C for 24 hours (Scheme 2). Initially, the synthesis of the silver complexes was attempted using the diimidazolium diiodide salt with Ag_2O in water for 24 hours at room temperature, followed by anion I^-/PF_6^- metathesis. Unfortunately, with this type of procedure, the obtained solids were not pure and contaminated by an appreciable quantity of the starting materials, as indicated by the presence in the ^{1}H-NMR spectra of the signal corresponding to the C2-H protons.

Complexes **1a-c** are light grey solids, soluble in common polar organic solvents (e.g. acetonitrile and dimethylsulfoxide). The deprotonation of the diimidazolium salt is confirmed by the absence of the C2-H signal in the ^{1}H NMR spectrum of the reaction products and the formation of the silver complexes is supported by the presence of the carbene carbon signal in the ^{13}C NMR spectra at δ 180-185 ppm, in the typical range of carbene carbons coordinated to a silver(I) center.[36,37] The dinuclear dicationic nature of the complexes with the two dicarbene ligands bridging the two metal centers is then further established with the ESI-MS spectra, which show the peaks corresponding to the $[Ag_2L_2PF_6]^+$, $[Ag_2L_2]^+$ and $[Ag_2L_2]^{2+}$ fragments. Analogous results have been reported by Hahn *et al.* with a *para*-phenylene dicarbene ligand having ethyl instead of methyl groups, as substituents to the nitrogen atoms in position 1.[28a]



1a, Y = *ortho*-phenylene
1b, Y = *meta*-phenylene
1c, Y = *para*-phenylene

Scheme 2. Synthesis of the silver(I) di(N-heterocyclic carbene) complexes.

The crystal structures of the compounds **1a** and **1b** have been fully elucidated by single crystal X-ray diffraction analysis. The crystals of **1a** and **1b** contain cationic complexes and PF_6^- anions. In particular in the unit cell of **1a** two crystallographically independent but very similar cationic complexes and four PF_6^- anions are present. The ORTEP views of one of the two cationic moieties in complex **1a** and the cation in **1b** are reported in Figure 1 and Figure 2 respectively together with the atomic labelling scheme; a list of the most important bond distances and angles is collected in the captions. Cationic complexes in **1a** as well as in **1b** are dinuclear with two dicarbene ligands bridging the two silver atoms. In **1a** the bridging ligands form a 14-membered ring while in **1b** the *meta* isomers of the bridging phenylene cause the formation of a 16-membered ring. The conformation of the two complexes is different, with the cationic moiety of **1b** being centrosymmetric with the inversion center located in the middle of the 16-membered ring thus forcing an 'anti' conformation, while the 14-membered ring in the cationic moiety of **1a** shows a 'syn' conformation.[38] The Ag-$C_{carbene}$ bond lengths span from 2.076(5) to 2.094(5) Å in **1a** and from 2.086(4) to 2.092(4) Å in **1b**, and fall in the typical range for $[Ag(NHC)_2]^+$ complexes. Considering the $C_{carbene}$-Ag-$C_{carbene}$ bond angle, it deviates only slightly from linearity in the case of complex **1b** (175.16(13)°), while in the case of **1a** it is more deviated (175.8(2) and 170.7(2)° in one of the two independent cationic moieties and 176.7(2) and 171.5(2)° in the other). Moreover while in **1b** the Ag···Ag separation is 7.165(2) Å, in **1a** the Ag···Ag distance is 3.289(2) and 3.265(1) in the two independent cationic moieties and this interatomic separation is slightly shorter than the sum of the Van der Waals radii for silver. Because of the centrosymmetry of complex **1b**, the mean planes of the phenyl rings are parallel at a distance of 4.306(2) Å (centroid to centroid separation of 4.409(2) Å), considering the crystal packing it is evident that π···π interactions are also present between the phenyl rings of adjacent molecules (centroid to centroid distance of 4.803(2) Å) and between the phenyl ring and the imidazole ring of facing molecules (centroid to centroid distance of 4.299(2) Å) (see Figure 3).

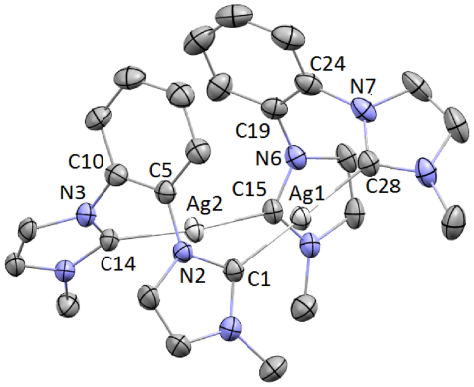


Figure 1. ORTEP view of one of the two cationic units of complex **1a**. Ellipsoids are drawn at their 30% probability. Hydrogen atoms and PF_6^- anions have been omitted for clarity. Selected bond distances (Å) and angles (deg) (data in squared parentheses are referred to the second cationic unit): C1-Ag1 2.076(5) [2.092(5)], C28-Ag1 2.076(5) [2.085(5)], C14-Ag2 2.088(5) [2.091(5)], C15-Ag2 2.088(5) [2.094(5)], C1-N2 1.345(7) [1.346(6)], C5-N2 1.430(7) [1.427(7)], C5-C10 1.387(8) [1.379(7)], C10-N3 1.414(7) [1.433(7)], C14-N3 1.347(7) [1.356(6)], C15-N6 1.360(6) [1.346(7)], C19-N6 1.410(7) [1.428(7)], C19-C24 1.383(7) [1.390(8)], C24-N7 1.422(7) [1.434(8)], C28-N7 1.346(6)

Published on 06 May 2016. Downloaded by University of California - Santa Barbara on 06/05/2016 11:22:19.
Dalton Transactions Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

View Article Online
DOI: 10.1039/C6DT01088B

[1.356(7)], Ag1···Ag2 3.289(2) [3.265(1)]; C1-Ag1-C28 175.8(2) [176.7(2)], C15-Ag2-C14 170.7(2) [171.5(2)].

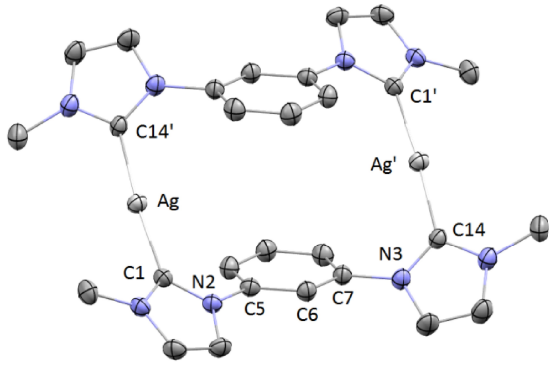


Figure 2. ORTEP view of the cationic part of complex **1b**. Ellipsoids are drawn at their 30% probability. Hydrogen atoms and PF6- anions have been omitted for clarity. Selected bond distances (Å) and angles (deg): C1-Ag 2.092(4), C14'-Ag 2.086(4), C1-N2 1.350(5), C5-N2 1.431(4), C5-C6 1.392(5), C6-C7 1.383(5), C7-N3 1.437(4), C14-N3 1.352(5); C14'-Ag-C1 175.16(13). Symmetry code for equivalent atoms: '= 1-x, -y, -z.

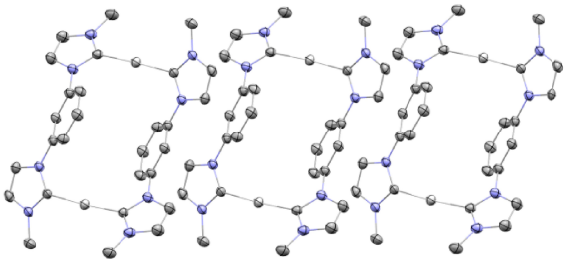


Figure 3. Packing diagram of cationic complexes in **1b** evidencing the stacking of adjacent molecules.

Interestingly, in the crystallization process of complex **1a** in acetonitrile, very few crystals of a second species, namely **1a***, have been obtained. The ORTEP view of **1a*** is shown in Figure 4 and a list of the most important bond distances and angles is collected in the caption.

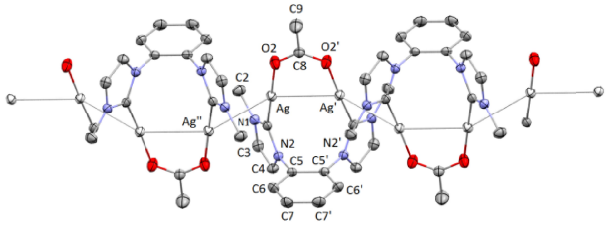
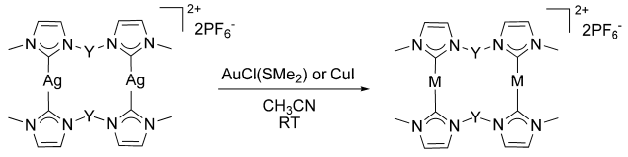


Figure 4. ORTEP view of the polymeric structure of complex **1a***. Ellipsoids are drawn at their 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): C1-N1 1.348(5), C1-N2 1.352(5), C1-Ag 2.067(4), C2-N1 1.462(5), C3-C4 1.340(6), C3-N1 1.378(5), C4-N2 1.382(5), C5-C6 1.379(5), C5-C5' 1.383(7), C5-N2 1.436(5), Ag-O2 2.111(3), Ag···Ag' 2.9279(8), Ag···Ag'' 3.0462(7); N1-C1-N2 104.6(3), N1-C1-Ag 128.8(3), N2-C1-Ag 126.6(3), C5'-C5-N2 119.73(18), C1-Ag-O2 176.63(14), C1-N1-C3 110.8(3), C1-N1-C2 124.1(3), C3-N1-C2 125.0(3), C1-N2-C4 111.1(3), C1-N2-C5 122.9(3), C4-N2-C5 126.0(3), C8-O2-Ag 126.6(3), Ag'···Ag···Ag'' 148.51(1). Symmetry code for equivalent atoms: ' = ½-x, y, z; '' = -x, 1-y, -z.

Compound **1a*** is a coordination cationic metallopolymer formed by infinite chains of dimers $[Ag_2(CH_3COO)(diNHC)]$ connected by Ag···Ag Van der Waals interactions. The polymeric structure develops along the *a* axis of the cell. The symmetric dinuclear complex, which is constructed over a mirror m orthogonal with respect to the metal···metal separation, is formed by two silver atoms bridged by the diNHC ligand and by an acetate anion. The diNHC ligand and the metal atoms form an eight membered ring with a boat conformation. The Ag atom is bonded to a carbene carbon atom (C1-Ag 2.067(4) Å), and an oxygen atom of an acetate anion (Ag-O2 2.111(3) Å) in a nearly linear arrangement (C1-Ag-O2 176.63(14)°). The mean planes of the imidazole rings of the bridging diNHC ligand form a dihedral angle of 64.01(2)°. The Ag'···Ag and Ag···Ag'' separations are 2.9279(8) and 3.0462(7) Å. The polymeric structure develops in a zig zag chain with an Ag'···Ag···Ag'' angle of 148.51(1)°. In the crystals of compound **1a***, PF_6^- anions are also present to neutralize the positive charges. The process leading to the formation of complex **1a*** should involve the hydrolysis of acetonitrile solvent to ammonium acetate.

