Silver (I) and mercury (II) complexes of *meta*- and *para*-xylyl linked bis(imidazol-2-ylidenes)

Murray V. Baker[1*] · David H. Brown[1,2] · Rosenani A. Haque[1,3] · Brian W. Skelton[1] · Allan H. White[1]

M. V. Baker · D. H. Brown · R. A. Haque · B. W. Skelton · A. H. White
[1]Chemistry M313, School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, 35 Stirling Hwy, Crawley, WA 6009, Australia

Email: murray.baker@uwa.edu.au

Tel: +61 8 6488 2576

Fax: +61 8 6488 1005

D. H. Brown.
[2]Nanochemistry Research Institute, Department of Applied Chemistry, Curtin University of Technology, Kent St, Bentley, WA 6102, Australia

R. A. Haque
[3]School of Chemical Sciences, Universiti Sains Malaysia, Minden, 11800 Penang, Malaysia

Dedicated to Jack Harrowfield on his retirement. An inimitable educator, scientist, colleague, friend, writer of mischievous anagrams...and still a good bloke.

Abstract

Mononuclear silver and mercury complexes bearing bis-*N*-heterocyclic carbene (NHC) ligands with linear coordination modes have been prepared and structurally characterised. The complexes form metallocyclic structures that display rigid solution behaviour. A larger metallocycle of the form $[L_2Ag_2]^{2+}$ [where L = *para*-bis(N-methylimidazolylidene)xylylene] has been isolated from the reaction of *para*-xylylene-bis(N-methylimidazolium) chloride and Ag_2O. Reaction of silver- and mercury-NHC complexes with $Pd(NCCH_3)_2Cl_2$ affords palladium-NHC complexes via NHC-transfer reactions, the mercury case being only the second example of a NHC-transfer reaction using a mercury-NHC complex.

Keywords

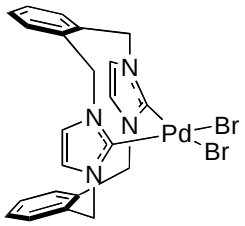
Silver · Mercury · N-Heterocyclic Carbenes · Carbene Transfer

Introduction

N-Heterocyclic carbene (NHC) complexes of silver have become common-place in the organometallic literature. The interest in Ag-NHC complexes is largely due to their ease of synthesis (from azolium salts and Ag_2O) and their ability to serve as useful precursors to other NHC-metal complexes by NHC-transfer reactions [1]. In recent years NHC-silver complexes have also been studied for possible antimicrobial and anti-cancer properties [2,3].

Wanzlick and Schönherr reported the synthesis of a mercury NHC complex via the reaction of an imidazolium salt with mercury(II) acetate in 1968 [4]. Despite the fact that this complex was one of the earliest examples of an NHC-metal complex, NHC-mercury complexes have received little attention compared to NHC-silver complexes, and applications of mercury carbene complexes have not been widely explored. We recently reported the use of NHC-mercury complexes for redox-transmetallation chemistry, where the reaction of a NHC-mercury(II) complex with a palladium(0) source afforded an NHC-palladium(II) complex [5]. Redox-transmetallation using mercury complexes is a well established route in organometallic synthesis outside of NHC chemistry [6].

We, and others, have an interest in xylyl-linked NHCs and their metal complexes, particularly systems where the NHCs form part of a cyclophane structure [5,7-18]. Cyclophane NHCs (comprising two NHC groups linked by two xylyl groups) provide a fascinating range of binding modes for metals, ranging from *cis*-chelating modes (e.g., **1**) and *trans*-spanning chelating modes (e.g., **2**, **3**) through to dinuclear modes involving two mono-NHC-bound metals (e.g., **4**) and dinuclear modes involving two bis(NHC)-bound metals (e.g., **5**, **6**). Metal complexes of cyclophane NHC ligands display interesting properties, including high stability compared to other complexes of unidentate and chelating NHCs and interesting catalytic properties (Pd-NHC complexes) [19] and anti-mitochondrial and luminescent properties (Au-NHC complexes) [20]. Compared to the cyclophane bis(NHC)s, bis(NHC) ligands containing only one xylyl linker (non-cyclophane structures) provide additional conformational flexibility that can permit additional metal-coordination modes (e.g. **7**) [21].



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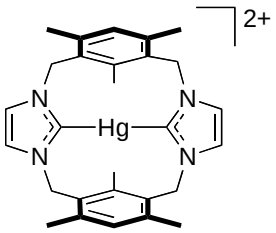

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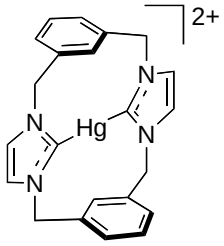

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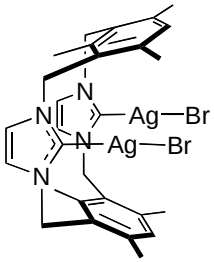

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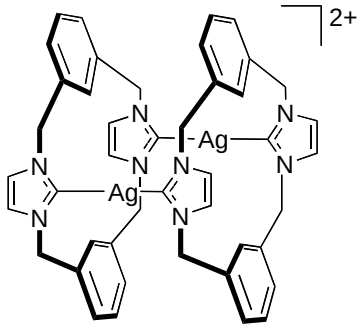

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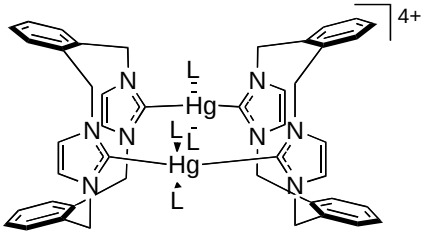

L = DMSO

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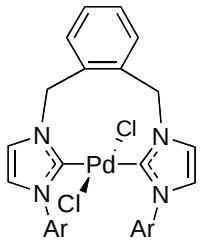

Ar = 2,6-$^{i}Pr_2C_6H_3$

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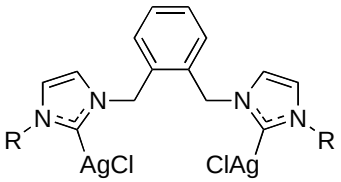
Silver complexes derived from non-cyclic xylyl-linked bis(NHC) ligands have been reported (e.g. **8**, **9**) [22-24]. Lutidinediyl analogues of the *meta*-xylyl linked structures have also been reported (**10**) [21,25,26]. In general metal complexes with *para*-xylyl linked bis(NHC) ligands are rare, though some interesting structures have been characterised in the solid-state (e.g. **11**) [27-29].



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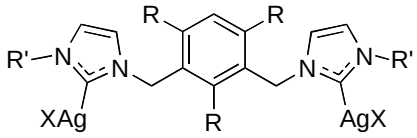

R = H, Me

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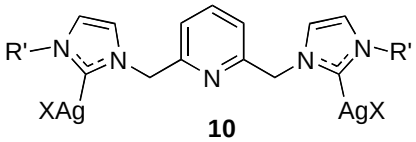

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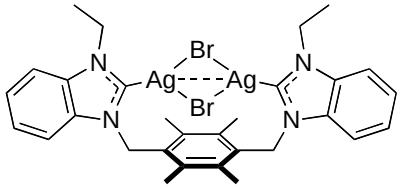

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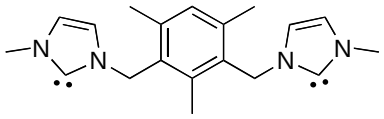
Here we report the synthesis and characterisation of silver and mercury complexes with NHC ligands **12** and **13**, derived from *meta*- and *para*-xylyl linked bis-imidazolium cations. We also report the transmetallation (carbene-transfer) reactions of silver and mercury complexes to form a palladium complex.



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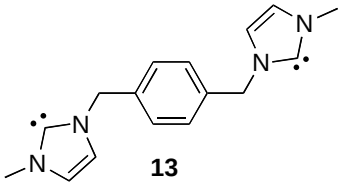

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Experimental Section

General experimental

Nuclear magnetic resonance spectra were recorded using Bruker Avance 500 (500.13 MHz for ^{1}H and 125.77 MHz for ^{13}C) and Bruker ARX300 (300.14 MHz for ^{1}H and 75.48 MHz for ^{13}C) spectrometers at ambient temperature. ^{1}H and ^{13}C chemical shifts were referenced to solvent resonances. Mass spectra were obtained by Dr A. Reeder using a VG Autospec Mass Spectrometer via electrospray ionisation (low resolution). Microanalyses were performed by the Microanalytical Laboratory at the Research School of Chemistry, Australian National University, Canberra.

Synthesis

$PdCl_2(NCCH_3)_2$ was prepared by the method of Wimmer et al. [30]. 1,3-Di(bromomethyl)-2,4,6-trimethylbenzene was prepared by the method of van der Made and van der Made [31].

