Homoleptic Crown N-Heterocyclic Carbene Complexes.
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Experimental Details

General Experimental

Mass spectra were carried out at the EPSRC Mass Spectroscopy centre, Swansea. Accurate masses were obtained using electron impact (ESI) on a QUATTRO mass spectrometer or on a Finnigan LCQ duo ion trap at Strathclyde University.

$^1$H NMR were run on either a Bruker DPX 400 spectrometer at 400 MHz or a Bruker AMX 400 spectrometer at 400 MHz, while $^{13}$C NMR were run at 100 MHz. Chemical shifts are in parts per million (ppm). The following abbreviations are used for multiplicities: s – singlet, d – doublet, t – triplet and m – multiplet.

Infra-Red Spectra were recorded on a Perkin Elmer Spectrum One FT IR Spectrometer. Melting points were run on a Gallenkamp Melting point apparatus.

All reagents were obtained from commercial suppliers unless otherwise stated. Dimethylformamide (99.8% anhydrous, Aldrich) was used without further purification. Solvents were purified using Pure-Solv 400 Solvent Purification System. Reactions were carried out under an argon atmosphere in glassware that was flame- or oven-dried to ensure complete dryness.

Synthesis of 1,3-bis(1-imidazolyl)propane

NaH (60% in mineral oil; 25.88g, 0.647mol) was washed with hexane (2 × 100ml) and suspended in DMF (100 ml). Imidazole (39.99g, 0.588mol) dissolved in DMF (150ml) was added to the suspension of NaH at 0 °C. A solid precipitated and more DMF (200ml) was added to effect re-dissolution. 1,3-Dibromopropane (29.9ml, 59g, 0.294mol) was added slowly and the solution stirred at room temperature for 18h. DCM (1.5L) was added resulting in a precipitate which was removed by filtration. The DCM was removed from the filtrate by rotary evaporation and subsequently, the DMF was distilled off under reduced pressure to give the crude product. The crude mixture was distilled at ca 200 °C in vacuo (0.3mbar) to give the title product (37.07g, 72%).

IR $\nu_{\text{max}}$(KBr disc)/cm$^{-1}$ 3106, 2939, 1599, 1508, 1452. $^1$H NMR (400 MHz, CDCl$_3$): $d$ 2.29 (quintet, J = 6.8 Hz, 2H), 3.91 (t, J = 6.8 Hz, 4H), 6.89 (s, 2H), 7.10 (s, 2H), 7.44 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$), $d$ 32.1 (CH$_2$), 43.5 (CH$_2$), 118.7 (CH), 130.4 (CH), 137.3 (CH); $m/z$ (ESI): 375 ([2M+Na], 53%), 353 ([2M+H], 100%), 177 ([M+H], 55%).

Synthesis of Di-imidazolium Salt, (5H$_2^{2+}$($\Gamma_2$) and Tetra-imidazolium Salt (6H$_4^{4+}$($\Gamma_4$))

To a three-necked flask equipped with a mechanical stirrer and a reflux condenser were added acetonitrile (4L), 1,3-bis(1-imidazolyl)propane (2.00g, 11.36mmol) and diiodopropane (3.36g, 11.36mmol). The mixture was heated at reflux for 24 h, after which time a further, equal quantity of the starting materials was added. One batch of starting material was added every
24 h, until, after 20 days, a total of 40.00 g of 1,3-bis(1-imidazolyl)propane and 67.2 g of diiodopropane had been added. During this period a white solid precipitated gradually. After addition was complete, the mixture was refluxed for a further four days. The reaction mixture was filtered hot to yield a white solid (crude tetraimidazolium salt), which after drying and recrystallization from hot methanol yielded the pure tetraimidazolium salt as a white crystalline solid (17.49 g, 0.0185 mol, 16.4%). The filtrate was taken to dryness in vacuo and the solid residue was recrystallized from methanol, yielding the diimidazolium salt as white crystals, (55.00 g, 0.116 mol, 51%).