Gold(I) and copper(I) complexes were synthesized via transmetalation of the dicarbene ligand from the corresponding silver(I) complexes (Scheme 3). The ^{1}H-NMR spectra of the gold(I) complexes are similar to those of the dinuclear silver(I) precursors, thus indicating that the symmetric dinuclear structure is maintained upon transmetalation of the ligand. In particular, the ^{1}H NMR signals of the two hydrogen atoms of the imidazole backbone and the aromatic signals of phenylene bridge are slightly shifted downfield in comparison with the corresponding silver(I) complex; the same shift is observed also in the ^{13}C NMR spectra for the C4 and C5 carbon atoms. A different behavior is generally observed for the carbene carbon signal, which is slightly upfield shifted due to the higher Lewis acidity of the gold(I) center with respect to the silver(I) one. The formation of the dinuclear gold(I) complexes is further confirmed by the ESI-MS spectra, which present the peaks of the $[Au_2L_2PF_6]^+$ and $[Au_2L_2]^{2+}$ fragments, whose nature is also supported by the simulation of the isotopic pattern.



1a, Y = *ortho*-phenylene
1b, Y = *meta*-phenylene
1c, Y = *para*-phenylene

2a, M = Au, Y = *ortho*-phenylene
2b, M = Au, Y = *meta*-phenylene
2c, M = Au, Y = *para*-phenylene
3a, M = Cu, Y = *ortho*-phenylene
3b, M = Cu, Y = *meta*-phenylene
3c, M = Cu, Y = *para*-phenylene

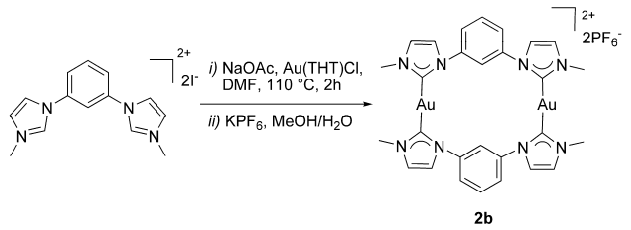
Scheme 3. Synthesis of the gold(I) and copper(I) di(N-heterocyclic carbene) complexes.

The dinuclear complex **2b** could be also prepared by heating the appropriate diimidazolium diiodide salt with (THT)AuCl in the presence of a weak base like sodium acetate (Scheme 4).[39] The reaction was carried out in DMF at 110 °C for 2 h, diethyl

Published on 06 May 2016. Downloaded by University of California - Santa Barbara on 06/05/2016 11:22:19.
Dalton Transactions Accepted Manuscript

View Article Online
DOI: 10.1039/C6DT01439B

ether was used to fully precipitate the crude product, which was then converted to the PF_6^- complex by way of anion metathesis reaction, using KPF_6 in water. The NMR characterisation of the complex obtained with this procedure fully matched that of the complex obtained via trasmetalation of the diNHC ligand.



Scheme 4. Direct synthesis of complex **2b**.

The structure of complexes **2a** and **2b** has been further confirmed on the basis of X-ray crystal structure analysis. In the crystals of **2a** cationic moieties, PF_6^- anions and acetonitrile solvent molecules are present. The ORTEP views of the cationic moieties in complexes **2a** and **2b** are reported in Figure 5 and Figure 6 respectively together with the atomic labelling scheme; a list of the most important bond distances and angles is collected in the captions. The cationic moieties are dinuclear with two dicarbene ligands bridging the two gold atoms in a very similar manner to what observed in the case of silver. In particular in complex **2a** the two bridging ligands form a 14-membered ring with a boat conformation. The complex is highly symmetric, being constructed over two mutually perpendicular mirror planes and shows a 'syn' conformation.[38] The Au···Au separation is 3.656(2) Å and the Au-$C_{carbene}$ bond distance (2.013(5) Å) is in the typical range for analogous NHC-Au(I) complexes. The $C_{carbene}$-Au-$C_{carbene}$ bond angle shows a slight deviation from linearity (174.1(2)°). In the crystal packing of complex **2a** there is no evidence of π···π stacking between adjacent molecules.

Compound **2b** is isostructural with the silver analogous **1b**. In the dinuclear dicationic moiety the two bridging ligands form a symmetric 16-membered ring, with 'anti' conformation. The Au···Au separation is 7.140(2) Å and the $C_{carbene}$-Au-$C_{carbene}$ bond angle shows a slight deviation from linearity (175.68(16)°). The mean planes of the phenyl rings are parallel at a distance of 4.363(2) Å (centroid to centroid separation of 4.416(2) Å). Considering the crystal packing, π···π interactions are also present between the phenyl rings of adjacent molecules (centroid to centroid separation of 4.775(2) Å) and between the phenyl ring and the imidazole ring of faced molecules (centroid to centroid distance of 4.423(2) Å) (see Figure 7), in a very similar way to that exhibited by the corresponding silver complex **1b**.

In the case of di(N-heterocyclic carbene) ligands bearing a 1,3-disubstituted arene linker, two possible structures are reported in the literature: (i) open ring stretched out conformation characterized by a long intramolecular Au···Au distance and by intermolecular π···π interactions and (ii) a twisted conformation with a short intramolecular Au···Au distance. Examples of both type (i)[40] and type (ii)[41,42] have been recently reported in the literature with silver(I), gold(I) and mercury(II) metal centers. The structure here reported for complex **2b** (as well as for complex **1b**) shows the open conformation (i).

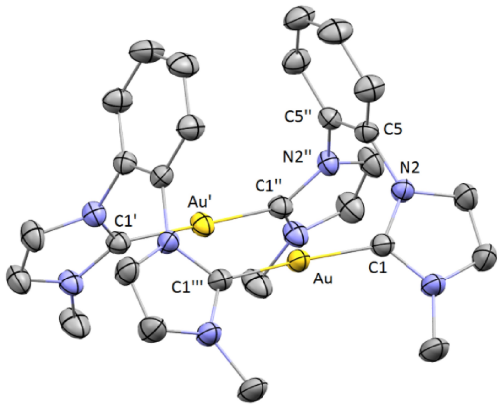


Figure 5. ORTEP view of the cationic complex **2a**. Ellipsoids are drawn at their 30% probability. Hydrogen atoms, PF_6^- anions and acetonitrile solvent molecule have been omitted for clarity. Selected bond distances (Å) and angles (deg): C1-Au 2.013(5), C1-N2 1.363(5), C5-N2 1.434(4), C5-C5'' 1.392(7); C1-Au-C1''' 174.1(2). Symmetry code for equivalent atoms: ' = 1-x, y, ½-z; '' = x, y, ½-z; ''' = 1-x, y, z.

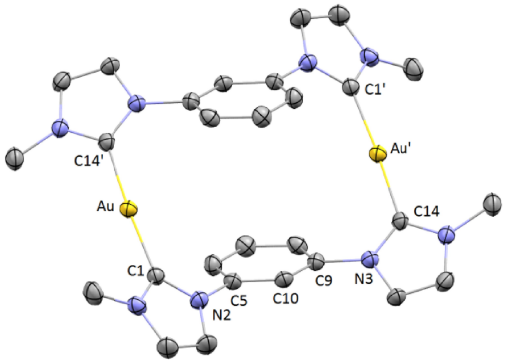


Figure 6. ORTEP view of the cationic complex **2b**. Ellipsoids are drawn at their 30% probability. Hydrogen atoms, PF_6^- anions and acetonitrile solvent molecule have been omitted for clarity. Selected bond distances (Å) and angles (deg): C1-Au 2.021(5), C14'-Au 2.025(5), C1-N2 1.359(6), C5-N2 1.437(6), C5-C10 1.392(6), C10-C9 1.388(6), C9-N3 1.447(6), C14-N3 1.343(6); C14'-Au-C1 175.7(2). Symmetry code for equivalent atoms: ' = -x, -y, 1-z.

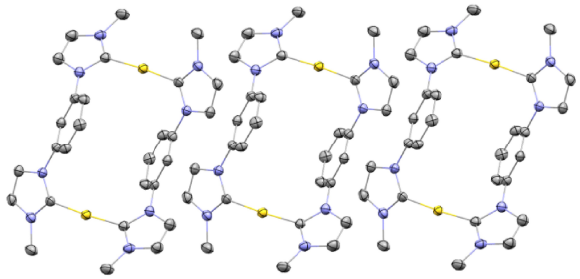


Figure 7. Packing diagram of cationic complexes in **2b** evidencing the stacking of adjacent molecules.

Published on 06 May 2016. Downloaded by University of California - Santa Barbara on 06/05/2016 11:22:19.

Dalton Transactions Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

Published on 06 May 2016. Downloaded by University of California - Santa Barbara on 06/05/2016 11:22:19.

The transmetalation route allows also the syntheses of the copper(I) complexes **3a** - **3c**. For example complex **3c**, with *para*-phenylene bridge, shows in the NMR spectra the expected set of signals, similar to the silver(I) analogue. Furthermore, in the ESI-MS spectrum, the fragments $[Cu_2L_2PF_6]^+$, $[Cu_2L_2]^+$ and $[Cu_2L_2]^{2+}$ can be observed. The copper complexes are fairly stable, even if a slight darkening of the powder and of their acetonitrile solution is observed with time (24-48 h). Particular care should be taken with the copper complex **3a**, with the *ortho*-phenylene diNHC, which could be synthesized and stored only in strictly anaerobic conditions, i.e. dry box. By exposure to air of an acetonitrile solution of complex **3a**, it quickly decomposes giving *inter alia* evolution products such as $[Cu(CH_3CN)_4]^+$ (evidenced by X-ray structure determination of few isolated crystals) and an organic species.[43] The NMR spectra of the evolved solution show the presence of the ligand functional groups albeit at markedly different chemical shift with respect to those observed in the pristine complex **3a**. The value of the C2 carbon resonance at 127.4 ppm, seems to rule out the possibility of coordination to the copper(I) center.