*Synthesis of the para-xylyl bis(imidazolium) salts **13**H_2·2Cl and **13**H_2·2PF_6*

N-Methylimidazole (3.0 g, 17.1 mmol) was added to a stirred solution of α,α'-dichloro-*p*-xylene (9.0 g, 51.4 mmol) in dioxane (150 mL). The mixture was heated at 100 °C for 24 h under nitrogen. The product precipitated from solution as a light yellow solid, which was collected and washed with diethyl ether. Recrystallisation from a mixture of ethanol and diethyl ether yielded the product as yellow crystals (4.7 g) Yield 81%; ^{1}H NMR (300.1 MHz, d_6-DMSO): δ 3.86 (6H, s, 2 x CH_3), 5.47 (4H, br s, $W_{h/2}$ = 2 Hz, 2 x CH_2), 7.50 (4H, br s, $W_{h/2}$ 2 Hz, 4 x Ar CH), 7.74 (2H, d, $^3J_{H,H}$ = 2 Hz, 2 x imidazolium H5), 7.86 (2H, d, $^3J_{H,H}$ = 2 Hz, 2 x imidazolium H4) and 9.49 (2H, s, 2 x imidazolium H2); ^{13}C NMR (75.5 MHz, d_6-DMSO): δ 35.9 (NCH_3), 51.3 (CH_2), 122.4 (imidazolium C5), 124.1 (imidazolium C4), 129.1 (Ar CH), 135.6 (imidazolium C2) and 136.9 (Ar C); Anal. Calc. for $C_{16}H_{20}N_4Cl_2$·$3H_2O$: C, 48.86; H, 6.36; N, 14.24. Found: C, 48.74; H, 6.36; N, 14.07%.

13H_2·2Cl was converted into its hexafluorophosphate salt (**13**H_2·2PF_6) by a salt metathesis reaction using **13**H_2·2Cl and KPF_6 in methanol and was obtained as white crystalline solid, in 71% yield after recrystallisation from hot water. Crystals suitable for X-ray diffraction studies were grown from slow evaporation of a concentrated solution of the imidazolium salt in acetonitrile at 4 °C. ^{1}H NMR (500.1 MHz, d_6-DMSO): δ 3.84 (6H, s, 2 x CH_3), 5.41 (4H, br s, $W_{h/2}$ 2 Hz, 4 x CH_2), 7.45 (4H, br s, $W_{h/2}$ 2 Hz, 4 x Ar CH), 7.70 (2H, d, $^3J_{H,H}$ = 2 Hz, 2 x imidazolium H5), 7.75 (2H, d, $^3J_{H,H}$ = 2 Hz, 2 x imidazolium H4) and 9.23 (2H, s, 2 x imidazolium H2); ^{13}C NMR (125.8 MHz, d_6-DMSO): δ 35.9 (CH_3), 51.3 (CH_2), 122.2 (imidazolium C5), 124.0 (imidazolium C4), 128.9 (Ar CH), 136.7 (imidazolium C2) and 135.4 (Ar C); Anal. Calc. for $C_{16}H_{20}N_4P_2F_{12}$: C, 34.42; H, 3.61; N, 10.04. Found: C, 34.29; H, 3.53; N, 9.92%. The tetrafluoroborate salt **13**H_2·2BF_4 was obtained by a similar procedure.

*Synthesis of the meta-mesitylene bis(imidazolium) salt **12**H_2·2PF_6*

A solution of 1,3-di(bromomethyl)-2,4,6-trimethylbenzene (1 g, 3.3 mmol) and 1-methylimidazole (0.84 g, 10 mmol) in 1,4-dioxane (13 mL) was heated at 100 °C, under nitrogen, for 24 h. The mixture was allowed to cool to room temperature and the precipitate was collected, washed with diethyl ether (5 mL) and dried over P_2O_5 to afford **12**H_2·2Br as a white powder (1.4 g, 90%). The bromide salt

12H_2·2Br was converted to its hexafluorophosphate salt by a metathesis reaction using **12**H_2·2Br and KPF_6 in methanol and was obtained as white crystalline solid, in 85% yield after recrystallisation from hot water. Crystals suitable for X-ray diffraction studies were grown from slow evaporation of a concentrated solution of the imidazolium salt in acetonitrile at 4 °C. ^{1}H NMR (500.1 MHz, d_6-DMSO): δ 2.21 (3H, s, 1 x C2-*C*H_3), 2.30 (6H, s, 1 x *C*4-CH_3/1 x *C*6-CH_3), 3.79 (6H, s, 2 x N-CH_3), 5.43 (4H, s, 2 x CH_2), 7.18 (1H, s, 1 x Ar H5), 7.60 (2H, d, $^3J_{H,H}$ = 2 Hz, 2 x imidazolium H5), 7.71 (2H, d, $^3J_{H,H}$ = 2 Hz, 2 x imidazolium H4) and 8.91 (2H, s, 2 x imidazolium H2); ^{13}C NMR (125.8 MHz, d_6-DMSO): δ 15.6 (C2-*C*H_3), 19.1 (C4-*C*H_3/C6-*C*H_3), 35.9 (NCH_3), 47.3 (CH_2), 122.2 (imidazolium C5'), 123.7 (imidazolium C4'), 131.2 (Ar CH), 136.0 (imidazolium C2'), 128.4 (Ar C), 139.0 (Ar C) and 139.7 (Ar C); Anal. Calc. for $C_{16}H_{20}N_4P_2F_{12}$: C, 38.01; H, 4.37; N, 9.33. Found: C, 37.87; H, 4.09; N, 9.50%.

*Synthesis of the dinuclear silver complex **17**·2Cl*

Ag_2O (85 mg, 367 mmol) was added to a solution of **13**H_2·2Cl (105 mg, 310 mmol) in methanol (15 mL). The mixture was heated at 60 °C for 2 h in darkness. A clear solution with some black suspension was obtained. The mixture was filtered and the filtrate was evaporated to dryness to give a white powder. Recrystallisation of the powder from minimum amount of hot methanol yielded white crystals (90 mg). Yield 52%. ^{1}H NMR (500.1 MHz, d_6-DMSO): δ 3.83 (12H, s, 4 x NCH_3), 5.29 (8H, br s, $W_{h/2}$ 2 Hz, 4 x CH_2), 7.14 (8H, br s, $W_{h/2}$ 2 Hz, 8 x ArH), 7.46 (4H, d, $^3J_{H,H}$ = 2 Hz, 4 x imidazolium H5) and 7.53 (4H, d, $^3J_{H,H}$ = 2 Hz, 4 x imidazolium H4); ^{13}C NMR (125.8 MHz, d_6-DMSO): δ 38.2 (NCH_3), 53.5 (CH_2), 122.2 (imidazolium C5'), 123.5 (imidazolium C4'), 127.7 (Ar CH), 137.2 (Ar C) and 180.1 (br C-Ag). Anal. Calc. for $C_{32}H_{36}Ag_2N_8Cl_2$·1.5CH_3OH·2H_2O: C, 44.54; H, 5.13; N, 12.40. Found: C, 44.70; H, 4.79; N, 12.19%.

*Synthesis of the dinuclear silver complex **17**·2PF_6*

Ag_2O (23 mg, 100 mmol) was added to a solution of **13**H_2·2PF_6 (50 mg, 90 mmol) in acetonitrile (10 mL). The mixture was heated at 60 °C for 2 hr in darkness. The mixture was filtered and the filtrate was concentrated in vacuo. The white resiude was washed with dichloromethane (2 x 2 mL) and was then recrystallised from a mixture of acetonitrile and diethyl ether to afford a white powder (36 mg). Yield

77 % ^{1}H NMR (500.1 MHz, d_6-DMSO): δ 3.83 (12H, s, 4 x NCH_3), 5.29 (8H, br s, $W_{h/2}$ 2 Hz, 4 xCH_2), 7.13 (8H, br s, $W_{h/2}$ 2 Hz, 8 x ArH), 7.46 (4H, d, $^{3}J_{H,H}$ = 2 Hz, 4 x imidazolium H4) and 7.53 (4H, d, $^{3}J_{H,H}$ = 2 Hz, 4 x imidazolium H5); ^{13}C NMR (125.8 MHz, d_6-DMSO): δ 38.1 (NCH_3), 53.5 (CH_2), 122.2 (imidazolium C5'), 123.5 (imidazolium C4'), 127.6 (Ar CH), 137.1 (Ar C) and 180.2 (d, $^{1}J_{C\text{-}109Ag}$ = 210 Hz, $^{1}J_{C\text{-}107Ag}$ = 180 Hz, Ag-C); ES-MS *m/z* 891 (55% relative intensity), 892 (30%), 893 (100%), 894 (40%), 895 (55%), 896 (15%) $[M\text{-}PF_6]^+ \equiv [\mathbf{17}\cdot PF_6]^+$; Anal. Calc. for $C_{32}H_{36}N_8Ag_2P_2F_{12}$: C, 37.02; H, 3.49; N, 10.79. Found: C, 36.77; H, 3.32; N, 10.71%.