**Diimidazolium salt, [5H₂₄(I)₂]**.

M.Pt. (284°C. Dec.). IR (KBr disc): £max/cm⁻¹ 3051, 3032, 1560, 1454, 1166. MS Found: [5+I]⁺ (ESI) 345.0569, C₁₂H₁₈N₄[5H₂] requires [5H₂+I]⁺ 345.0571; ¹H NMR (400 MHz, DMSO-d₆): δ 2.34 (m, 2H), 2.49 (m, including DMSO peak, 2H), 4.45 (m, 4H), 4.62 (m, 4H), 7.65 (s, 4H), 9.07 (s, 2H). ¹³C NMR (100 MHz, DMSO-d₆): δ 28.6 (CH₂), 49.2 (CH₂), 124.0 (CH), 138.9 (CH); m/z (ESI) 345 ([5H₂+I]⁺, 8%), 217 ([5H₂-H]⁺, 65%), 109 ([5H₂]⁺, 100%).

**Tetraimidazolium salt, [6H₄⁺(I)₄]**

M.Pt. (264°C. Dec.) IR (KBr disc): £max/cm⁻¹ 3413, 3132, 3069, 1571, 1450. [Found: [6H₄+2I-H]⁺ (ESI) 689.1079, C₂₄H₃₆N₈ requires [6H₄+2I-H]⁺ 689.1069; ¹H NMR (400 MHz, DMSO-d₆): δ 2.50 (m including DMSO peak, 8H), 4.28 (t, J= 6.8 Hz, 16H), 7.86 (s, 8H), 9.50 (s, 4H). ¹³C NMR (100 MHz, DMSO-d₆): δ 29.0 (CH₂), 45.8 (CH₂), 122.6 (CH), 136.5 (CH); m/z (ESI) 966 ([6H₄+4I+Na]⁺, 5%), 816 ([6H₄+3I]⁺, 30%), 689 ([6H₄+2I-H]⁺, 100%), 561 ([6H₄+I-2H]⁺, 30%).

**Disilver tetracarbene complex [Ag₂(6)]²⁺(I)₂**

![Disilver tetracarbene complex][1]

Tetraimidazolium salt, 6H₄⁺(I)₄ (1.01 g, 1.07 × 10⁻³ mol), silver(I) oxide (0.50 g, 2.17 × 10⁻³ mol) and sodium acetate (0.35 g, 4.23 × 10⁻³ mol) were suspended in DMSO (100 ml) and stirred at room temperature for 18 h. The initial black suspension was converted to a white suspension. The mixture was heated to 90°C and then filtered. On cooling the filtrate a precipitate formed which was separated by filtration and dried under high vacuum. The disilver tetracarbene complex was collected as white needles (0.47 g, 2.25 × 10⁻⁴ mol, 21%). Crystals suitable for X-ray diffraction were obtained by recrystallization from hot DMSO with very slow cooling.

M.Pt. (282°C. Dec.) IR (KBr disc): £max/cm⁻¹ 3096, 2928, 1569, 1421. [Found: [Ag₂(6)+I]⁺ (ESI) 772.9897, Ag₂C₂H₂N₈ requires [Ag₂(6)+I]⁺ 772.9891; ¹H NMR (400 MHz, DMSO-d₆): δ 2.37 (m, 8H), 3.67 (m, 8H), 4.14 (m, 8H), 7.78 (s, 8H); m/z (ESI) 775 ([Ag₂(6)+I]⁺, 10%), 541 ([Ag₂(6)-Ag]⁺, 12%), 324 ([Ag₂(6)]⁺, 100%).

**Dicopper tetracarbene complex ([Cu₂(6)]²⁺(I)₂**

![Dicopper tetracarbene complex][2]
Tetraimidazolium salt, 6H$_4$($\Gamma$)$_4$ ($0.50$g, $5.34 \times 10^{-4}$mol), copper(I) oxide ($0.10$g, $7.46 \times 10^{-4}$mol) and sodium acetate ($0.18$g, $2.18 \times 10^{-3}$mol) were suspended in DMSO (25ml) and heated to 90°C for 3h. The red solid dissolved to give a pale blue-green solution. The volume of DMSO was decreased to 5ml and methanol (10ml) was added to precipitate a solid, which was recovered by filtration and dried in vacuo to give the dicopper tetracarbene complex as a white powder ($0.23$g, $2.82 \times 10^{-4}$mol, 53%).