The photophysical properties of both gold(I) and silver(I) complexes have been investigated at room temperature in the solid state as powder. All the excitation profiles, reported in Figure 8 and recorded by monitoring the emission maxima, are centered in the UV region (below 400 nm) and can be attributed to the π–π* Ligand Centered (LC) transitions (see further in the text).[19b]

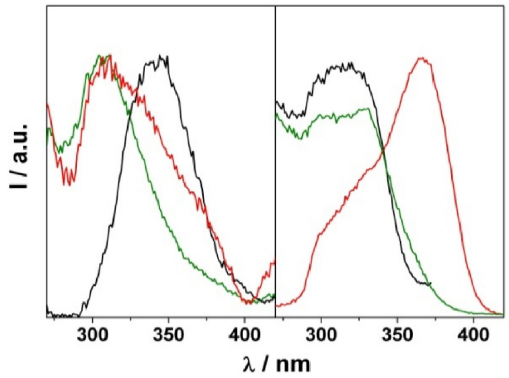


Figure 8. Excitation spectra ($\lambda_{em} = \lambda_{max}$) in the solid state as powder at 298 K. Left window: **1a** (black), **1b** (red) and **1c** (green). Right window: **2a** (black), **2b** (red) and **2c** (green).

View Article Online
DOI: 10.1039/C6DT01129B

Table 1. Photophysical data of the investigated complexes in the solid state (as powder) at room temperature.

Complex	λ_{max} (nm)a	Φ (%)[a]	τ (μs)[b]	M···M distance (Å)
1a	410	< 1%	c	3.266
1b	420	< 1%	c	7.165
1c	460	< 1%	15.0 - 234	-
2a	380	1.0	1.1	3.657
2b	450	5.7	0.4	7.140
2c	478	2.8	22 - 140	7.213d

[a] λ_{exc} = 300 or 330 nm; [b] λ_{exc} = 330 nm; [c] Not detected due to the weakness of the signal. [d] From Ref.28

The emission spectra, reported in Figure 9, are centred in the 410 - 480 nm window (blue region). The gold(I) complexes show a discrete quantum efficiency (up to ~6% for **2b,** Table 2) while the corresponding silver(I) compounds are weak emitters (PLQY < 1%). Both the shape profiles and the relative lifetime decays indicate the presence of two emitting states. For instance, the complexes **1c** and **2c** show broader and red-shifted profiles compared to those involving ligands **a** and **b**. Moreover, their lifetimes follow a biexponential decay and are much longer (up to two order of magnitude) than **2a-b** (unfortunately, the lifetimes of **1a** and **1b** could not be measured because of the weakness of the signals). These optical features suggest a Metal Centered (MC) emission for **1-2c** and a predominant LC character for **1-2a** and **1-2b**.[19b,42]
In order to rationalize the dependence of the PL performances on the geometrical factors, the aurophilic interaction model[44] can be taken into account since it states the central role of the metal-metal distance to this regard. Unfortunately, in the present case the samples have different emitting states (MC and LC) and a proper correlation cannot be made for the whole series. For example complexes **2a** and **2b** (M-M distance of 3.66 and 7.14 Å, respectively), having both LC emissive nature, show different quantum efficiencies (1.0 and 5.7%, respectively) suggesting that additional factors, rather than the distance between metals, such as sample geometry and π···π crystal stacking, influence the optical properties of the dinuclear gold(I) complexes.

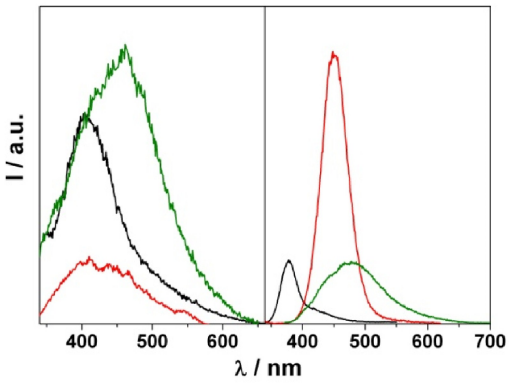


Figure 9. Emission spectra (λ_{exc} = 300 or 330 nm) in the solid state as powder at 298 K. Left window: **1a** (black), **1b** (red) and **1c** (green). Right window: **2a** (black), **2b** (red) and **2c** (green). For each window, the profile intensities have been normalized according to the corresponding quantum efficiencies.

Dalton Transactions Accepted Manuscript

Published on 06 May 2016. Downloaded by University of California - Santa Barbara on 06/05/2016 11:22:19.

Complex **2b** was found to be non-emissive in acetonitrile solution both at room temperature and in frozen solution at 77 K. Nonetheless, considering the interesting emitting properties of complex **2b** in the solid state, we decided to further explore the nature of the observed Uv-vis transitions for this complex by performing TDDFT calculations.

The geometry of the cationic part of complex **2b** was optimised at the M06-L/def2-SVP level of theory, and the results were in good agreement with the available X-ray crystal structure. In particular, the Au···Au distances is ca. 0.15 Å greater than that obtained from X-ray crystallography, and the near-linear $C_{carbene}$-Au-$C_{carbene}$ geometry is predicted with an average bond angle of 174.1°, in agreement with 175.4° from the available crystal structure.

Furthermore, natural bond orbital (NBO) calculations provide for an analysis of the electronic structure and interaction between Au atoms. The Wiberg bond index (WBI) for the Au···Au interaction in the open form is 0.002-0.005, indicative of insignificant aurophilic interactions.[45] The Au atoms are calculated to be positively charged (NPA average of +0.26), which results in a breaking of the formal $5d^{10}$ $6s^{0}$ electronic structure of Au(I): the electronic configuration is $5d^{9.61}$ $6s^{1.01}$ $6p^{0.12}$ from NBO calculations, and the small amount of hybridization is a further confirmation of very weak (or non-existent) aurophilic interaction in this system. The simple van der Waals interaction between two M^{+} centres may be calculated using the London formula as

$$E_{\text{int}} \approx \frac{-3I_{M+}\alpha^{2}_{M+}}{4\left[r(M_1 - M_2)\right]^{6}}$$

where I_{M+} is the ionization potential (20.5 eV for Au^{+}), α_{M+} is the polarizability (1.72 $Å^3$), and $r(M_1\text{-}M_2)$ is the metal-metal distance. For complex **2b**, E_{int} is 0.04 kJ/mol at the optimized bond distance, again reflecting the small Au···Au interaction in the complex.[46]

Molecular orbital contour plots for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of complex **2b** were calculated at the CAM-B3LYP/def2-SVP level of theory and are shown in Figure 10. These contour plots show that the LUMO is primarily associated with a π* antibonding orbital located on the aryl-linker with a smaller component lying on the NHC units. The HOMO is primarily ligand centred (69%), with a smaller contribution (31%) from the Au(I) 5*d* orbitals. TD-DFT has been employed to calculate the nature of the transitions involved in the electronic absorption spectra (Table 2), which are, as expected, best described as a combination of LC and ML-LCT processes.

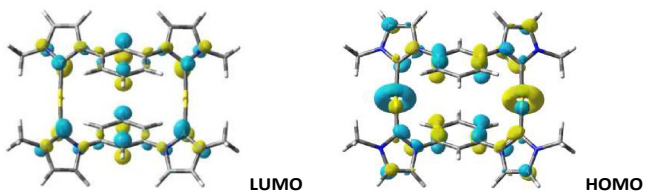


Figure 10. CAM-B3LYP/def2-SVP molecular orbitals of the cationic part of complex **2b**.

Table 2. CAM-B3LYP/def2-SVP calculated absorbance transitions with acetonitrile solvent for complex **2b.**

View Article Online
DOI: 10.1039/C6DT01129B

λ (nm)	f	Assignment	
237	0.27	H → L+2	ML-LCT
235	0.13	H-1→ L	ML-LCT
218	0.94	H → L+4	LC
217	0.95	H-1 → L+1	LC
205	0.27	H-3 → L	LC
202	1.32	H → L+3	ML-LCT
188	0.29	H → L+6	LC, LMCT

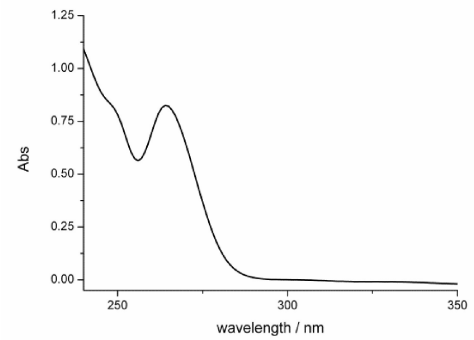


Figure 11. UV-visible absorbance spectra from acetonitrile solution for complex **2b** (3.0×10^{-5} M).

Synthesis of Ir(III) and Ru(II) diNHC complexes

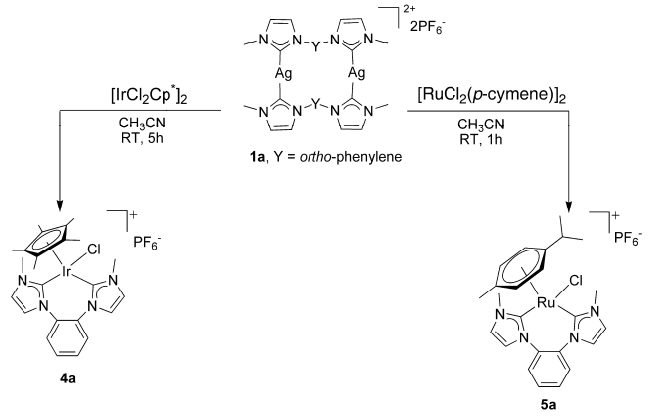
The transmetalation synthetic procedure was then used with partial success for the synthesis of dicarbene ruthenium(II) and iridium(III) complexes. The reaction of the silver(I) complex **1a** with $[IrCl_2Cp^*]_2$ or $[RuCl_2(p\text{-cymene})]_2$ at room temperature in acetonitrile, using a Ag:M ratio 1:1 (M = Ir) or 1:2 (M = Ru), affords complexes **4a** and **5a** respectively (Scheme 5).

In both cases monocationic complexes are obtained, in which one di(N-heterocyclic carbene) ligand is chelating the metal center. The coordination sphere is completed by one chloride ligand and by an aromatic ring (Cp* for the iridium(III) and *p*-cymene for the ruthenium(II) complex). The ESI-MS spectra support indeed this formulation and show the fragments corresponding to $[IrClCp^*L]^{+}$ or to $[RuClL(p\text{-cymene})]^{+}$ respectively. The coordination of the carbene ligand to the metal center is further supported by the chemical shift of the carbene carbon in the ^{13}C-NMR spectra, 157.0 for C2-Ir and 179.5 for C2-Ru, in the typical range of carbene carbons coordinated respectively to an iridium(III) or ruthenium(II) center.[47]

Dalton Transactions Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins



Scheme 5. Synthesis of the iridium(III) and ruthenium(II) di(N-heterocyclic carbene) complexes.