*Synthesis of the silver complex **15**·PF$_6$*

Ag_2O (30 mg, 129 mmol) was added to a solution of **12**H_2·2Br (25 mg, 104 mmol) in methanol (20 mL). The mixture was heated at 50 °C for 2 h in darkness. The mixture was filtered and the filtrate was concentrated in vacuo to afford **15**·Br as a white solid. The white solid residue was dissolved in water (10 mL) and the resulting solution was filtered into an aqueous solution of KPF_6 (38 mg, 206 mmol, 5 mL). A grey precipitate formed, which was collected and dried under reduced pressure (44 mg). Yield 76%; Analytically pure samples were obtained by recrystallisation of the complex from acetonitrile. ^{1}H NMR (500.1 MHz, d_6-acetone): δ 2.17 (6H, s, 2 x C4/C6-CH_3), 2.73 (3H, s, 1 x C2-CH_3), 3.85 (6H, s, 2 x NCH_3), 5.48 (2H, A part of AB multiplet, $^{2}J_{H,H}$ = 14 Hz, 2 x benzylic C*H*H), 5.57 (2H, B part of AB multiplet, $^{2}J_{H,H}$ = 14 Hz, 2 x benzylic CH*H*), 7.12 (1H, s, 1 x Ar H5), 7.42 (2H, d, $^{3}J_{H,H}$ = 2 Hz, 2 x imidazolium H5) and 7.64 (2H, d, $^{3}J_{H,H}$ = 2 Hz, 2 x imidazolium H4); ^{13}C NMR (125.8 MHz, d_6-DMSO): δ 17.0 (C4/C6-CH_3), 19.1 (C2-CH_3), 39.4 (NCH_3), 47.9 (CH_2), 122.1 (imidazolium-C5'), 123.7 (imidazolium-C4'), 131.7 (Ar CH), 131.5 (Ar C), 136.4 (Ar C), 138.0 (Ar C) and 178.7 (d, Ag-C, $^{1}J_{C\text{-}109Ag}$ = 212 Hz, $^{1}J_{C\text{-}107Ag}$ = 188 Hz); Anal. Calc. for $C_{19}H_{24}N_4AgPF_6\cdot 0.5H_2O$: C, 40.02; H, 4.42; N, 9.82. Found: C, 40.25; H, 4.36; N, 9.90%.

*Synthesis of the mercury complex **16**·2PF$_6$*

$Hg(OAc)_2$ (35 mg, 109 mmol) was added to a solution of **12**H_2·2PF_6 (50 mg, 100 mmol) in acetonitrile (40 mL). The mixture was heated at reflux for 3 days. A clear colourless solution resulted. The solution was concentrated in vacuo. The

solid residue was washed with water (2 x 5 mL) and recrystallised from acetonitrile to afford colourless crystals (45 mg). Yield 55%; Analytically pure samples and crystals suitable for X-ray diffraction studies were obtained by the slow evaporation of a solution of the salt in acetonitrile/water at room temperature; ^{1}H NMR (500.1 MHz, d_3-acetonitrile): δ 2.16 (6H, s, 2 x C4/C6-CH_3), 2.53 (3H, s, 1 x C2-CH_3), 3.79 (6H, s, 2 x NCH_3), 5.58 (2H, A part of AB pattern, $^{2}J_{H,H}$ = 15 Hz, 2 x benzylic C*H*H), 5.62 (2H, B part of AB pattern, $^{2}J_{H,H}$ = 15 Hz, 2 x benzylic CH*H*), 7.34 (1H, s, 1 x Ar H5), 7.42 (2H, m, $^{3}J_{H,H}$ = 2 Hz, 2 x imidazolium H5) and 7.68 (2H, d, $^{3}J_{H,H}$ = 2 Hz, 2 x imidazolium H4); ^{13}C NMR (125.8 MHz, d_6-acetonitrile): δ 16.7 (C4/C6-CH_3), 17.0 (C2-CH_3), 39.9 (NCH_3), 49.6 (CH_2), 126.4 (imidazolium-C5'), 126.6 (imidazolium-C4'), 132.0 (Ar CH), 135.4 (Ar C), 137.4 (Ar C), 142.4 (Ar C) and 173.3 (C-Hg); Anal. Calc. for $C_{19}H_{24}N_4HgP_2F_{12}$: C, 28.56; H, 3.03; N, 7.01. Found: C, 28.74; H, 3.09; N, 7.13%.

Synthesis of a palladium complex via NHC-transfer reactions

Method A (via a silver complex): Ag_2O (28 mg, 120 mmol) was added to a solution of **13**H_2·2Cl (32 mg, 94 mmol) in methanol (10 mL). The mixture was heated at 60 °C for 2 h in darkness. A clear solution with some black suspension was obtained. The mixture was filtered and the filtrate was evaporated to dryness to give a white powder. The white powder was suspended in acetonitrile (10 mL) and $PdCl_2(NCCH_3)_2$ (49 mg, 188 mmol) was added. The resulting mixture was stirred at 60 °C for 24 h, which resulted in a yellow solution with a dark precipitate. The mixture was filtered and the filtrate was dried in vacuo to leave a yellow solid. The solid was washed with a minimum amount of dichloromethane and then recrystallised from acetonitrile, collected and dried in vacuo to afford a yellow powder (38 mg). Yield: 59%. Crystals suitable for X-ray diffraction studies were grown from slow evaporation of a concentrated solution of the complex in acetonitrile at 4 °C.

Method B (via a mercury complex): $Hg(OAc)_2$ (40 mg, 125 mmol) was added to a solution of **13**H_2·2Cl (40 mg, 118 mmol) in methanol (50 mL). The mixture was heated at reflux for 24 h resulting in a clear colourless solution. The solution was concentrated in vacuo to afford a white solid. The white solid was washed with water (2 x 6 mL), diethyl ether (2 x 6 mL) and dried under vacuum (64 mg). [^{1}H

NMR (300.1 MHz, d_6-DMSO): δ 3.89 (12H, s, 4 x NCH_3), 5.48 (8H, br s, 4 x CH_2), 7.46 (8H, s, 8 x ArH), 7.68 (4H, d, $^3J_{H,H}$ = 2 Hz, 4 x imidazolium H5) and 7.73 (4H, d, $^3J_{H,H}$ = 2 Hz, 4 x imidazolium H4)] A portion of the solid (30 mg, 38 mmol) was suspended in acetonitrile (10 mL). A solution of $PdCl_2(NCCH_3)_2$ (20 mg, 77 mmol) in acetonitrile (10 mL) was added and the mixture was heated at 60 °C. After 30 min, a precipitate began to form. The reaction was continued until all the original white solid dissolved (18 h). A yellow solution with grey precipitate resulted. The solution was filtered and the filtrate was concentrated in vacuo to give a yellow solid, which was then washed with water (2 x 5 mL) and dried (23 mg) Yield 91%.

^{1}H NMR (500.1 MHz, d_3-acetonitrile): δ 4.01 (6H, s, 2 x CH_3), 5.67 (4H, br s, 2 x CH_2), 6.94 (2H, d, $^3J_{H,H}$ = 2 Hz, 2 x imidazolium H5), 7.07 (2H, d, $^3J_{H,H}$ = 2 Hz, 2 x imidazolium H4) and 7.50 (4H, s, 4 x ArH); ^{13}C NMR (125.8 MHz, d_3-acetonitrile): δ 39.0 (N-CH_3), 55.0 (CH_2), 123.6 (imidazolium-C5'), 125.9 (imidazolium-C4'), 130.6 (Ar CH), 137.9 (Ar C) and 147.3 (C-Pd); Anal. Calc. for $C_{16}H_{18}N_4Pd_2Cl_4$: C, 30.95; H, 2.92; N, 9.02. Found: C, 31.01; H, 3.22; N, 8.85%.

Structure determinations

Full spheres of CCD area-detector diffractometer data were measured (monochromatic Mo Kα radiation, λ = 0.7107$_3$ Å, ω-scans) yielding $N_{t(otal)}$ reflections, these merging to N unique (R_{int} cited) after 'empirical'/multiscan 'absorption correction', these being used in the full matrix least squares refinements on F^2 (anisotropic displacement parameter refinement for the non-hydrogen atoms, hydrogen atom treatment following a riding model; reflection weights: $(\sigma^2(F_o^2) + (aP)^2) (+ bP))^{-1}$ ($P = (F_o^2 + 2F_c^2/3)$); N_o with $F_o > 4\sigma(F_o)$ were considered 'observed'. Pertinent details are given below in the Figures, the latter showing 50% probability amplitude displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Neutral atom complex scattering factors were employed within the SHELXL 97 program [32]. Full *.cif* depositions (excluding structure factor amplitudes) reside with the Cambridge Crystallographic Data Centre, CCDC 736772-736777, 737102.

Crystal/refinement data

13H_2·$2PF_6$ ≡ $C_{16}H_{20}F_{12}N_4P_2$, M = 558.3. Monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), a = 7.1194(8), b = 12.1150(10), c = 13.055(2) Å, β = 105.019(2)º, V = 1088 Å^3 (T ca. 153 K). D_c (Z = 2) = 1.70$_5$ g cm^{-3}. μ_{Mo} = 0.32 mm^{-1}; specimen: 0.43 x 0.31 x 0.25 mm; 'T'$_{min/max}$ = 0.82. $2\theta_{max}$ = 66º; N_t = 14578, N = 3980 (R_{int} = 0.022), N_o = 3382. $R1$ = 0.041, $wR2$ = 0.123 (a = 0.067, b = 0.326), S = 1.05. $|\Delta\rho_{max}|$ = 0.45 e Å^{-3}.