M.Pt. (164°C. Dec.) IR (KBr disc): $\gamma_{\text{max}}$/cm$^{-1}$ 3155, 3074, 2954, 1439, 1418, 1236. [Found: [Cu$_2$(6)]$^+$ (ESI) 685.0382, Cu$_2$C$_2$H$_2$N$_2$ requires [Cu$_2$(6)]$^+$ 685.0381; $^1$H NMR (400 MHz, DMSO-d$_6$): $d$ 2.20 (br s, 8H), $d$ 3.62 (m, 8H), $d$ 4.06 (m, 8H), $d$ 7.60 (s, 8H). $^{13}$C NMR (100 MHz, DMSO-d$_6$): $d$ 33.3 (CH$_3$), 45.4 (CH$_2$), 122.6 (CH), 178.2 (C); $m/z$ (ESI) 685 ([Cu$_2$(6)]$^+$, 50%), 495 ([Cu$_2$(6)-Cu], 25%), 279 ([Cu$_2$(6)]$^{2+}$, 100%).

Palladium Tetracarbene complex ([Pd(6)]$^2$($\Gamma$)$_2$)

![Pd(6)2Gamma2](image)

Tetraimidazolium salt, 6H$_4$($\Gamma$)$_4$ ($0.29$g, $3.09 \times 10^{-4}$mol), palladium diiodide ($0.09$g, $2.62 \times 10^{-4}$mol), sodium iodide ($0.19$g, $1.29 \times 10^{-3}$mol) and sodium acetate ($0.11$g, $1.35 \times 10^{-3}$mol) were suspended in DMSO (25ml) and heated at reflux for 18h. The initial black suspension was converted to a colourless solution. The volume of DMSO was reduced to 5ml and methanol (10ml) was added to precipitate a solid, which was filtered and dried under vacuum gave the tetracarbene palladium complex as a white powder ($0.18$g, $2.27 \times 10^{-4}$mol, 87%).

M.Pt. (>300°C. Dec.). IR (KBr disc): $\gamma_{\text{max}}$/cm$^{-1}$ 3428, 3151, 3094, 2956, 2917, 1630, 1474, 1411. [Found: [Pd(6)]$^+$ (ESI) 665.0823, PdC$_2$H$_2$N$_2$ requires [Pd(6)]$^+$ 665.0824; $^1$H NMR (400 MHz, DMSO-d$_6$): $d$ 1.85-1.90 (m, 8H), 2.38-2.46 (m, 4H), 4.44 (m, 8H), 4.70 (m, 8H), 7.30 (s, 8H). $^{13}$C NMR (100 MHz, DMSO-d$_6$): $d$ 32.6 (CH$_2$), 53.2 (CH$_2$), 123.8 (CH), 170.0 (C); $m/z$ (ESI) 665 ([Pd(6)]$^+$, 50%), 537 ([Pd(6)-H]), 35%, 269 ([Pd(6)]$^{2+}$, 100%).

X-ray Crystallography

Crystals were coated in oil and mounted on glass fibres. Data were collected on Nonius Kappa CCD (6H$_4$($\Gamma$)$_4$) and Bruker-Nonius FR591 rotating anode CCD ([Pd(6)]$^+$) Cu; [Ag$_2$(6)]$^+$, [Ag$_4$I$_4$]; [Cu$_2$(6)] I$_2$) diffractometers using graphite monochromated Mo Ka radiation. The heavy atom positions were determined by Patterson methods and developed by routine Fourier synthesis. Full matrix least-squares refinement was based on F$^2$, with all non-hydrogen atoms anisotropic. While hydrogen atoms were mostly observed in the difference maps, they were placed in calculated positions riding on the parent atom. The structure solution and refinement used the program SHELX-97 and the graphical interface WinGX.

X-ray Structure Determinations: [6]$^{4+}$ (Pd$_4$): 1.3 CH$_2$O (C$_5$H$_4$I$_4$L$_4$O$_{13}$): M$_f$ = 985.86, colourless plate, 0.25 $\times$ 0.20 $\times$ 0.04 mm, a = 7.6944(4), b = 9.5717(6), c = 12.3057(8) Å, $\alpha$ = 76.506(3) °, $\beta$ = 83.023(4), $\gamma$ = 80.749(4) °, V = 866.48(9) Å$^3$, Triclinic, P-1, Z = 1, $\rho_{\text{calc}}$ = 1.889 g cm$^{-3}$, $\mu$ = 3.626 mm$^{-1}$, Mo Kα radiation (λ = 0.71069 Å), T = 150(2) K. 2$\gamma_{\text{max}}$ = 27.21 °, 16447 reflections measured, 3822 independent reflections (R$_{int}$ = 0.0554), of which 2692 had I > 2s(I). R = 0.0393, wR(all) = 0.0758, gof = 1.063, residual electron density in the range 0.818 to -0.729 e Å$^{-3}$.