The iridium(III) complex tends to slowly (in ca. 10 days) react in solution and, in the NMR spectra, appears a second set of signal, related to the new species **4a'**, formed by replacement of the chloride ligand with a deuterated acetonitrile solvent molecule. The formation of the dicationic complex $[IrCp^*L(CD_3CN)]^{2+}$ (**4a'**) has been supported by a qualitative test, that is by addition of $AgPF_6$ to a freshly prepared solution of complex **4a**: a new set of NMR signal emerges and coincides with that observed on **4a** standing. The changes observed in the ^1H and ^{13}C-NMR spectra further point to the formation of a dicationic complex: in particular, the signals of the dicarbene ligand move downfiled, as a consequence of the increased positive charge on the complex, with the exception of the carbene carbon, which instead moves upfield (150.3 for **4a'** and 157.0 for **4a**). This is a consequence of the higher Lewis acidity of the metal center and a similar behavior has been already reported for other iridium(III) or palladium(II) complexes.[47a,48]

The crystal structure of complex **5a** has been fully elucidated by X-ray diffraction analysis and in the crystals of **5a**, cationic moieties, PF_6^- anions and acetonitrile solvent molecules are present. The ORTEP view of the cationic complex in **5a** is reported in Figure 12 together with the atomic labelling scheme; a list of the most important bond distances and angles is collected in the caption.

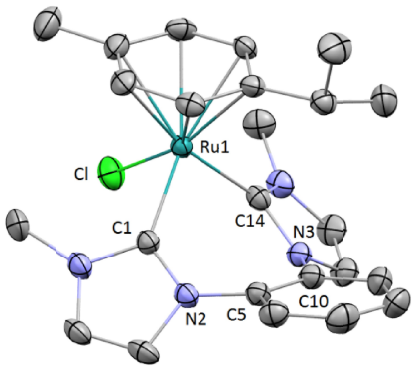


Figure 12. ORTEP view of the cationic complex in **5a**. Ellipsoids are drawn at their 30% probability. Hydrogen atoms, PF_6 anions and acetonitrile molecules have been omitted for clarity. Selected bond distances (Å) and angles (deg): C1-Ru1 2.051(5), C1-N2 1.353(7), C5-N2 1.428(7), C5-C10 1.396(7), C10-N3 1.424(7), C14-N3 1.381(7), C14-Ru1 2.035(5), Cl-Ru1 2.4182(13), Ru1-CT 1.734(5), CT-Ru1-Cl 126.7(2), CT-Ru1-C1 128.2(2), CT-Ru1-C14 128.9(2), C14-Ru1-C1 88.4(2), C14-Ru1-Cl 84.4(2), C1-Ru1-Cl 85.4(2). CT is the centroid of the *p*-cymene ligand.

View Article Online DOI: 10.1039/C6DT01124B

The ruthenium center shows a distorted tetrahedral coordination environment considering the two carbene carbon atoms of the chelating ligand, the chlorine atom and the centroid of the *p*-cymene molecule. The chelating ligand forms a 7-member coordination ring with a boat conformation. The $C_{carbene}$-Ru-$C_{carbene}$ bond angle is 88.4(2)°, and the $C_{carbene}$-Ru-Cl bond angles are 84.4(2) and 85.4(2)° while the bond angles at the ruthenium atom involving the centroid of the *p*-cymene ligand are wider spanning from 126.7(2) to 128.9(2)° as usually observed in other ruthenium (arene) NHC complexes in the literature.[49] The $C_{carbene}$-Ru, Ru-Cl and Ru-C bond distances for the *p*-cymene ligand lie in the usual range.

Unfortunately, reaction of the silver complexes **1b**,**c** with $[RuCl_2(p\text{-cymene})]_2$ or $[IrCl_2Cp^*]_2$ in acetonitrile in different reaction conditions (molar ratios of the reagents, temperature, reaction time) does not allow the isolation of a pure product. For example the ^1H-NMR spectra of the ruthenium(II) reaction mixtures show the signals of free *p*-cymene, probably due to decomposition processes, whose presence is also apparent from the dark-green color of the reaction mixture. In the literature[22a,24a] the coordination of *meta*-phenylene based dicarbene is often accompanied also by the metalation of the C2 carbon atom of the aromatic bridge; however, it is important to underline that generally the adopted synthetic procedure is different from the one used in this work and involves the deprotonation of the carbene proligand with a strong base in the presence of the proper metal precursor.

Conclusions

In this work, we have synthesized three different dinuclear silver(I) complexes of general formula $[Ag_2(diNHC)_2](PF_6)_2$ bearing bridging di(N-heterocyclic carbene) ligands with phenylene linkers between the carbene moieties. The transmetalation of the diNHC ligand from silver(I) complexes to gold(I) and copper(I) was successful, and the copper(I) and gold(I) complexes displayed the same coordination geometries as the precursor Ag(I) complexes. The same transmetallation procedure furnished chelating complexes of ruthenium(II) and iridium(III) with the *ortho*-phenylene bridged dicarbene ligand. We are currently exploring possible catalytic applications of the resulting complexes, for example in transfer hydrogenation.

Experimental

All manipulations of air and moisture sensitive compounds were carried out using standard Schlenk techniques under an atmosphere of argon or nitrogen or using a dry-box. The reagents were commercially available and generally used as received. All solvents were purified and dried by standard methods. The 1,1'-(phenylene)bis(imidazole) precursors were

Published on 06 May 2016. Downloaded by University of California - Santa Barbara on 06/05/2016 11:22:19.

Dalton Transactions Accepted Manuscript

Please do not adjust margins

View Article Online
DOI: 10.1039/C6DT01129B

Published on 06 May 2016. Downloaded by University of California - Santa Barbara on 06/05/2016 11:22:19.

prepared according to literature procedures.[35] Generally NMR spectra were recorded either on a Bruker Avance 300 (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P) or on a Bruker Avance 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) at 298 K unless otherwise stated; chemical shifts (δ) are reported in units of ppm relative to the residual solvent signals (for ^{1}H and ^{13}C) or to 85% H_3PO_4 (for ^{31}P). ESI-MS analyses were performed using a LCQ-Duo (Thermo-Finnigan) operating in positive ion mode. Instrumental parameters: capillary voltage 10 V, spray voltage 4.5 kV, capillary temperature 200 °C, mass scan range from 150 to 2000 amu, N_2 was used as sheath gas, and the He pressure inside the trap was kept constant. The pressure directly read by an ion gauge (in the absence of the N_2 stream) was 1.33×10^{-5} Torr. Sample solutions were prepared by dissolving the compounds in acetonitrile and were directly infused into the ESI source by a syringe pump at 8μL/min flow rate. Elemental analysis were carried out by the microanalytical laboratory of Chemical Sciences Department (University of Padova) with a Fisons EA 1108 CHNS-O apparatus.

General procedure for the synthesis of the 1,1'-dimethyl-3,3'-(phenylene)bis(imidazolium) diiodide salts $[H_2L]I_2$.

CH_3I (120 μL, 1.9 mmol) was added to a solution of the appropriate 1,1'-(phenylene)bis(imidazole) (0.55 g, 0.74 mmol) in DMSO (1 mL). The reaction mixture was stirred for 24 hours at room temperature and an orange solution was obtained. Addition of CH_2Cl_2 (35 mL) affords the product as an off-white solid, which was filtered and dried under vacuum. The NMR spectra of the diimidazolium salts compare well with those reported in the literature.[32b,33,35]

$[H_2(L^{ortho})]I_2$. White solid, yield 94%. ^{1}H NMR (d_6-DMSO, 300 MHz): δ 3.92 (s, 6H, CH_3), 7.74 (s, 2H, CH), 7.85 (s, 2H, CH), 7.93 (s, 4H, CH Ar), 9.45 (s, 2H, NCHN).

$[H_2(L^{meta})]I_2$. White solid, yield 95%. ^{1}H NMR (d_6-DMSO, 300 MHz): δ 3.99 (s, 6H, CH_3), 7.99 (s, 3H, CH Ar), 8.02 (s, 2H, CH), 8.29 (s, 1H, CH Ar), 8.36 (s, 2H, CH), 9.86 (s, 2H, NCHN).

$[H_2(L^{para})]I_2$. White solid, yield 91%. ^{1}H NMR (d_6-DMSO, 300 MHz): δ 3.97 (s, 6H, CH_3), 8.00 (s, 2H, CH), 8.09 (s, 4H, CH Ar) 8.38 (s, 2H, CH), 9.87 (s, 2H, NCHN).

General procedure for the synthesis of the 1,1'dimethyl-3,3'-(phenylene)bis(imidazolium) bis(hexafluorophosphate) salts $[H_2L](PF_6)_2$.

A solution of NH_4PF_6 (0.28 g, 1.7 mmol) in MeOH (1 mL) was added to a solution of 1,1'-dimethyl-3,3'-(phenylene)bisimidazolium diiodide (0.30 g, 0.61 mmol) in MeOH (4 mL). The mixture was stirred for two hours at room temperature, giving a white solid that was filtered and dried under vacuum.

$[H_2(L^{ortho})](PF_6)_2$. White solid, yield 76%. ^{1}H NMR (CD_3CN, 300 MHz): δ 3.90 (s, 6H, CH_3), 7.35 (d, $^{3}J_{HH}$ = 1.8 Hz, 2H, CH), 7.46 (d, $^{3}J_{HH}$ = 1.8 Hz, 2H, CH), 7.73 - 7.76 (m, 2H, CH Ar), 7.88 - 7.91 (m, 2H, CH Ar), 8.66 (s, 2H, NCHN). ^{31}P{^{1}H} NMR (CD_3CN, 121 MHz): δ -144.6 (heptet, PF_6).

$[H_2(L^{meta})](PF_6)_2$. White solid, yield 76%. ^{1}H NMR (CD_3CN, 300 MHz): δ 3.98 (s, 6H, CH_3), 7.60 (s, 2H, CH), 7.81 - 7.88 (m, 3H, CH Ar), 7.91 (s, 2H, CH), 8.02 - 8.04 (m, 1H, CH Ar), 9.25 (s, 2H, NCHN). ^{31}P{^{1}H} NMR (CD_3CN, 121 MHz): δ -144.6 (heptet, PF_6).

$[H_2(L^{para})](PF_6)_2$. White solid, yield 80%. ^{1}H NMR (CD_3CN, 300 MHz): δ 3.96 (s, 6H, CH_3), 7.58 (s, 2H, CH), 7.82 (s, 2H, CH), 7.85 (s, 4H, CH Ar), 8.96 (s, 2H, NCHN). ^{31}P{^{1}H} NMR (CD_3CN, 121 MHz): δ -144.6 (heptet, PF_6).