13H_2·$2BF_4$ ≡ $C_{16}H_{20}B_2F_8N_4$, M = 442.0. Monoclinic, space group $P2_1/c$, a = 4.9639(8), b = 12.913(2), c = 15.401(3) Å, β = 92.932(3)º, V = 985.$_9$ Å^3 (T ca. 153 K). D_c (Z = 2) = 1.48$_9$ g cm^{-3}. μ_{Mo} = 0.14 mm^{-1}; specimen: 0.48 x 0.15 x 0.10 mm; 'T'$_{min/max}$ = 0.80. $2\theta_{max}$ = 50º; N_t = 9070, N = 1730 (R_{int} = 0.036), N_o = 1454. $R1$ = 0.058, $wR2$ = 0.148 (a = 0.068, b = 1.03), S = 1.05. $|\Delta\rho_{max}|$ = 0.46 e Å^{-3}.

17·$2NO_3$·$2CH_3OH$ ≡ $C_{34}H_{44}Ag_2N_{10}O_8$, M = 936.5. Triclinic, space group $P\bar{1}$, a = 9.363(2), b = 9.460(2), c = 21.779(4) Å, α = 94.308(4), β = 91.836(3), γ = 93.606(3)º, V = 1919 Å^3 (T ca. 170 K). D_c (Z = 2) = 1.62$_1$ g cm^{-3}. μ_{Mo} = 1.08 mm^{-1}; specimen: 0.49 x 0.15 x 0.12 mm; 'T'$_{min/max}$ = 0.85. $2\theta_{max}$ = 58º; N_t = 15090, N = 8356 (R_{int} = 0.047), N_o = 6607. $R1$ = 0.050, $wR2$ = 0.116 (a = 0.040, b = 5.58); S = 1.08. $|\Delta\rho_{max}|$ = 1.17 e Å^{-3}.

18·$2CH_3CN$ ≡ $C_{24}H_{30}Cl_4N_8Pd_2$, M = 785.2. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a = 7.2833(6), b = 7.8832(7), c = 14.8010(10) Å, α = 80.196(2), β = 81.669(2), γ = 65.593(2)º, V = 759.$_9$ Å^3 (T ca. 170 K). D_c (Z = 1) = 1.56$_4$ g cm^{-3}. μ_{Mo} = 1.56 mm^{-1}; specimen: 0.48 x 0.20 x 0.08 mm; 'T'$_{min/max}$ = 0.81. $2\theta_{max}$ = 67º; N_t = 10432, N = 5365 (R_{int} = 0.026), N_o = 4826. $R1$ = 0.029, $wR2$ = 0.074 (a = 0.021, b = 0.71), S = 1.10. $|\Delta\rho_{max}|$ = 0.86 e Å^{-3}.

12H_2·$2PF_6$ ≡ $C_{19}H_{26}F_{12}N_4P_2$, M = 600.4. Monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14; variant), a = 8.1345(5), b = 26.145(2), c = 11.9508(5) Å, β = 108.052(5)º, V = 2417 Å^3 (T ca. 100 K). D_c (Z = 4) = 1.65$_0$ g cm^{-3}. μ_{Mo} = 0.29 mm^{-1}; specimen: 0.32 x 0.20 x 0.07 mm; 'T'$_{min/max}$ = 0.81. $2\theta_{max}$ = 68º; N_t =

30072, N = 9496 (R_{int} = 0.033), N_o = 4980. $R1$ = 0.041, $wR2$ = 0.106 (a = 0.058), S = 0.87. $|\Delta\rho_{max}|$ = 0.45 e Å^{-3}.

15·HCO_3·H_2O ≡ $C_{20}H_{27}AgN_4O_4$, M = 495.3. Triclinic, space group $P\bar{1}$, a = 8.3300(10), b = 10.8710(10), c = 11.9050(10) Å, α = 72.493(3), β = 82.538(3), γ = 77.284(3)º, V = 1001 Å^3 (T ca. 150 K). D_c (Z = 2) = 1.64$_4$ g cm^{-3}. μ_{Mo} = 1.04 mm^{-1}; specimen: 0.22 x 0.15 x 0.10 mm; 'T'$_{min/max}$ = 0.74. $2\theta_{max}$ = 75º; N_t = 19861, N = 10153 (R_{int} = 0.025), N_o = 8618. $R1$ = 0.039, $wR2$ = 0.13 (b = 3.7), S = 1.28. $|\Delta\rho_{max}|$ = 1.93 e Å^{-3}.

Variata. Hydrogen atoms, located in associated with residues modelled as bicarbonate and water, were refined in (x, y, z, U_{iso}).

16·2PF_6 ≡ $C_{19}H_{24}F_{12}HgN_4P_2$, M = 799.0. Monoclinic, space group $P2_1$ (C_2^2, No. 4), a = 8.5280(6), b = 12.5400(9), c = 11.7590(8) Å, β = 96.925(2)º, V = 1248 Å^3 (T ca. 153 K). D_c (Z = 2) = 2.12$_6$ g cm^{-3}. μ_{Mo} = 6.4 mm^{-1}; specimen: 0.38 x 0.37 x 0.33 mm; 'T'$_{min/max}$ = 0.58. $2\theta_{max}$ = 75º; N_t = 24232, N = 12340 (R_{int} = 0.038), N_o = 10236. $R1$ = 0.036, $wR2$ = 0.077 (a = 0.035), S = 1.05. $|\Delta\rho_{max}|$ = 3.25 e Å^{-3}. x_{abs} = –0.018(4).

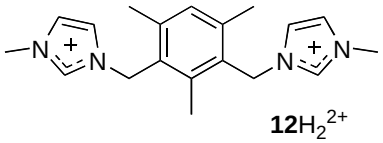
Results and discussion

Synthesis, reactivity and solution behaviour

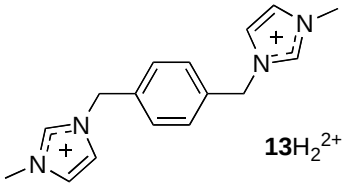
*Imidazolium salts **12**H_2·2Br, **12**H_2·2PF_6, **13**H_2·2Cl, and **13**H_2·2PF_6*

The *meta*- and *para*-xylyl linked bis(imidazolium) salts **12**H_2·2Br and **13**H_2·2Cl were prepared by procedures based on the method used by Dias and Jin for the synthesis of a tri-imidazolium analogue of **12**H_2^{2+} [33]. The reaction of α,α'-dichloro-*p*-xylene with two equivalents of *N*-methylimidazole in refluxing dioxane for 24 h afforded **13**H_2·2Cl, after recrystallisation from ethanol-diethyl ether. In a similar fashion, **12**H_2·2Br was prepared by the reaction of 1,3-di(bromomethyl)-2,4,6-trimethylbenzene with two equivalents of *N*-methylimidazole in refluxing dioxane. The bis-imidazolium salts **12**H_2·2Br and

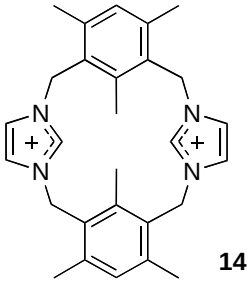
13H_2·2Cl are very soluble in polar solvents such as ethanol, methanol, DMSO, DMF and water, but are insoluble in less polar solvents such as dichloromethane, acetone, acetonitrile and diethyl ether. The halide salts **12**H_2·2Br and **13**H_2·2Cl were converted to their hexafluorophosphate counterparts by salt metathesis in methanol using KPF_6. The ^1H and ^{13}C NMR spectra for solutions of the imidazolium cations **12**H_2^{2+} and **13**H_2^{2+}, as the halide and hexafluorophosphate salts, display the expected signals.



12H_2^{2+}



13H_2^{2+}



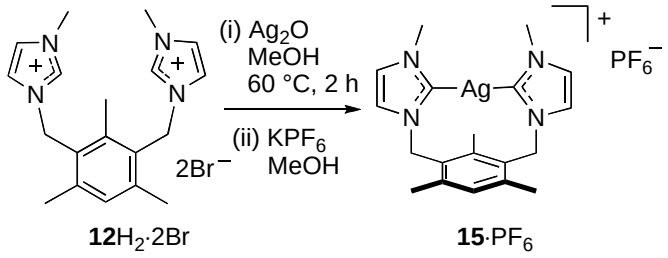
14

Complexes derived from the meta*-linked di(imidazolium) cation* ***12****H*$_2$

The reaction of **12**H_2·2Br with Ag_2O in methanol afforded complex **15**·Br (Scheme 1). The imidazolium salt **12**H_2·2Br reacts relatively quickly under these conditions to form the silver complex **15**. This reactivity is substantial higher than that of the cyclophane analogue **14** [11], a result that may be a consequence of higher conformational mobility and/or accessibility of the imidazolium C2 positions in **12**H_2^{2+} *vs*. **14**. Salt metathesis by the addition of an aqueous solution of **15**·Br to an aqueous solution of KPF_6 afforded **15**·PF_6 as a grey precipitate, which was isolated in an overall yield of 76%. The bromide salt **15**·Br is freely soluble in highly polar solvents such as DMF, DMSO and water, while **15**·PF_6 is

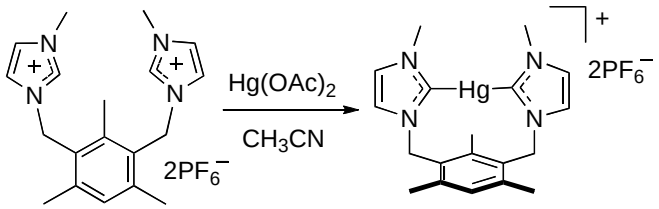
poorly soluble in water but dissolves well in acetonitrile and acetone at room temperature.

