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The first dicarbene double helical mercury complex

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An intermediate and a double helical complex of mercury with a new tridentate carbene based ligand were obtained and structurally characterized.

Helical complexes have a very important place in the field of supramolecules. One of the reasons is their similarity in the self-assembly process and topology to natural α-helical polypeptides and double-helical nucleic acids.[1] To design ligands that facilitate self-assembly and recognition in the formation of helical complexes is a major task that has received considerable attention in the last decade. Among the reported ligands, nitrogen and oxygen donor ligands have been the most commonly used.[2] Ligands with sulfur[3] donor atoms have received less attention and there is only one report[4] of metal–carbon complexes exhibiting a mononuclear double helical structure.

As an alternative ligand system we have chosen N-heterocyclic carbene-based ligands, which have a basicity comparable to that of alkylphosphanes and can stabilize a wide range of metals with different oxidation numbers.[5] We have recently reported the facile synthesis of carbene complexes of Ag^I, Au^I and Pd^{II}, and their properties such as aggregation, luminescence and mesomorphism.[6] It occurs to us that stable metal–carbene complexes would be good candidates for the study of supramolecules. Here we report preliminary results of the first double helical carbene complex of mercury. The ligand in this complex has potentially two carbon and one nitrogen binding sites. The mercury ions selectively bind to the carbene but not the pyridine nitrogen sites. An intermediate, in which only one mercury ion bonds to one carbene, was also structurally characterized. The isolation of this intermediate provides a clue to the formation pathway of the double helicate.

2,6-Bis(1-methylimidazolium-3-yl)pyridine dibromide $[HimypyimyH]Br_2$ **1**, which after deprotonating the 2-carbene hydrogens, has a topography analogous to tridentate ligands such as 2,6-bis(1-methylimidazol-2-yl)pyridine, terpyridine[2] and 2,6-bis(pyrazol-1-yl) pyridine,[7] all of which have three potential nitrogen binding sites and have been widely used as tridentate ligands in the formation of supramolecules. The potential binding sites of the deprotonated **1**, are two carbene carbons and one pyridine nitrogen atom. The ligand precursor **1**† was synthesized by mixing a two to one molar ratio of 1-methylimidazole and 2,6-dibromopyridine thoroughly, followed by heating the mixture at 140 °C without solvent for 20 hours. The solubility of **1** in common organic solvents is very poor and therefore to prepare metal complexes from **1** is a difficult task. Ligand precursor **2**,† which has two PF_6^- anions, is more soluble in CH_3CN and acetone and is used for the synthesis of metal–carbene complexes (Scheme 1).

The complexes $[(OAc)Hg(Himypyimy)][(PF_6)_2]$, **3**† and $[Hg_2(impyimy)_2](PF_6)_4$, **4**,† were prepared by refluxing a 2 : 1 molar ratio of **2** and $Hg(OAc)_2$ in CH_3CN for different durations. A similar method has been used for the preparation of monomercury carbene complexes.[8] If one follows the reaction by ^1H NMR spectrometry, one finds that during the early stages (≈1 h), **3** is the predominant species observed. Other minor species are unreacted starting materials and traces of **4**. No other species has been observed. If the reaction continues, the amount of **4** increases while **3** decreases. Again no side product was observed. Compound **3** was also obtained when the reaction was carried out at room temperature.

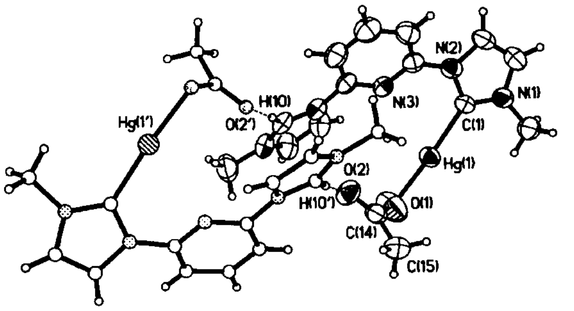
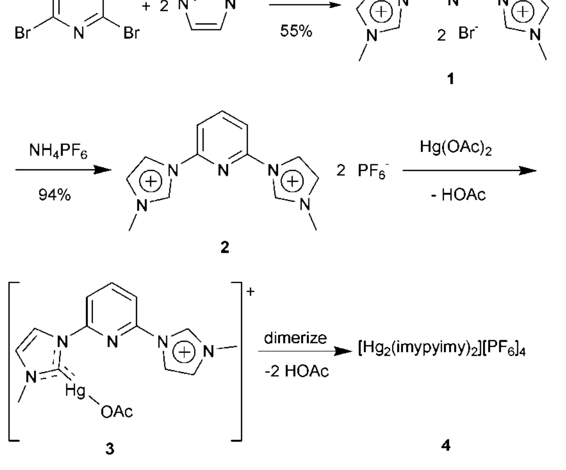