General procedure for the syntheses of the silver(I) complexes $[Ag_2L_2](PF_6)_2$, 1a-1c.

$[H_2L](PF_6)_2$ (0.10 g, 0.19 mmol) and Ag_2O (0.12 g, 0.52 mmol) were placed in a two neck round bottom flask. Subsequently, CH_3CN (10 mL) was added and the reaction mixture was stirred for 24 hours at 65 °C. Afterwards, it was filtered through Celite and the filtrate was concentrated at low pressure. Addition of diethyl ether (10 mL) afforded the product as a white solid, that was filtered and dried under vacuum.

1a. Grey solid, yield 40%. ^{1}H NMR (CD_3CN, 300 MHz): δ 3.81 (s, 6H, CH_3), 7.04 (s, 2H, CH), 7.20 (s, 2H, CH), 7.37 (m, 2H, CH Ar), 7.47 (m, 2H, CH Ar). ^{13}C{^{1}H} NMR (CD_3CN, 75 MHz): δ 39.1 (CH_3), 123.6 (CH), 124.2 (CH), 128.7 (CH Ar), 131.3 (CH Ar), 135.8 (C Ar), 186.7 (CAg). ESI-MS^{+} (CH_3CN): *m/z* 836.88 $[Ag_2L_2PF_6]^{+}$, 690.97 $[Ag_2L_2]^{+}$, 346.09 $[Ag_2L_2]^{2+}$. Crystals of complex **1a** were obtained by slow diffusion of diethyl ether into a solution of the complex.

1b. Grey solid, yield 32%. ^{1}H NMR (CD_3CN, 300 MHz): δ 3.97 (s, 6H, CH_3), 7.31 (m, 1H, CH Ar), 7.38 (d, $^{3}J_{HH}$ = 1.8 Hz, 2H, CH), 7.48 (d, $^{3}J_{HH}$ = 1.8 Hz, 2H, CH), 7.56 (m, 3H, CH Ar). ^{13}C{^{1}H} NMR (CD_3CN, 75 MHz): δ 39.2 (CH_3), 120.5 (CH Ar), 122.7 (CH), 124.5 (CH), 124.9 (CH Ar), 131.0 (CH Ar), 141.5 (C Ar), 181.7 (CAg). ESI-MS^{+} (CH_3CN): *m/z* 836.88 $[Ag_2L_2PF_6]^{+}$, 691.04 $[Ag_2L_2]^{+}$, 346.19 $[Ag_2L_2]^{2+}$. Crystals of complex **1b** were obtained by diffusion of vapours between diethyl ether and an acetonitrile solution of the complex.

1c. Grey solid, yield 20%. ^{1}H NMR (CD_3CN, 300 MHz): δ 3.98 (s, 6H, CH_3), 7.39 (s, 2H, CH), 7.54 (s, 2H, CH), 7.65 (s, 4H, CH Ar). ^{13}C{^{1}H} NMR (CD_3CN, 75 MHz): δ 39.7 (CH_3), 122.3 (CH), 124.4 (CH), 125.4 (CH Ar), 141.0 (C Ar), 180.0 (CAg). ESI-MS^{+} (CH_3CN): *m/z* 836.89 $[Ag_2L_2PF_6]^{+}$, 691.04 $[Ag_2L_2]^{+}$, 346.22 $[Ag_2L_2]^{2+}$.

General procedure for the syntheses of gold(I) complexes $[Au_2L_2](PF_6)_2$ 2a-2c.

A solution of $AuCl(SMe_2)$ (0.031 g, 0.105 mmol) in acetonitrile (5 mL) was added to a solution of $[Ag_2L_2](PF_6)_2$ (0.051 g, 0.052 mmol) in the same solvent (5 mL). The reaction mixture was stirred for 2 hours at room temperature. Afterwards, it was filtered on Celite and the filtrate was concentrated at low pressure. Addition of diethyl ether (15 mL) afforded the product as a white solid, which was filtered and dried under vacuum.

2a. White solid, yield 30%. Anal. Calcd for $C_{28}H_{28}N_8Au_2F_{12}P_2$: C, 28.98; H, 2.43; N, 9.66%. Found: C, 29.09; H, 2.40; N, 9.36%. ^{1}H NMR (CD_3CN, 300 MHz): δ 3.82 (s, 6H, CH_3), 7.03 (d, $^{3}J_{HH}$ = 1.5 Hz, 2H, CH), 7.21 (d, $^{3}J_{HH}$ = 1.5 Hz, 2H, CH), 7.42 (m, 2H, CH Ar), 7.51 (m, 2H, CH Ar). ^{13}C{^{1}H} NMR (CD_3CN, 75 MHz): δ 38.0 (CH_3), 123.9 (CH), 124.5 (CH), 129.1 (CH Ar), 131.9 (CH Ar), 135.5 (C Ar), 185.3 (CAu). ESI-MS^{+} (CH_3CN): *m/z* 1015.08 $[Au_2L_2PF_6]^{+}$, 435.42 $[Au_2L_2]^{2+}$. Crystals of complex **2a** were

Dalton Transactions Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

View Article Online
DOI: 10.1039/C6DT01129B

obtained by diffusion of vapours between diethyl ether and an acetonitrile solution of the complex.

2b. White solid, yield 38%. Anal. Calcd for $C_{28}H_{28}N_8Au_2F_{12}P_2$: C, 28.98; H, 2.43; N, 9.66%. Found: C, 28.75; H, 2.49; N, 10.06%. ^{1}H NMR (CD_3CN, 300 MHz): δ 3.98 (s, 6H, CH_3), 7.36 - 7.44 (m, 6H, CH + CH Ar), 7.64 (m, 2H, CH Ar). $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz): δ 38.5 (CH_3), 122.4 (CH Ar), 123.3 (CH), 124.5 (CH), 126.6 (CH Ar), 131.2 (CH Ar), 140.3 (C Ar), 183.2 (CAu). ESI-MS$^+$ (CH_3CN): *m/z* 1015.09 $[Au_2L_2PF_6]^+$, 435.40 $[Au_2L_2]^{2+}$. Crystals of complex **2b** were obtained by diffusion of vapours between diethyl ether and an acetonitrile solution of the complex.

2c. White solid, yield 46%. Anal. Calcd for $C_{30}H_{31}Au_2F_{12}N_9P_2$ (**2c**·CH_3CN) C, 29.99; H, 2.60; N, 10.49%. Found: C, 30.97; H, 2.65; N, 10.19%. ^{1}H NMR (CD_3CN, 300 MHz): δ 4.00 (s, 6H, CH_3), 7.40 (s, 2H, CH), 7.52 (s, 2H, CH), 7.74 (s, 4H, CH Ar). $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz): δ 39.2 (CH_3), 122.5 (CH), 124.6 (CH), 126.1 (CH Ar), 139.8 (C Ar), 183.8 (CAu). ESI-MS$^+$ (CH_3CN): *m/z* 1015.07 $[Au_2L_2PF_6]^+$, 435.33 $[Au_2L_2]^{2+}$.

Direct synthesis of gold(I) complex 2b.

To a stirred slurry of (THT)AuCl (0.09 g, 0.28 mmol) and the diimidazolium diiodide salt (0.15 g, 0.28 mmol) in DMF (10 mL) at 110 °C was added sodium acetate (0.09 g, 1.21 mmol). The reaction mixture was stirred at this temperature for 2 h and filtered while hot. The filtrate was cooled to room temperature and diethyl ether (50 mL) was added to precipitate the complex as a white powder. The crude product was dissolved in water, filtered and a saturated solution of KPF_6 in water (2 mL) was added. The resultant precipitate was recrystallized from a mixture of acetonitrile and diethyl ether. Yield: 0.06 g, 37%. ^{1}H NMR (d_6-DMSO, 400 MHz): δ 4.01 (s, 12H, CH_3), 7.45 (t, $^3J_{HH}$ = 8.0 Hz, 2H, CH Ar), 7.63 (t, J_{HH} = 2.0 Hz, 2H, CH Ar), 7.70 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.0 Hz, 4H, CH Ar), 7.75 (d, $^3J_{HH}$ = 1.7 Hz, 4H, CH), 7.81 (d, $^3J_{HH}$ = 1.7 Hz, 4H, CH). ^{13}C NMR (d_6-DMSO, 100 MHz): δ 37.9 (NCH_3), 121.3 (CH Ar), 123.0 (CH), 124.2 (CH), 125.5 (CH Ar), 130.3 (CH Ar), 139.0 (CH Ar), 181.8 (*C*Au). ESI-MS$^+$ (CH_3OH): *m/z* 1015.2 $[C_{28}H_{28}N_8Au_2]PF_6^+$, calcd 1015.14. m/z 435.3 $[C_{28}H_{28}N_8Au_2]^{2+}$, calcd 435.26.

General procedure for the syntheses of the copper(I) complexes $[Cu_2L_2](PF_6)_2$, 3b and 3c.

CuI (0.032 g, 0.017 mmol) was added to a solution of the appropriate complex $[Ag_2L_2](PF_6)_2$ (0.041 g, 0.042 mmol) in acetonitrile (5 mL). The reaction mixture was stirred for one hour. Afterwards, it was filtered through Celite and the filtrate was concentrated at low pressure. Addition of diethyl ether (10 mL) affords the product as a white/grey solid, which was filtered and dried under vacuum. Unfortunately, the instability of the products does not allow to obtain good elemental analyses. For this reason, the products were characterised only by means of spectroscopic techniques.

3b. Off-white solid, yield 29%. ^{1}H NMR (CD_3CN, 300 MHz): δ = 4.00 (s, 6H, CH_3), 7.09 (m, 1H, CH Ar), 7.35 (d, $^3J_{HH}$ = 1.8 Hz, 2H, CH), 7.49, (s, 1H, CH Ar), 7.52 (d, $^3J_{HH}$ = 1.8 Hz, 2H, CH), 7.58 (m, 2H, CH Ar). $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz): δ 39.2 (CH_3), 122.2 (CH Ar), 124.1 (CH Ar), 124.7 (CH), 130.5 (CH Ar), 177.7 (CCu), CAr not detected. ESI-MS$^+$ (CH_3CN): *m/z* 746.95 $[Cu_2L_2PF_6]^+$, 601.25 $[Cu_2L_2]^+$, 301.33 $[Cu_2L_2]^{2+}$.