^{13}C NMR spectra of solutions of **15**·PF_6 in d_6-DMSO display two doublets centred at ca. δ 179, due to the carbene carbons bound to the silver centre. The presence of ^{13}C-^{109}Ag and ^{13}C-^{107}Ag coupling of ca. 200 Hz in these signals is consistent with the absence of NHC-exchange processes at the Ag centre [1,11,34]. The ^{1}H NMR spectra of solutions of **15**·PF_6 in d_6-acetone display an AX pattern due to the benzylic methylene protons, indicating that **15** is conformationally rigid on the NMR time-scale at room temperature (i.e., that the mesitylene ring does not "flip", e.g., by a process involving the 2-methyl group passing through the metallocyclic ring). In d_6-DMSO solutions prepared from **15**·PF_6, **15** displayed excellent thermal stability, no decomposition being observed by ^{1}H NMR when the solution was heated at 100 °C for 2 days.



Scheme 1

The mononuclear mercury complex **16** was obtained by the reaction of **12**H_2·2PF_6 with $Hg(OAc)_2$ in acetonitrile at reflux for 3 days (Scheme 2). The salt **16**·2PF_6 was obtained as colourless crystals in 55% yield after recrystallisation from a mixture of acetonitrile and water. The NMR spectra for solutions of **16**·2PF_6 were similar to those of the silver analogue **15**·PF_6. The ^{1}H NMR spectra of solutions of **16**·2PF_6 in d_3-acetonitrile display an AB pattern due to the benzylic methylene protons, indicating some conformational rigidity in the structure. In the ^{13}C NMR spectra, for the same solution, a signal at ca. δ 173 is attributed to the carbene carbon bound to mercury, which is consistent with the literature [5].



12H_2·2PF_6 **16**·2PF_6

Scheme 2

Complexes derived from the para*-linked di(imidazolium) cation* ***13****H*$_2$

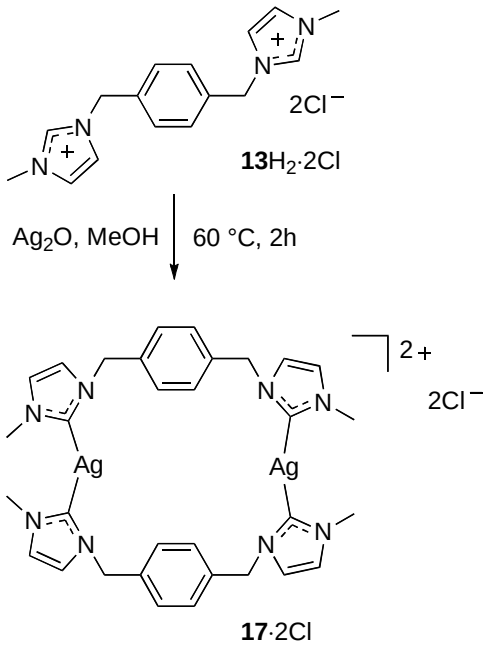
Reaction of **13**H_2·2Cl with an excess of Ag_2O in methanol (Scheme 3) afforded the salt **17**·2Cl in 52% yield after recrystallisation from hot methanol. The reaction also proceeds well in DMF or DMSO. The salt **17**·2Cl is soluble in DMF, DMSO and ethanol, and sparingly soluble in methanol. The hexafluorophosphate salt **17**·2PF_6 was prepared similarly, by reacting **17**·2PF_6 with Ag_2O in acetonitrile, and was isolated in 77% yield. Removal of the associated $AgPF_6$ by-product proved problematic. One procedure that can be used to isolate a hexafluorophosphate salt from a reaction mixture is the selective precipitation of the salt by addition of water ($AgPF_6$ remains dissolved). This method could not be used here because on addition of water to the reaction mixture the material darkened immediately. However, careful washing of the crude reaction product with dichloromethane, followed by recrystallisation from acetonitrile/diethyl ether, afforded pure **17**.2PF_6.

The results of an electrospray ionisation mass spectrometry study were consistent with the dimeric structure $[L_2Ag_2]^{2+}$ for the cation **17**. The study showed a molecular ion cluster with prominent peaks near 891 (55% relative intensity), 892 (30%), 893 (100%), 894 (40%), 895 (55%), and 896 (15%) amu, as expected for the [**17**·PF_6]$^+$ ion pair (*i.e.*, $\{[L_2Ag_2]PF_6\}^+$). The ^{1}H NMR spectra for solutions of **17**·2PF_6 in d_6-DMSO indicate that the cation **17** exhibits some conformational flexibility in solution at ambient temperature. For example, the ^{1}H NMR signal attributed to the benzylic protons appears as a singlet, which is consistent with a situation where the two protons on each benzylic carbon have their environments rendered chemically equivalent by conformational changes that are rapid on the NMR timescale. Similar to the situation for of **15**·PF_6, the ^{13}C NMR spectra for solutions of **17**·2PF_6 in d_6-DMSO displayed two doublets

centred near δ 180, attributed to the carbene carbons bound to ^{107}Ag and ^{109}Ag centres. For a solution of **17**·2Cl in d_6-DMSO, however, the ^{13}C NMR spectrum displayed only one broad signal at ca. δ 180. The lack of any observed ^{13}C-$^{107/109}$Ag coupling is common for silver complexes with halide counter anions, and has been attributed to halide-mediated Ag-NHC exchange processes [1,35].

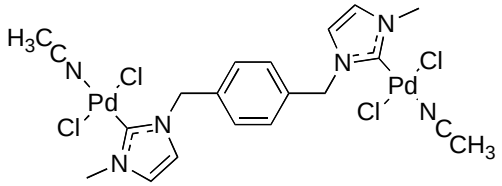
It is interesting that the *para*-linked di(imidazolium) salt **13**H_2.2Cl reacted with Ag_2O to form a dimeric structure $[L_2Ag_2]^{2+}$ (**17**), whereas **11** was isolated from the reaction of Ag_2O with a *para*-linked di(benzimidazolium) salt [29]. Two factors that might be responsible for the different courses of these reactions are the reaction solvents employed and the presence or absence of methyl substituents on the *para*-phenylene linker. In the reaction leading to **17**, solvent was methanol, from which AgCl precipitates, leaving only one Ag^+ per bis(NHC) ligand, whereas for the reaction leading to **11**, the solvent was dichloromethane, from which silver halides are less likely to precipitate, leaving excess silver and bromide in solution to form the Ag_2Br_2 core in **11**. Alternatively, the per-methylation of the *para*-phenylene linker in **11** may serve to disfavour formation of a product of form $[L_2Ag_2]^{2+}$, with the methyl groups providing the extra steric encumbrance that destabilise the L_2Ag_2 macrocycle.

Similar to those of **15**.PF_6, solutions of **17**.2PF_6 in d_6-DMSO displayed no decomposition (as observed by ^{1}H NMR) when heated at 100 °C for two days.

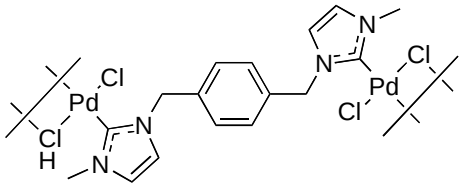


Scheme 3

Silver-NHC complexes provide a synthetic pathway to other NHC-metal complexes *via* transmetallation reactions [1]. Since examples of palladium complexes of *para*-xylyl-linked bis(NHC) ligands are rare [27], we have explored the use of **17**·2Cl in transmetallation reactions. The silver complex **17**·2Cl, prepared by the reaction of **13**H_2·2Cl with Ag_2O in methanol, was treated with two equivalents of $PdCl_2(NCCH_3)_2$ in acetonitrile at 60 °C. A precipitate, presumably AgCl, formed immediately. Filtration of the mixture, followed by drying of the filtrate under vacuum afforded a yellow powder. Results of elemental analysis of the bulk material were consistent with structures involving bridging chlorides, such as **19** (intermolecular chloride bridges) or **20** (intramolecular chloride bridges). However, the ^{1}H and ^{13}C NMR spectra of solutions of the powder in d_3-acetonitrile were consistent with formation of a solvated complex of structure **18**. Disruption of the chloride bridging to afford a solvated complex **18** would occur on dissolution of either **19** or **20** in acetonitrile. While the reaction of **17**·2Cl with $PdCl_2(NCCH_3)_2$ was conducted in acetonitrile and thus might be expected to yield the solvated complex **18**, the vacuum-drying step presumably resulted in the isolation of a non-solvated product. It has been shown previously that the acetonitrile ligand in complexes of the type *trans*-(NHC)$PdX_2(NCCH_3)$ is extremely labile, such that even washing the complex with diethyl ether can result in loss of the coordinated acetonitrile and formation of non-solvated bridging-halide complexes [36,37]. After the yellow powder was carefully recrystallised by very slow evaporation of an acetonitrile solution and isolated without any drying step, an X-ray study indicated that the crystals contained the solvated structure **18** (see below).