[Ag$_2$(6)];[Ag$_4$I$_4$]: 2 C$_2$H$_4$O$_2$S$_1$. 2 C$_2$O$_2$S$_1$ (C$_5$H$_3$Ag$_4$I$_4$N$_6$O$_2$S$_2$), M$_f$ = 1521.88, colourless slab, 0.24 $\times$ 0.14 $\times$ 0.06 mm, a = 12.3163(2), b = 12.8750(3), c = 15.2227(3) Å, $\alpha$ = 114.8265(9), $\beta$ = 96.1581(13), $\gamma$ = 97.8441(13) °, V = 2133.66(8)
Å³, Triclinic, P-1, Z = 2, \( \rho_{\text{calc}} = 2.369 \) g cm\(^{-3} \), \( \mu = 4.836 \) mm\(^{-1} \), Mo Ka radiation (\( ? = 0.71069 \) Å), T = 120(2) K, \( 2\theta_{\text{max}} = 27.6 ^\circ \), 44761 reflections measured, 9793 independent reflections (\( R_{\text{int}} = 0.0325 \)), of which 9167 had I > 2s(I). R = 0.0413, wR(all) = 0.0931, gof = 1.032, residual electron density in the range 2.551 to -2.304 e Å\(^{-3} \).

\[ \text{[Cu}_2(6)\text{]} I_2 \cdot 1.5 \text{C}_2\text{O}_3\text{S}_1 \cdot (\text{C}_2\text{H}_1\text{Cu}_2\text{N}_6\text{O}_1\text{S}_1\text{S}_1), M_r = 930.67, \text{light green rhombus, 0.12 x 0.10 x 0.05 mm}, a = 25.8310(8), b = 12.6143(5), c = 23.1549(8) \text{Å}, \beta = 113.219(2) ^\circ, V = 6933.7(4) \text{Å}^3, \text{Monoclinic, C 2/c, Z = 8, } \rho_{\text{calc}} = 1.782 \text{ g cm}^{-3}, \mu = 3.133 \text{ mm}^{-1}, \text{Mo Ka radiation (} ? = 0.71069 \text{ Å), T = 120(2) K, } 2\theta_{\text{max}} = 27.56 ^\circ, \text{31692 reflections measured, 7226 independent reflections (} R_{\text{int}} = 0.0357 \), of which 6721 had I > 2s(I). R = 0.0886, wR(all) = 0.1895, gof = 1.121, residual electron density in the range 1.890 to -1.433 e Å\(^{-3} \).

\[ \text{[Pd}(6)\text{]} I_2 \cdot 0.25 \text{C}_2\text{O}_3\text{S}_1 \cdot 0.75 \text{C}_3\text{H}_6\text{O}_1 \cdot 0.25 \text{H}_2\text{O} \cdot (\text{C}_{26.75}\text{H}_{38}\text{I}_2\text{N}_8\text{O}_{12.25}\text{Pd}_1\text{S}_{0.25}), M_r = 859.89, \text{colourless slab, 0.18 x 0.06 x 0.03 mm}, a = 9.6438(2), b = 11.1519(3), c = 16.9242(4) \text{Å}, a = 92.8046(12) \beta = 103.9323(14), ? = 115.2879(14) ^\circ, V = 1573.23(7) \text{Å}^3, \text{Triclinic, P-1, Z = 2, } \rho_{\text{calc}} = 1.815 \text{ g cm}^{-3}, \mu = 2.604 \text{ mm}^{-1}, \text{Mo Ka radiation (} ? = 0.71069 \text{ Å), T = 120(2) K, } 2\theta_{\text{max}} = 27.58 ^\circ, \text{39619 reflections measured, 7943 independent reflections (} R_{\text{int}} = 0.0520 \), of which 6549 had I > 2s(I). R = 0.0274, wR(all) = 0.0513, gof = 1.086, residual electron density in the range 0.539 to -0.910 e Å\(^{-3} \).

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