3c. Off-white solid, yield 30%. ^{1}H NMR (CD_3CN, 300 MHz): δ 3.99 (s, 6H, CH_3), 7.34 (d, $^3J_{HH}$ = 1.8 Hz, 2H, CH), 7.47 (d, $^3J_{HH}$ = 1.8 Hz, 2H, CH) 7.61 (s, 4H, CH Ar). $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz): δ 39.1 (CH_3), 122.2 (CH), 124.7 (CH), 125.9 (CH Ar), 137.2 (C Ar), 177.2 (CCu). ESI-MS$^+$ (CH_3CN): *m/z* 747.05 $[Cu_2L_2PF_6]^+$, 601.13 $[Cu_2L_2]^+$, 301.22 $[Cu_2L_2]^{2+}$.

***In situ* synthesis of the copper complex 3a.**

This compound was prepared *in situ* using the same procedure described in the previous section, however the reaction was carried out in a dry box in deuterated acetonitrile and the colorless solution was analyzed. ^{1}H NMR (CD_3CN, 300 MHz): δ 3.75 (s, 6H, CH_3), 7.01 (d, $^3J_{HH}$ = 1.8 Hz, 2H, CH), 7.05 (d, $^3J_{HH}$ = 1.8 Hz, 2H, CH), 7.56 (m, 2H, CH Ar), 7.64 (m, 2H, CH Ar). $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz): δ = 38.8 (CH_3), 123.2 (CH), 123.3 (CH), 129.3 (CH Ar), 131.0 (CH Ar), 137.4 (C Ar), 180.1 (CCu). Upon standing 12 hours in air, the color of the solution turned yellow and a new spectrum was recorded. The main signals are assigned to species **3a***. ^{1}H NMR (CD_3CN, 300 MHz): δ 4.51 (s, 6H, CH_3), 8.08 (m, 2H, CH Ar), 8.19 (d, $^3J_{HH}$ = 2.1 Hz, 2H, CH), 8.49 (m, 2H, CH Ar), 8.65 (d, $^3J_{HH}$ = 2.1 Hz, 2H, CH). $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz): δ = 42.6 (CH_3), 119.3 (CH), 119.5 (CH Ar), 123.7 (C Ar), 127.4 (NCN), 131.7 (CH), 132.7 (C Ar). ^{1}H NMR (d_6-DMSO, 400 MHz): δ 4.60 (s, 6H, CH_3), 8.12 (m, 2H, CH Ar), 8.67 (bs, 2H, CH), 8.80 (m, 2H, CH Ar), 9.50 (bs, 2H, CH). $^{13}C\{^1H\}$ NMR (d_6-DMSO, 100 MHz): δ 41.7 (CH_3), 118.3 (CH), 118.9 (CH Ar), 123.2 (C Ar), 127.4 (NCN), 130.8 (CH), 131.7 (C Ar).

Synthesis of the iridium(III) complex [IrClCp*(L^{ortho})](PF$_6$), 4a.

A solution of $[IrCl_2Cp^*]_2$ (0.026 g, 0.033 mmol) in CH_3CN (7 mL) was added to a solution of the silver complex **1a** (0.031 g, 0.031 mmol) in the same solvent (7 mL). The reaction mixture was stirred for 5 hours at room temperature. Afterwards, it was filtered through Celite and the filtrate was concentrated at low pressure. Addition of diethyl ether (15 mL) afforded the product as a yellow solid, which was filtered and dried under vacuum. Yield 20%. Anal. Calcd for $C_{24}H_{29}N_4ClF_6IrP$: C, 38.63; H, 3.92; N, 7.51%. Found: C, 36.34; H, 3.71; N, 6.61%. The elemental analysis confirm the expected C/H/N ratio, however the values are lower than the estimated ones probably because of a small amount of silver salt. ^{1}H NMR (CD_3CN, 300 MHz): δ 1.42 (s, 15H, CH_3), 3.92 (s, 6H, CH_3), 7.38 (d, $^3J_{HH}$ = 2.1 Hz, 2H, CH), 7.49 (d, $^3J_{HH}$ = 2.1 Hz, 2H, CH), 7.52 (m, 2H, CH Ar), 7.62 (m, 2H, CH Ar). $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz): δ 9.1 (CH_3), 40.1 (NCH_3), 94.0 (CCp*), 124.7 (CH), 127.3 (CH), 129.6 (CH Ar), 130.7 (CH Ar), 134.2 (C Ar), 157.0 (CIr). ESI-MS$^+$ (CH_3CN): *m/z* 601.26 $[IrClCp^*L]^+$, 363.19 $[IrClCp^*]^+$. The NMR solution of complex **4a** slowly evolves and in ca. 10 days a second similar set of signals emerges. The new signals can be attributed to the dicationic species $[IrCp^*L(CD_3CN)](PF_6)_2$ (**4a'**), in which the chloride ligand has been substituted by an deuterated acetonitrile solvent molecule. To confirm this, $[IrClCp^*L](PF_6)$ **4a** (5.5 mg, 0.0074 mmol) and $AgPF_6$ (7.5 mg, 0.0134 mmol, 3.5 eq.) were placed in a vial. Afterwards CD_3CN (1.0 ml) was added and the solution was heated at 50 °C for two hours,

Published on 06 May 2016. Downloaded by University of California - Santa Barbara on 06/05/2016 11:22:19.

Dalton Transactions Accepted Manuscript

View Article Online
DOI: 10.1039/C6DT01120B

Published on 06 May 2016. Downloaded by University of California - Santa Barbara on 06/05/2016 11:22:19.

giving complete conversion of complex **4a** in **4a'**. ^{1}H NMR (CD_3CN, 300 MHz): δ 1.50 (s, 15H, CH_3), 3.77 (s, 6H, CH_3), 7.50 (d, $^{3}J_{HH}$ = 2.1 Hz, 2H, CH), 7.58 (m, 4H, CH + CH Ar), 7.68 (m, 2H, CH Ar). $^{13}C\{^{1}H\}$ NMR (CD_3CN, 75 MHz): δ 9.3 (CH_3), 39.8 (NCH_3), 96.4 (CCp*), 125.8 (CH), 127.3 (CH), 129.8 (CH Ar), 131.3 (CH Ar), 133.2 (C Ar), 150.3 (CIr). ESI-MS^{+} (CH_3CN): *m/z* 585.17 $[IrCp^*L(HDO)]^{+}$, 565.34 $[IrCp^*L]^{+}$, 303.38 $[IrCp^*L(CH_3CN)]^{2+}$, 283.32 $[IrCp^*L]^{2+}$.

Synthesis of the ruthenium(II) complex [RuCl(L^{ortho})(*p*-cymene)](PF_6), 5a.

Complex **1a** (0.042 g, 0.043 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (0.053 g, 0.086 mmol) were placed in a two neck round bottom flask. Subsequently, CH_3CN (5 mL) was added and the reaction mixture was stirred for one hour at room temperature. Afterwards, it was filtered through Celite and the filtrate was concentrated at low pressure. Addition of diethyl ether (10 mL) afforded the product as an orange solid, which was filtered and dried under vacuum. Yield 23%. Anal. Calcd for $C_{24}H_{28}N_4ClF_6PRu{\cdot}CH_3CN$: C, 44.93; H, 4.50; N, 10.08. Found: C, 44.98; H, 4.25; N, 10.30%. ^{1}H NMR (CD_3CN, 300 MHz): δ 0.85 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.65 (hept, 1H, $CH(CH_3)_2$), 1.94 (s superimposed to the deuterated solvent signal, 3H, CH_3), 4.04 (s, 6H, NCH_3), 5.20 (d, $^{3}J_{HH}$ = 6.3 Hz, 2H, CH Ar *p*-cymene), 5.32 (d, $^{3}J_{HH}$ = 6.3 Hz, 2H, CH Ar *p*-cymene), 7.39 (s, 2H, CH), 7.48 (m, 4H, CH Ar + CH), 7.62 (m, 2H, CH Ar). $^{13}C\{^{1}H\}$ NMR (CD_3CN, 75 MHz): δ 18.7 (CH_3 *p*-cymene), 22.7 ($CH(CH_3)_2$), 31.8 ($CH(CH_3)_2$), 40.8 (NCH_3), 86.1 (CH Ar *p*-cymene), 91.6 (CH Ar *p*-cymene), 124.5 (CH), 127.2 (CH), 128.9 (CH Ar), 130.2 (CH Ar), 134.4 (C Ar), 179.5 (CRu). ESI-MS^{+} (CH_3CN): *m/z* 509.05 $[RuClL(p\text{-cymene})]^{+}$, 415.82 $[RuCl(p\text{-cymene})PF_6]^{+}$, 375.01 $[RuClL]^{+}$, 311.86 $[RuCl(CH_3CN)(p\text{-cymene})]^{+}$. Crystals of complex **5a** were obtained by diffusion of vapours between diethyl ether and an acetonitrile solution of the complex.

X-ray crystal structure determination of compounds 1a, 1a*, 1b, 2a, 2b and 5a.

The crystallographic data for all complexes were collected on a Bruker Smart Apex II single-crystal diffractometer working with monochromatic Mo-Kα radiation and equipped with an area detector.[50] The structures were solved by direct methods and refined against F^2 with SHELXL-2014/7[51] with anisotropic thermal parameters for all non-hydrogen atoms. Idealized geometries were assigned to the hydrogen atoms. Details for the X-ray data collection are reported in the supporting information. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

Photophysical measurements

Uncorrected emission spectra were obtained with an Edinburgh FLS980 spectrometer equipped with a peltier-cooled Hamamatsu R928 photomultiplier tube (185-850 nm). An Edinburgh Xe900 450 W Xenon arc lamp was used as exciting light source. Corrected spectra were obtained *via* a calibration curve supplied with the instrument. Emission lifetimes in the ns-μs range were determined with the single photon counting technique by means of the same Edinburgh FLS980 spectrometer using pulsed NanoLED excitation sources at 330 nm, (pulse width ≤ 0.3 ns, after deconvolution). Solid samples, Φ_{em} have been calculated by corrected emission spectra obtained from an apparatus consisting of a barium sulphate coated integrating sphere (4 or 6 inches), a 450W Xe lamp and a R928 photomultiplier tube signal detectors, following the procedure described by De Mello et al.[52] Experimental uncertainties are estimated to be ± 8% for lifetime determinations, ± 20% for emission quantum yields.

Theoretical Methods

Density functional theory (DFT) calculations were carried out within the Gaussian 09 suite of programs.[53] Ground state geometries were optimised in the absence of solvent with the M06-L functional[54] in conjunction with the def2-SVP basis set and associated core potential.[55] Single-point energy calculations were carried out with the def2-TZVP basis set and core potential. The polarisable continuum model (PCM)[56] self-consistent reaction field (SCRF) was used to model solvent effects at the gas-phase optimised geometries with a solvent of acetonitrile, consistent with the experimental system. Frontier MO energies were calculated using DFT MOs (including solvent effects) with M06-L and CAM-B3LYP[57] An SCF convergence criteria of 10^{-8} a.u. was employed throughout.