Fig. 1 The molecular structure of **3**. The unlabelled portion is the symmetry equivalent of the labelled portion and is drawn with 50% probability thermal ellipsoids. Selected bond lengths [Å] and angles [°]: Hg(1)–C(1) 2.091(5); Hg(1)–O(1) 2.087(7); C(1)–Hg(1)–O(1) 175.5(2). The intermolecular hydrogen bond distance of O(2)···H(10′) and O(2′)···H(10) is 2.136(6) Å.



Scheme 1 Synthesis of the ligand, intermediate and double helical carbene complex.

The crystal structure ‡ of compound **3** (Fig. 1) shows that the mercury ion linearly bonds to a monodentate acetate through an oxygen atom O(1) and to a monodentate $[Himypyimy]^+$ through the carbene carbon atom C(1). All the bond angles and bond distances are comparable to those reported for mercury carbene and acetate complexes.[9] The important bond angles and distances are listed in the figure caption. The distances Hg(1)–C(1) 2.091(5) Å and Hg(1)–O(1) 2.087(7) Å, suggest that the *trans* influence of the carbene is greater than that of the acetate. Among the three potential binding sites of $[HimpyimyH]^{2+}$, only one imidazolium cation has been deprotonated in this compound. The undeprotonated imidazolium ring tilts 24.9(6)° from the pyridine ring with the 2-position C–H proton pointing outward. It is noteworthy that the two molecular cations are associated with two hydrogen bonds in which the dangling acetate oxygen atom acts as a proton acceptor and the

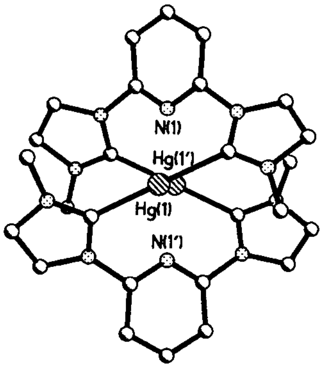


Fig. 2 The molecular structure of **4**.

C–H hydrogen atom in the 2-position of the imidazolium ring acts as a proton donor (Fig. 1). The arrangement of the dimer is such that if deprotonation of the imidazolium proton by the intermolecular H-bonded acetate does occur, it leads to the formation of the helical dimercury compound **4**.

The double helical structure of **4** analyzed by X-ray diffraction ‡ is given in Fig. 2. The helix is formed by bridging two mercury(II) ions with two [imypyimy] strands through the carbene sites. The geometry around each mercury(II) deviates from linearity by ≈10°. It appears that weak van der Waals interactions[10] between the PF_6^- anion and Hg^{2+} cation ($Hg \cdots F$ distance, ≈3.07 Å) push the geometry toward a tetrahedral arrangement. Deviation from linear geometry due to the weak interactions with counter anions has been observed for other mercury carbene compounds, such as $[Hg(MeImyMe)_2]Cl_2$ and $[Hg(MeBimyFc)_2]I_2$ where MeImyMe is 1,3-dimethylimidazol-2-ylidene and MeBimyFc is 1-ferrocenylmethyl-3-methyl benzimidazol-2-ylidene.[11] The PF_6^- anion also forms hydrogen bonds with neighbouring cations with $H \cdots F$ bonds in the range from 2.24(5) to 2.50(5) Å, within the range of a typical hydrogen bond.[12] The PF_6^- anions thus hold two adjacent cations through $Hg \cdots F$ interactions and $H \cdots F$ hydrogen bonds. Further discussion is not possible due to the highly disordered PF_6 anions which lead to the poor level of accuracy of the crystal structure determination.