18



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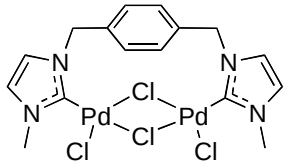


20

We recently reported the first example of redox-transmetallation using a mercury-NHC complex [5]. In view of the apparently labile nature of mercury-NHC complexes, we have explored their use in non-redox transmetallation ("carbene-transfer") reactions. The reaction of **13**H_2·2Cl with $Hg(OAc)_2$ in methanol at reflux for 24 hours afforded the mercury analogue of **17**. The Hg complex was identified on the basis of the similarity of its ^{1}H NMR spectrum with that of the Ag analog **17**. The mercury complex was treated with two equivalents of $PdCl_2(NCCH_3)_2$ in acetonitrile and heated at 60 °C. After 18 hours the reaction mixture consisted of a yellow solution and a grey precipitate (presumably $HgCl_2$ with traces of palladium black). The mixture was filtered and the yellow solution was evaporated to dryness under vacuum to leave a yellow powder. Solutions of this yellow powder in d_3-acetonitrile gave ^{1}H and ^{13}C NMR spectra identical to those of the solvated complex **18** isolated from the silver transfer reaction.

We have found that both the silver and the mercury transmetallation experiments can be performed without the need to use inert-atmosphere conditions. The mercury transmetallation route proceeded as well as, if not better than, the silver transmetallation. The mercury complexes made from $Hg(OAc)_2$ proved easy to purify, and any excess $Hg(OAc)_2$ or acetic acid was easily

removed by washing with water. Silver complexes, especially those made from the bis-imidazolium systems in this study darken easily if exposed to light and therefore need to be protected during synthesis and isolation. Mercury complexes do not need special experimental conditions and perhaps, in this respect, have an advantage over silver complexes.

Structure determinations

Cation **13**H_2^{2+} has been defined in both bis-hexafluorophosphate and -tetrafluoroborate salts. In both, one half of the formula unit comprises the asymmetric unit, i.e. one anion, devoid of crystallographic symmetry, and one half of the cation, the latter disposed about a crystallographic centre of symmetry in both cases. Both structures are well-ordered. The imidazole ring is twisted out of the plane of the central *p*-xylyl ring in each case (C_3N_2/C_6 interplanar dihedral angles 77.75(5), 86.7(3)º respectively) (Fig. 1). In both salts there are cation...anion H...F contacts; in the BF_4 salt these are all ≥ 2.4 Å, but, in the PF_6 salt, contacts to the imidazole hydrogen atoms *ortho* to the xylyl attachment are 2.2_4, 2.3_9 Å.

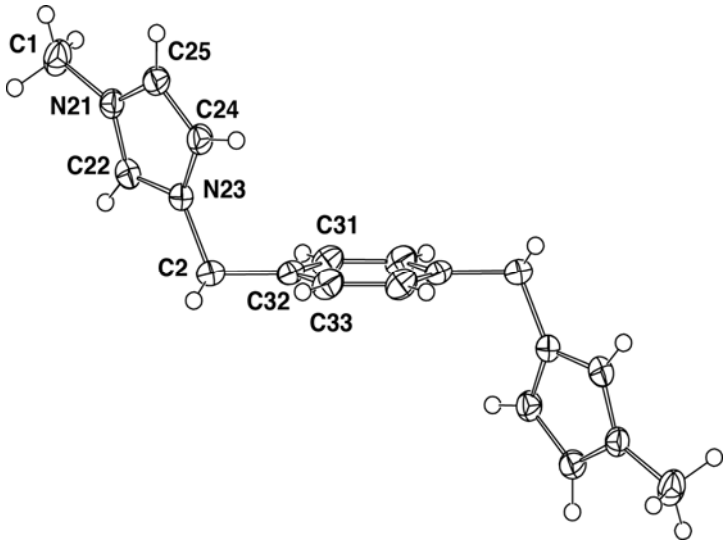


Fig. 1 (Centrosymmetric) Cation **13**H_2^{2+} in its hexafluorophosphate salt; the conformation in the tetrafluoroborate is similar.

Although silver(I) complexes of **13** and **12** were obtained in bulk as chloride and hexafluorophosphate, and hexafluorophosphate respectively, as described above, the materials obtained were inappropriate for single crystal X-ray studies; smaller quantities of other salts suitable for the X-ray work were obtained adventitiously in the course of variations on the described syntheses. With **13**H_2, a nitrate complex was obtained from methanol solution in ambience:

17·2NO$_3$·2MeOH is an elegant structure, in which, although there is only one formula unit in the asymmetric unit of the structure, that is comprised of halves of independent dimers disposed pseudo-symmetrically about inversion centres in a triclinic cell (Fig. 2(a)). The two independent cations are very similar, each comprising a pair of **17** units with their pendant groups oriented quasi-trans about a quasi-inversion centre at the centre of the xylyl ring except that the imidazole rings are oriented so that the carbene groups are directed to the same 'side' of the ligand. The pair of ligands may then be bridged by a pair of silver atoms to form a 22-membered (centrosymmetric) metallocycle (Fig. 2(b)(i)), the ring in projection through the xylyl centroids (or nearly so) having a 'Z' aspect (Fig. 2(b)(ii)). Ag-C are 2.116,2.088;2.107,2.082(4) Å (units 1;2), with C-Ag-C 172.8;175.4(2)º comparable to other silver-carbene distances, below and elsewhere [35]. C_3N_2/C_6 interplanar dihedral angles are 73.8,75.2;81.0,77.0(2)º. Within the nitrate ions, N-O are 1.212,1.243(6),1.263(5);1.247(6),1.247,1.250(5) Å, with opposed O-N-O angles 121.3(5),121.4(4),117.3;120.8,119.3,119.9(5)º. The methanol C-O distances are 1.379(7);1.393(8) Å, the hydroxyl groups being hydrogen-bonded to the nitrate ions (H,O...O 1.96(6),2.800(7);2.11(7),2.864(7) Å).

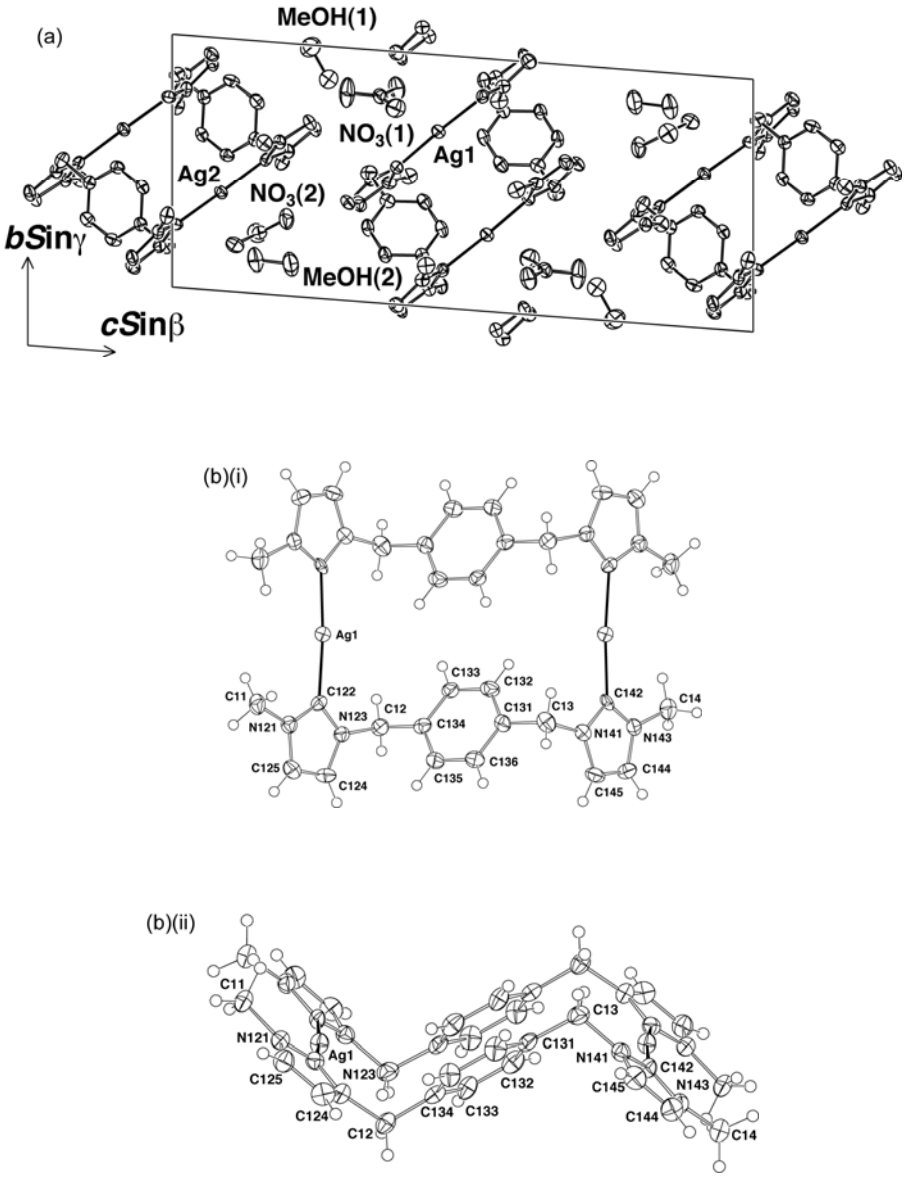


Fig. 2 (a) Unit cell contents of **17**·2NO_3·2CH_3OH projected down *a*; (b) Projections of cation 1 (cation 2 is similar): (i) normal to, and (ii) through, the Ag_2(xylyl centroid)$_2$ plane.