Acknowledgements

C.T. thanks the University of Padova for financial support (CPDA140431). M.M. thanks Fondazione Cassa di Risparmio di Padova e Rovigo (www.fondazionecariparo.it) for a PhD grant. G.A. thanks thanks Italian projects PON R&C 2007-2013 "MAAT" Molecular NAnotechnology for HeAlth and EnvironmenT (PON02 00563 3316357) and EFOR-Energia da FOnti Rinnovabili (Iniziativa CNR per il Mezzogiorno L. 191/2009 art. 2 comma 44).

Notes and references

1 (a) S. P. Nolan, N-Heterocyclic Carbenes, Effective Tools for Organometallic Synthesis. Weinheim: Wiley-VCH; 2014. (b) S. Diez-Gonzalez, N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools. Cambridge: RSC Catalysis Series, RSC; 2010. (c) C. S. J. Cazin, N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis, in Catalysis by Metal Complexes. vol. 32. Heidelberg: Springer; 2010. (d) O. Kühl, Functionalised N-heterocyclic carbene complexes. John Wiley and Sons; 2010. (e) F. Glorius, N-Heterocyclic Carbenes in Transition Metal Catalysis, in Topics in Organometallic Chemistry, vol. 21, Heidelberg: Springer; 2007.

2 (a) F. E. Hahn and M. C. Jahnke, *Angew. Chem. Int. Ed.*, 2008, **47**, 3122. (b) W. A. Herrmann, *Angew. Chem. Int. Ed.*, 2002, **41**, 1290. (c) D. Bourissou, O. F. Guerret, P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39. (d) A. J. Arduengo, R. L. Harlow and M. J. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361. (e) W. A. Herrmann, T. Weskamp and V. P. W. Böhm, *Adv. Organomet. Chem.*, 2001, **48**, 1.

Dalton Transactions Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

View Article Online
DOI: 10.1039/C6DT01123B

Published on 06 May 2016. Downloaded by University of California - Santa Barbara on 06/05/2016 11:22:19.

3 (a) M. Scholl, T. M. Trnka, J. P. Morgan and R. H. Grubbs, *Tetrahedron Lett.*, 1999, **40**, 2247. (b) J. Huang, H. Z. Schanz, E. D. Stevensenand S. P. Nolan, *Organometallics*, 1999, **18**, 5375. (c) W. A. Herrmann, M. Elison, J. Fischer, C. Köcher and G. R. J. Artus, *Angew Chem. Int. Ed.*, 1995, **34**, 2371. (d) L. Mercs and M. Albrecht, *Chem. Soc. Rev.*, 2010, **39**, 1903.

4 (a) M. C. Gather, A. Köhnen and K. Meerholz, *Adv. Mater.*, 2011, **23**, 233. (b) R. D. Costa, E. Ortí, H. J. Bolink, S. Graber, C. E. Housecroft and E. C. Constable, *Adv. Funct. Mater.*, 2010, **20**, 1511. (c) T. Sajoto, P. I. Djurovich, A. Tamayo, M. Yousufuddin, R. Bau, M. E. Thompson, R. J. Holmes and S. R. Forrest, *Inorg. Chem.*, 2005, **44**, 7992. (d) Y. Unger, A. Zeller, S. Ahrens and T. Strassner, *Chem. Commun.*, 2008, 3263.

5 (a) K. M. Hindi, M. J. Panzner, C. A. Tessier, C. L. Cannon and W. J. Youngs, *Chem. Rev.*, 2009, **109**, 3859. (b) A. Melaiye, R. S. Simons, A. Milsted, F. Pingitore, C. Wesdemiotis, C. A. Tessier and W. J. Youngs, *J. Med. Chem.*, 2004, **47**, 973. (c) M. L. Teyssot, A. S. Jarrousse, M. Manin, A. Chevry, S. Roche, F. Norre, C. Beaudoin, L. Morel, D. Boyer, R. Mahiou and A. Gautier, *Dalton Trans.*, 2009, **34**, 6894. (d) D. Brackemeyer, A. Hervé, C. Schulte to Brinke, M. C. Jahnke and F. E. Hahn, *J. Am. Chem. Soc.*, 2014, **136**, 7841. (e) C. Bazzicalupi, M. Ferraroni, F. Papi, L. Massai, B. Bertrand, L. Messori, P. Gratteri, A. Casini, *Angew. Chem. Int. Ed.*, 2016, **55**, 4256. (f) J.-J. Zhang, C.-M. Che and I. Ott, *J. Organomet. Chem.*, 2015, **782**, 37. (g) J. F. Arambula, R. McCall, K. J. Sidoran, D. Magda, N. A. Mitchell, C. W. Bielawski, V. M. Lynch, J. L. Sesslerg and K. Arumugam, *Chem. Sci.*, 2016, **7**, 1245.

6 R. Visbal and M. C. Gimeno, *Chem. Soc. Rev.*, 2014, **43**, 3551.

7 (a) K. Matsumoto, N. Matsumoto, A. Ishii, T. Tsukuda, M. Hasegawa and T. Tsubomura, *Dalton Trans.*, 2009, 6795. (b) V. J. Catalano, L. B. Munro, C. E. Strasser and A. F. Samin, *Inorg. Chem.*, 2011, **50**, 8465.

8 (a) X. Zhang, S. Gu, Q. Xia and W. Chen, *J. Organomet. Chem.*, 2009, **694**, 2359. (b) A. Poethig and T. Strassner, *Organometallics*, 2011, **30**, 6674.

9 (a) R. Visbal, I. Ospino, J. M. López-de-Luzuriaga, A. Laguna and M. C. Gimeno, *J. Am. Chem. Soc.*, 2013, **135**, 4712. (b) S. Gonell, M. Poyatos and E. Peris, *Dalton Trans.*, 2016, **45**, 5549. (c) F.-F. Hung, W.-P. To, J.-J. Zhang, C. Ma, W.-Y. Wong and C.-M. Che, *Chem.-Eur. J.*, 2014, **20**, 8604.

10 E.Q.-X. Liu, F.-B. Xu, Q.-S. Li, H.-B. Song and Z.-Z. Zhang, *Organometallics*, 2004, **23**, 610.

11 Q.-X. Liu, H.-B. Song, F.-B. Xu, Q.-S. Li, X.-S. Zeng, X.-B. Leng and Z.-Z. Zhang, *Polyhedron*, 2003, **22**, 1515.

12 (a) Y. Unger, D. Meyer and T. Strassner, *Dalton Trans.*, 2010, **39**, 4295. (b) Y. Unger, D. Meyer, O. Molt, C. Schildknecht, I. Münster, G. Wagenblast and T. Strassner, *Angew. Chem., Int. Ed.*, 2010, **49**, 10214. (c) R. Wai-Yin Sun, A. Lok-Fung Chow, X.-H. Li, J. J. Yan, S. Sin-Yin Chui and C.-M. Che, *Chem. Sci.*, 2011, **2**, 728-736. (d) P. Pinter, H. Mangold, I. Stengel, I. Münster and T. Strassner, *Organometallics*, 2016, **35**, 273. (e) M. Tenne, S. Metz, G. Wagenblast, I. Münster and T. Strassner, *Organometallics*, 2015, **34**, 4433. (f) H. Leopold, A. Tronnier, G. Wagenblast, I. Münster and T. Strassner, *Organometallics*, 2016, **35**, 959.

13 (a) F. Kessler, R. D. Costa, D. Di Censo, R. Scopelliti, E. Orti, H. J. Bolink, S. Meier, W. Sarfert, M. Grätzel, M. K. Nazeeruddin and E. Baranoff, *Dalton Trans.*, 2012, **41**, 180. (b) F. Monti, F. Kessler, M. Delgado, J. Frey, F. Bazzanini, G. Accorsi, N. Armaroli, H. J. Bolink, E. Ortí, R. Scopelliti, M. K. Nazeeruddin and E. Baranoff, *Inorg. Chem.*, 2013, **52**, 10292. (c) Y. Zhou, J. Jia, W. Li, H. Fei and M. Zhou, *Chem. Commun.*, 2013, **49**, 3230. (d) G. J. Barbante, E. H. Doeven, P. S. Francis, B. D. Stringer, C. F. Hogan, P. R. Kheradmand, D. J. D. Wilson and P. J. Barnard, *Dalton Trans.*, 2015, **44**, 8564. (e) B. D. Stringer, L. M. Quan, P. J. Barnard, D. J. D. Wilson and C. F. Hogan, *Organometallics*, 2014, **33**, 4860.

14 (a) U. Son, K. H. Park, Y.-S. Lee, B. Y. Kim, C. H. Choi, M. S. Lah, Y. H. Jang, D.-J. Jang and Y. K. Chung, *Inorg. Chem.*, 2004, **43**, 6896. (b) G. Duan and V. W.-W. Yam, *Chem. - Eur. J.*, 2010, **16**, 12642. (c) J. Dinda, S. Liatard, J. Chauvin, D. Jouvenot and F. Loiseau, *Dalton Trans.*, 2011, **40**, 3683. (d) D. G. Brown, N. Sanguantrakun, B. Schulze, U. S. Schubert and C. P. Berlinguette, *J. Am. Chem. Soc.*, 2012, **134**, 12354. (e) G. J. Barbante, P. S. Francis, C. F. Hogan, P. R. Kheradmand, D. J. D. Wilson and P. J. Barnard, *Inorg. Chem.*, 2013, **52**, 7448. (f) V. Leigh, W. Ghattas, R. Lalrempuia, H. Müller-Bunz, M. T. Pryce and M. Albrecht, *Inorg. Chem.*, 2013, **52**, 5395.

15 (a) M. Poyatos, J. A. Mata and E. Peris, *Chem. Rev.*, 2009, **109**, 3677. (b) J. A. Mata, M. Poyatos and E. Peris, *Coord. Chem. Rev.*, 2007, **251**, 841. (c) A. Biffis, C. Tubaro and M. Baron, *Adv. Organomet. Chem.*, 2015, **63**, 203.

16 P. J. Barnard, M. V. Baker, S. J. Berners-Price, B. W. Skelton and A. H. White, *Dalton Trans.*, 2004, 1038.

17 V. J. Catalano and A. O. Etogo, *J. Organomet. Chem.*, 2005, **690**, 6041.

18 P. J. Barnard, L. E. Wedlock, M. V. Baker, S. J. Berners-Price, D. A. Joyce, B. W. Skelton and J. H. Steer, *Angew. Chem., Int. Ed.*, 2006, **45**, 5966.