Results from ^1H NMR and crystal structure suggest that the double helical mercury(II) carbene complex **4** is formed in the following ways. First deprotonation of an imidazolium cation by acetate followed by coordination to mercury(II) to give intermediate $[(OAc)Hg(Himypyimy)][PF_6]_2$, **3**. Association of two molecular cations of **3** through intermolecular hydrogen bonding gives an approximate double helical topology. Further deprotonating of a second imidazolium cation by a hydrogen bonded acetate from other molecular cation generates a second carbene which coordinates readily with an adjacent mercury(II) ion to produce **4**. The formation pathway of the double helical complex **4**, is different from that reported for the oligopyridine systems.[13]

In this work, we have succeeded in the synthesis of the first double helical organometallic carbene complex together with a mercury(II)–carbene intermediate from a new tridentate carbene based ligand. Experimental results suggest that the double helix is formed through a single strand mercury(II)–carbene intermediate followed by dimerization, deprotonation and coordination. Through van der Waals forces and hydrogen bonds, helicates form an infinite 3D supramolecular architecture. Stable metal–carbene compounds are therefore very promising for the formation of supramolecules and we believe that the pyridine will have the ability to coordinate to other metals. The synthesis of carbene complexes with different metal ions is underway. We are also currently developing other carbene ligands, which will form different architectures and may facilitate assembly between molecules.

Acknowledgements

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Notes and references

† Elemental analysis. Found (requires): for **1**: C, 36.67 (37.41); H, 4.14 (4.11); N, 16.48 (16.79%); for **2**: C, 29.49 (29.39); H, 2.67 (2.85); N, 13.10 (13.18%); for **4**: C, 21.48 (21.39); H, 1.76 (1.80); N, 9.43 (9.60%). The content of **3** was assessed by ^1H NMR (CD_3CN, 300 MHz): δ 9.42 (s, 1H, imH), 8.45 (dd, ^3J(H,H) = 7 Hz, 7 Hz, 1H, pyH), 8.19 7.63 (dd, ^3J(H,H) = 2 Hz, 2 Hz, 2H, imH), 8.01, 7.65 (d, ^3J(H,H) = 2 Hz, 2H, imH), 7.93, 7.90 (d, ^3J(H,H) = 7 Hz, 2H, pyH), 4.06, 3.99 (s, 6H, CH_3), 1.83 (s, 3H, CH_3CO_2). Yields: **1**, 55%; **2**, 94%; **3**, 54%, **4**, 76%.

‡ Crystal data for **3**: $C_{15}H_{17}F_{12}HgN_5O_2P_2$, M = 789.87, monoclinic, a = 13.786(2), b = 11.755(2), c = 16.049(3) Å, β = 108.433(3)°, U = 2467.4(7) Å^3, T = 294(2) K, space group $P2_1/n$, Z = 4, μ(Mo-Kα) = 6.484 mm^{-1}, 14074 reflections measured, 5387 unique (Rint = 0.0378) which were used in all calculations. The final $R1$ = 0.0374, $wR2$ = 0.1029 and for all data $R1$ = 0.0524, $wR2$ = 0.1078. The structure was solved by standard direct methods and refined against F^2 by least squares.[14] All non-hydrogen atoms of **3** were readily located and refined anisotropically. For H-atoms a riding model was employed.

For **4**: $C_{26}H_{26}F_{24}Hg_2N_{10}P_4$, M = 1459.63, orthorhombic, a = 23.7267(16), b = 23.8877(17), c = 30.6000(20) Å, U = 117343(2) Å^3, T = 296(2) K, space group $Fddd$, Z = 16, μ(Mo-Kα) = 7.361 mm^{-1}, 24313 reflections measured, 4920 unique (Rint = 0.1193) which were used in all calculations. The final $R1$ = 0.1239, $wR2$ = 0.2813 and for all data $R1$ = 0.1440, $wR2$ = 0.2918. The structure was solved by standard direct methods and refined against F^2 by least squares.[14] All non-hydrogen atoms of **4** were refined anisotropically except the two highly disordered hexafluorophosphate anions. For H-atoms a riding model was employed. All diffraction data of these two compounds were collected on a Siemens SMART diffractometer equipped with a CCD area detector, ω scans, graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). CCDC reference number 186/1845. See http://www.rsc.org/suppdata/dt/b0/b000971g/ for crystallographic files in .cif format.

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