As a ligand, **13** also forms a bis(carbene) complex with acetonitrile solvated palladium(II) chloride, shown to be **18**·2CH_3CN, the neutral complex molecule also a centrosymmetric species, with one half of the array comprising the asymmetric unit of the structure (Fig. 3); the C_3N_2/C_6 interplanar dihedral angle is 81.4(1)º. The pair of *trans*-Pd-Cl distances in the quasi-square-planar palladium environment are 2.2964,2.2998(6) Å, Cl-Pd-Cl 178.46(2)º. Pd-N(CH_3CN) is 2.081(2) and Pd-C(carbene) 1.950(2) Å, N-Pd-C being 177.89(8)º,

N-Pd-Cl are 90.50,91.04(6) and C-Pd-Cl 88.92,89.55(6)º. The Cl_2PdNC array is essentially planar (χ^2 293), the dihedral angle to the associated C_3N_2 plane being 66.99(8)º. Distances of the palladium atom to methyl and methylene hydrogen atoms to either side are 2.9 Å. The solvating acetonitrile molecules have an association which presents the aspect of a proto-inclusion complex (Fig. 3), lying above and below the central *p*-xylyl ring and quasi-parallel to it and to the imidazole ring to one side. Their closest contact, however, is from the nitrogen atom to methylene and imidazole hydrogen atoms of an adjacent complex (N...H, 2.6 Å (x2)).

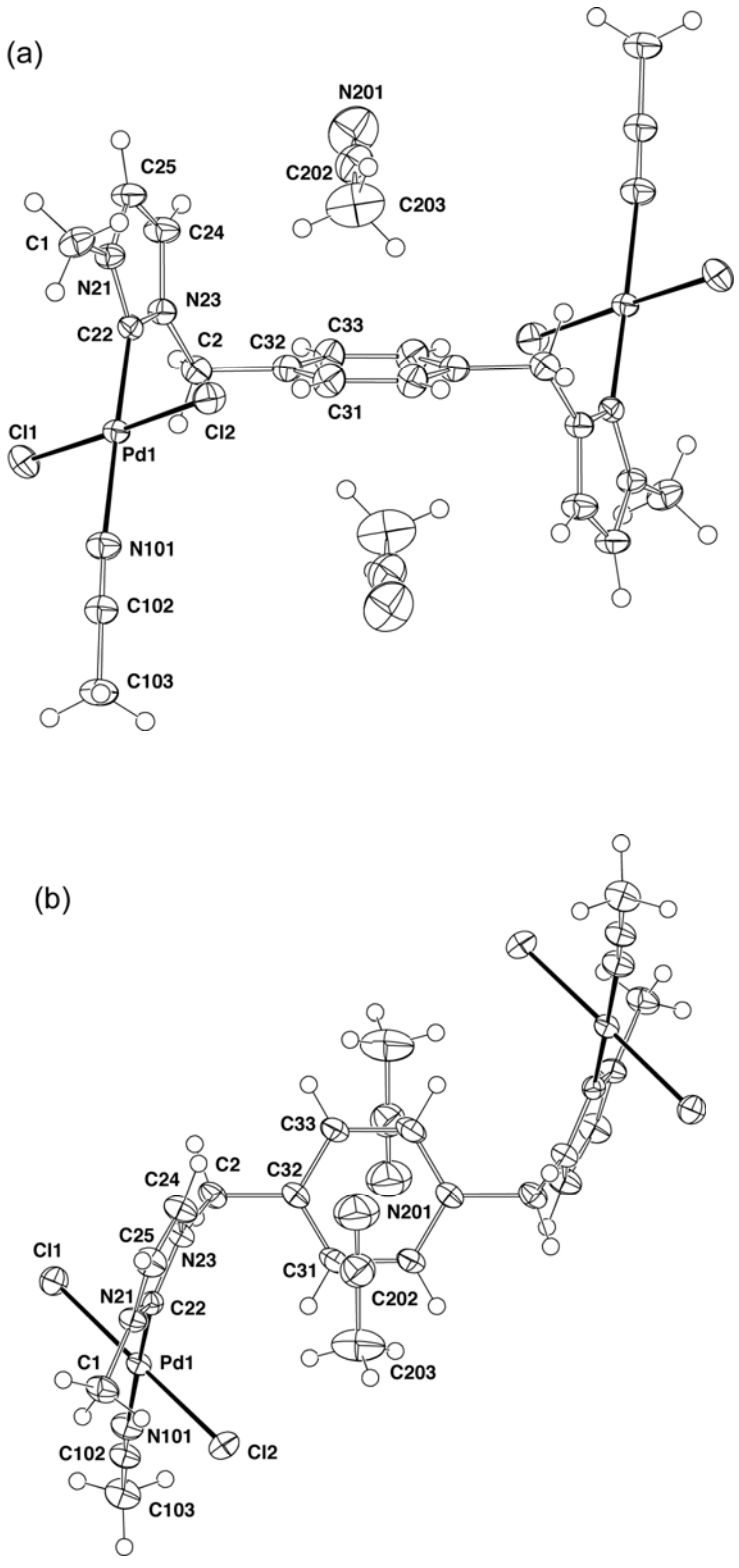


Fig. 3 Projections of **18**·2CH_3CN (a) through and (b) normal to, the central *p*-xylyl ring

Cation **12**H_2^{2+} has also been isolated as a bis(hexafluorophosphate) salt. Here, the imidazole pendants lie to the same side of the central ring, both inclined at similar angles (C_3N_2/C_6 interplanar dihedrals: 84.82,79.58(5)º), so that the cation has quasi-m symmetry, (to which the imidazole methyl substituents do not conform), with a pair of ring hydrogen atoms, ortho to the pendants, directed 'inwards'/towards each other, so as to 'chelate' one of the fluorine atoms of one of the anions (H...F 2.2_5, $2.3_{\mathbf{x}}$ Å), while one of the other ortho hydrogen atom contacts one of the fluorine atoms of the other anion (H...F 2.2_8 Å) (Fig. 4). The 'chelation' mode is consummated, with replacement of the pair of 'chelating' hydrogen atoms by a single metal atom in a bis(carbene) complex, in two crystallographically characterized derivatives of silver(I) and mercury(II):

15·HCO_3·H_2O. Here all hydroxylic hydrogen atoms are confirmed by refinement in (x, y, z, U_{iso}) using good quality data, unambiguously establishing the nature of the complex, deposited from a solution of the bromide on standing in ambience. The pair of imidazole rings now lie quasi-normal to the central ring (C_3N_2/C_6 interplanar dihedrals: 89.7,88.9(1); C_3N_2/C_3N_2: 2.2(1)º), and almost mutually coplanar (Fig. 5(a)), Ag-C are 2.093,2.094(3) Å, C-Ag-C 178.3(1)º, similar to values recorded for other bis(carbene)silver(I) arrays elsewhere [35] and above. The cation symmetry is quasi-m. The anions and solvent molecules form a separate one-dimensional array, disposed about crystallographic centres of symmetry along *b:* ...OCO.OH(*i*)HO.OCO$(H\overset{i}{O}H)_2$OCO.OH... (Fig. 5(b)). Within the bicarbonate anion, C-O(2,3) are 1.265,1.206(4) Å with O(2)-C-O(3) 126.6(3)º; C-O(1)(H) is 1.356(4) Å, with O(1)-C-O(2,3) 116.8,116.6(3)º. O(3)...O(4,4') are 2.809(5), 2.871(4) Å, with H...O distances 1.98,2.03(3) Å. O(1)...O(2) are 2.610(3) with H(1)...O(2) 1.79(5) Å. A similar cation disposition is found in:

16·2PF_6 (Fig. 6). Here the C_3N_2/C_6 interplanar dihedral angles are 80.0,77.6(2)º, the C_3N_2/C_3N_2 inclination here being greater (22.4(2)º), although M-C distances here are almost identical to those of the silver(I) complex (Hg-C 2.078,2.086(4) Å; C-Hg-C 176.8(1)º); again Hg-C are similar to those recorded in other mercury/carbene arrays [5]. In this complex the two anions approach the mercury atom from either side of the $Hgim_2$ 'plane', Hg...F(11,12) being 3.085,3.228(4), and Hg...F(21,22) 3.065,3.040(4) Å (Fig. 6(b)).

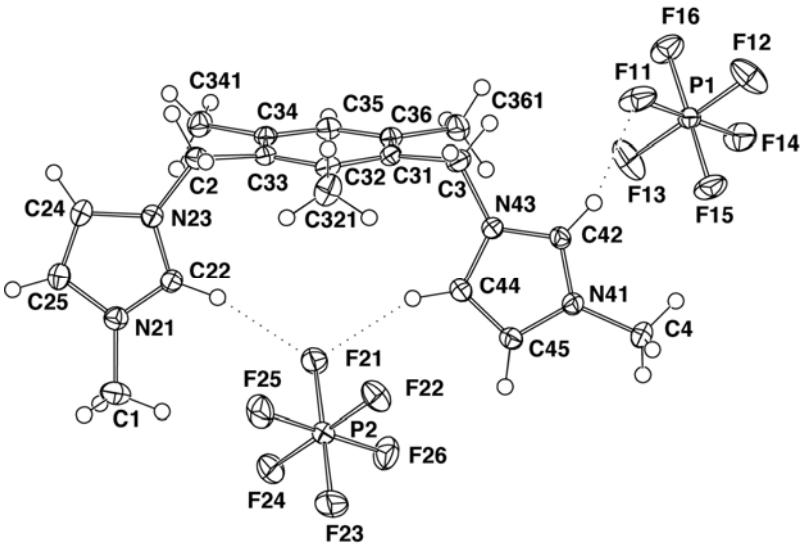


Fig. 4 The asymmetric unit of **12**H_2·2PF_6, showing the H...F interactions, and the 'chelation' of one of the anions by the cation of quasi-m symmetry.

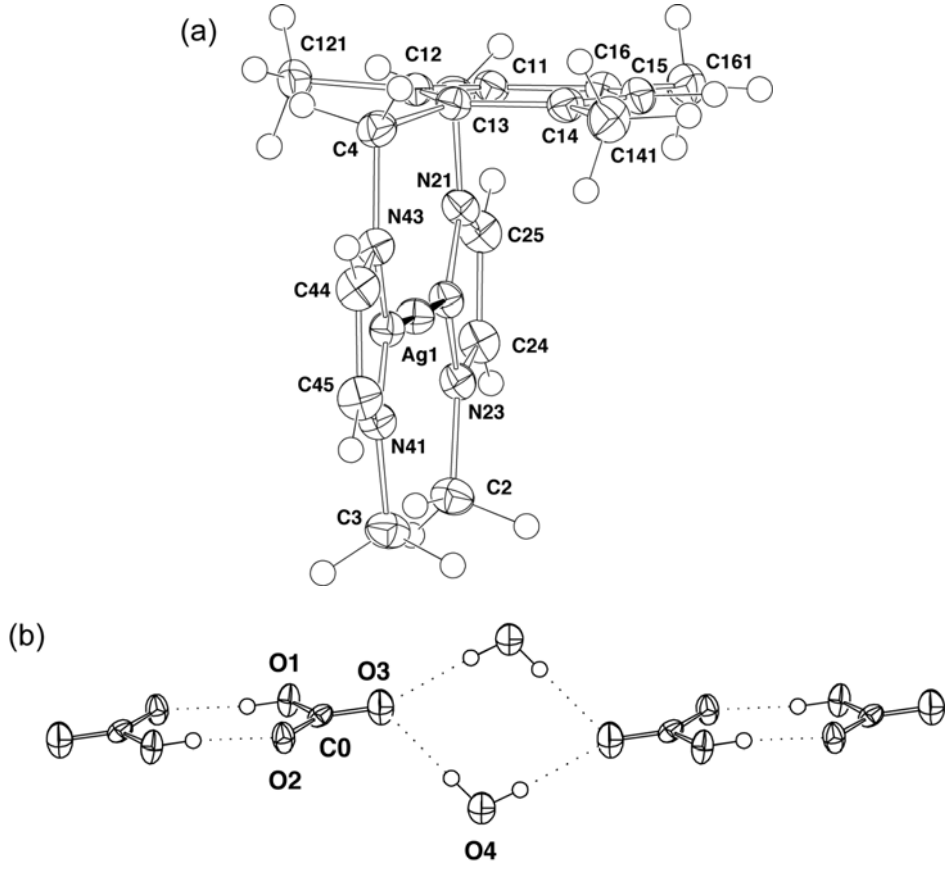


Fig. 5 (a) The cation **15** in **15**·HCO_3·H_2O. (b) The bicarbonate/water molecule polymeric strand.

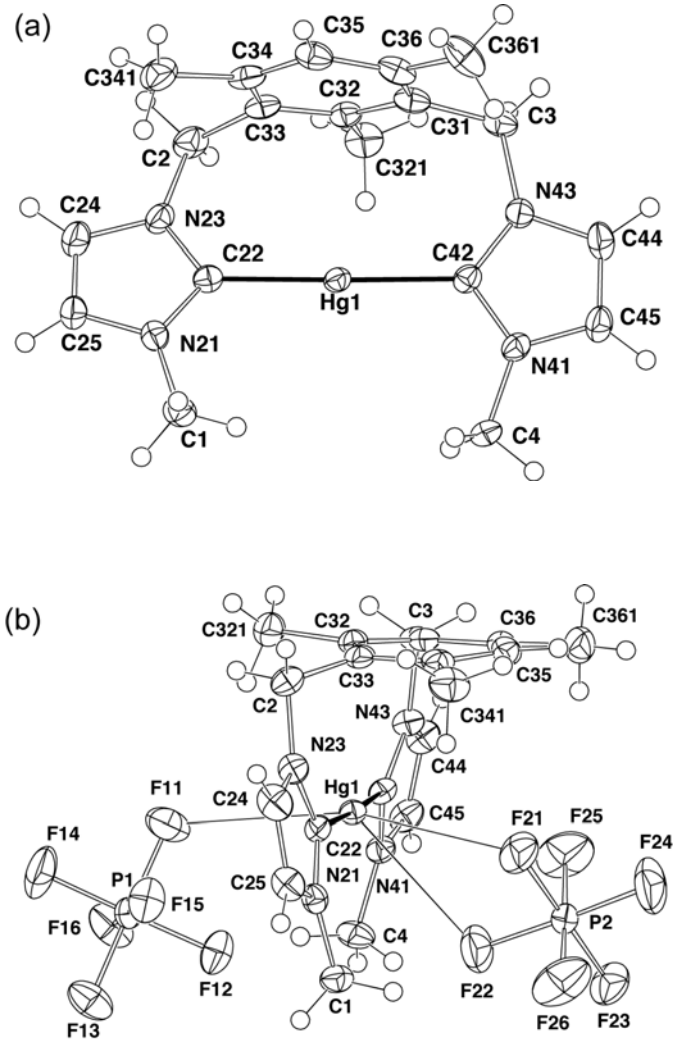
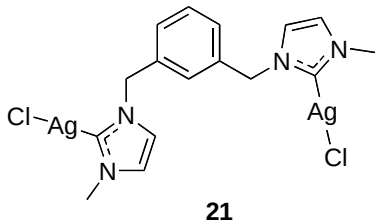


Fig. 6 (a) The cation **16** in **16**·2PF_6. (b) Projection showing the approaches of the anions.

The structure of the cation **15** contrasts with structures such as **21** and **22** , which are also based on bis(NHC)s with meta-xylyl-type linking motifs [16,24,26]. Different coordination modes may arise due to the presence of coordinating vs non-coordinating anions (**21** was formed in the presence of chloride), solvent effects, etc. In the present case, however, internal steric hindrance between the mesityl C2 methyl substituent and the imidazolyl units may disfavour dinuclear binding motifs such as exemplified by **22** [26] and **23** [11]. In the latter, for example, the mesityl groups are distinctly distorted from planarity, with the C2 methyl group pushed out of the arene plane away from the imidazolyl groups. The ligand **12** can be thought of as derived from the cyclophane ligand found in **23**,

and the absence of the *ortho*-xylyl linker leaves **12** with conformational freedom to adopt the interesting trans-spanning chelating coordinating mode rather than a sterically disfavoured dinuclear structure.



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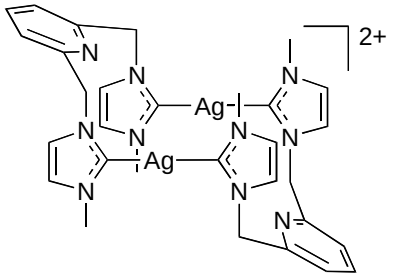

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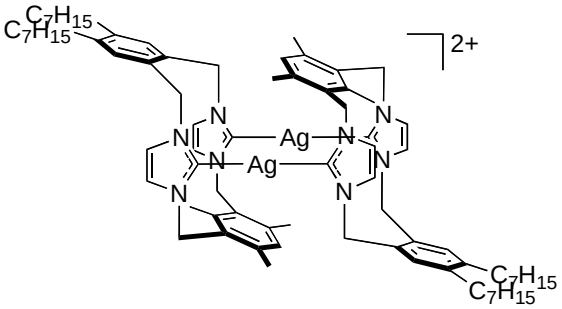

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