19 (a) C. Tubaro, M. Baron, M. Costante, M. Basato, A. Biffis, A. Gennaro, A. A. Isse, C. Graiff and G. Accorsi, *Dalton Trans.*, 2013, 10952. (b) M. Baron, C. Tubaro, A. Biffis, M. Basato, C. Graiff, A. Poater, L. Cavallo, N. Armaroli and G. Accorsi, *Inorg. Chem.*, 2012, **51**, 1778.

20 A. Biffis, M. Cipani, C. Tubaro, M. Basato, M. Costante, E. Bressan, A. Venzo and C. Graiff, *New J. Chem.*, 2013, **37**, 4176.

21 T. P. Pell, D. J. D. Wilson, B. W. Skelton, J. L. Dutton and P. J. Barnard, *Inorg. Chem.*, 2016, http://dx.doi.org/10.1021/acs.inorgchem.6b00222.

22 (a) R. J. Rubio, G. T. S. Andavan, E. B. Bauer, T. K. Hollis, J. Cho, F. S. Tham and B. Donnadieu, *J. Organomet. Chem.*, 2005, **690**, 5353. (b) G. T. S. Andavan, E. B. Bauer, C. S. Letko, T. K. Hollis and F. S. Tham, *J. Organomet. Chem.*, 2005, **690**, 5938. (c) J. Cho, T. K. Hollis, T. R. Helgerta and E. J. Valente, *Chem. Commun.*, 2008, 5001. (d) J. Cho, T. K. Hollis, E. J. Valente and J. M. Trate, *J. Organomet. Chem.*, 2011, **696**, 373. (e) X. Zhang, A. M. Wright, N. J. DeYonker, T. K. Hollis, N. I. Hammer, C. E. Webster and E. J. Valente, *Organometallics*, 2012, **31**, 1664. (f) T. R. Helgert, T. K. Hollis and E. J. Valente, *Organometallics*, 2012, **31**, 3002. (g) A. J. Huckaba, T. K. Hollis, T. O. Howell, H. U. Valle and Y. Wu, *Organometallics*, 2013, **32**, 69. (h) X. Zhang, B. Cao, E. J. Valente and T. K. Hollis, *Organometallics*, 2013, **32**, 752. (i) S. W. Reilly, G. Akurathi, H. K. Box, H. U. Valle, T. K. Hollis and C. E. Webster, *J. Organomet. Chem.*. 2016, **802**, 32. (j) S. W. Reilly, C. E. Webster, T. K. Hollis and H. U. Valle, *Dalton Trans*., 2016, **45**, 2823.

23 M. Albrecht, R. H. Crabtree, J. Mata and E. Peris, *Chem. Commun.*, 2002, 32.

24 Y. Canac, C. Lepetit, M. Abdalilah, C. Duhayon and R. Chauvin, *J. Am. Chem. Soc.*, 2008, **130**, 8406.

25 (a) M. Raynal, R. Pattacini, C. S. J. Cazin, C. Vallée, H. Olivier-Bourbigou and P. Braunstein, *Organometallics*, 2009, **28**, 4028. (b) W. Zuo and P. Braunstein, *Organometallics*, 2010, **29**, 5535. (c) W. Zuo and P. Braunstein, *Dalton Trans.*, 2012, **41**, 636. (d) N. Darmawan, C.-H. Yang, M. Mauro, M. Raynal, S. Heun, J. Pan, H. Buchholz, P. Braunstein and L. De Cola, *Inorg. Chem.*, 2013, **52**, 10756. (e) M. Jagenbrein, A. A. Danopoulos and P. Braunstein, *J. Organomet. Chem.*, 2015, **775**, 169.

26 L. Mercs, A. Neels, H. Stoeckli-Evans and M. Albrecht, *Inorg. Chem.*, 2011, **50**, 8188.

27 (a) A. R. Chianese, A. Mo, N. L. Lampland, R. L. Swartz and P. T. Bremer, *Organometallics*, 2010, **29**, 3019. (b) A. R.

Dalton Transactions Accepted Manuscript

View Article Online
DOI: 10.1039/C6DT01125B

Chianese, S. E. Shaner, J. A. Tendler, D. M. Pudalov, D. Y. Shopov, D. Kim, S. L. Rogers and A. Mo, *Organometallics*, 2012, **31**, 7359. (c) A. R. Chianese, M. J. Drance, K. H. Jensen, S. P. McCollom, N. Yusufova, S. E. Shaner, D. Y. Shopov and J. A. Tendler, *Organometallics*, 2014, **33**, 457.
28 (a) A. Rit, T. Pape and F. E. Hahn, *Organometallics*, 2011, **30**, 6393. (b) R. Maity, A. Rit, C. Schulte to Brinke, J. Kösters and F. E. Hahn, *Organometallics*, 2013, **32**, 6174.
29 Y.-M. Zhang, J.-Y. Shao, C.-J. Yao and Y.-W. Zhong, *Dalton Trans.*, 2012, **41**, 9280.
30 B. K. Rana, V. Bertolasi, S. Pal, P. Mitra and J. Dinda, *J. Mol. Struct.*, 2013, **1049**, 458.
31 S. Zlatogorsky, C. A. Muryn, F. Tuna, D. J. Evans and M. J. Ingleson, *Organometallics*, 2011, **30**, 4974.
32 (a) D. Munz, A. Poethig, A. Tronnier and T. Strassner, *Dalton Trans.*, 2013, **42**, 7297. (b) A. Tronnier and T. Strassner, *Dalton Trans.*, 2013, **42**, 9847.
33 A. R. Naziruddin, Z.-J. Huang, W.-C. Lai, W.-J. Lin and W.-S. Hwang, *Dalton Trans.*, 2013, **42**, 13161.
34 (a) W. D. Clark, G. E. Tyson, T. K. Hollis, H. U. Valle, E. J. Valente, A. G. Oliver and M. P. Dukes, *Dalton Trans.*, 2013, **42**, 7338. (b) V. Charra, P. de Frémont, P.-A. R. Breuil, H. Olivier-Bourbigou and P. Braunstein, *J. Organomet. Chem.*, 2015, **795**, 25.
35 (a) V. C. Vargas, R. J. Rubio, T. K. Hollis and M. E. Salcido, *Org. Lett.*, 2003, **5**, 4847. (b) C. Tubaro, A. Biffis, C. Gonzato, M. Zecca and M. Basato, *J. Mol. Catal. A: Chem.*, 2006, **248**, 93. (c) J. Z. Vlahakis, S. Mitu, G. Roman, E. P. Rodriguez, I. E. Crandall and W. A. Szarek, *Biorg. Med. Chem.*, 2011, **19**, 6525.
36 (a) H. M. J. Wang and I. J. B. Lin, *Organometallics*, 1998, **17**, 972. (b) J. C. Garrison and W. J. Youngs, *Chem. Rev.*, 2005, **105**, 3978.
37 Y.-F. Han, G.-X. Jin and F. E. Hahn, *J. Am. Chem. Soc.*, 2013, **135**, 9263.
38 R. Zhong, A. Pöthig, D. C. Mayer, C. Jandl, P. J. Altmann, W. A. Herrmann and F. E. Kühn, *Organometallics*, 2015, **34**, 2573
39 P. J. Barnard, M. V. Baker, S. J. Berners-Price, B. W. Skelton and A. H. White, *Dalton Trans.*, 2004, 1038.
40 (a) A. Herbst, C. Bronner, P. Dechambenoit and O. S. Wenger, *Organometallics*, 2013, **32**, 1807. (b) J. Vaughan, D. J. Carter, A. L. Rohl, M. I. Ogden, B. W. Skelton, P. V. Simpson and D. H. Brown, *Dalton Trans.*, 2016, **45**, 1484. (c) T. P. Pell, B. D. Stringer, C. F. Hogan, D. J. D. Wilson and P. J. Barnard, unpublished results.
41 (a) D. H. Brown, G. L. Nealon, P. V. Simpson, B. W. Skelton, and Z. Wang, *Organometallics*, 2009, **28**, 1965. (b) J. C. C. Chen and I. J. B. Lin, *J. Chem. Soc., Dalton Trans.*, 2000, 839. (c) A. Caballero, E. Díez-Barra, F. A. Jalón, S. Merino, A. M. Rodríguez and J. Tejeda, *J. Organomet. Chem.*, 2001, **627**, 263.
42 F. Jean-Baptiste dit Dominique, H. Gornitzka, A. Sournia-Saquet and C. Hemmert, *Dalton Trans.*, 2009, 340.
43 (a) J. R. Ames, M. A. Houghtaling, D. L. Tellian and T. P. Mitchell, *Can. J. Chem.*, 1997, **75**, 28. (b) Z. Shi and R. P. Thummel, *J. Org. Chem.*, 1995, **60**, 5935.
44 P. Pyykkö, *Angew. Chem. Int. Ed.*, 2004, **43**, 4412.
45 J. Muñiz, E. Sansores, J. A. Reyes-nava, V. H. Ramos-sanchez and A. Olea, *Int. J. Quant. Chem.*, 2011, **111**, 4378.
46 L. Magnko, M. Schweizer, G. Rauhut, M. Schütz, H. Stoll and H.-J. Werner, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1006.
47 (a) A. Volpe, A. Sartorel, C. Tubaro, L. Meneghini, M. Di Valentin, C. Graiff and M. Bonchio, *Eur. J. Inorg. Chem.*, 2014, 665. (b) C. Tubaro, D. Bertinazzo, M. Monticelli, O. Saoncella, A. Volpe, M. Basato, D. Badocco, P. Pastore, C. Graiff and A. Venzo, *Eur. J. Inorg. Chem.*, 2014, 1524.
48 G. Buscemi, M. Basato, A. Biffis, A. Gennaro, A. A. Isse, M. M. Natile and C. Tubaro, *J. Organomet. Chem.*, 2010, **695**, 2359.
49 (a) J. DePasquale, M. Kumar, M. Zeller and E. T. Papish, *Organometallics*, 2013, **32**, 966. (b) M. Poyatos, F. Mas, Marzá, M. Sanaú and E. Peris, *Inorg. Chem.*, 2004, **43**, 1793.
50 APEX II v2012.2-0 Software User Guide, SAINT, version 7.06a, SADABS, version 2.01, Bruker AXS Inc., Madison, WI, 2008.
51 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112-122.
52 J. C. De Mello, H. F. Wittmann and R. H. Friend, *Adv. Mat.*, 1997, **9**, 230.
53 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.1, Gaussian 09, Revision A.1, Gaussian, Inc.: Wallingford CT, 2009.
54 Y. Zhao and D. G. Truhlar, *J. Chem. Phys.*, 2006, **125**, 194101.
55 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.
56 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.
57 T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51.

Published on 06 May 2016. Downloaded by University of California - Santa Barbara on 06/05/2016 11:22:19.

Dalton Transactions Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx