# Synthesis, Structures and Luminescent Properties of σ-Alkynyl Complexes of Orthomercuriated Schiff Bases

**Wai-Yeung Wong,*[a] Guo-Liang Lu,[a] Li Liu,[a] Jian-Xin Shi,[a,b] and Zhenyang Lin[c]**

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A novel series of σ-alkynyl complexes of orthomercuriated Schiff bases of substituted benzylideneanilines and anthracenylmethyleneanilines were synthesised in good yields by alkynylation of the mercuric chlorides of the appropriate Schiff bases with terminal alkynes RC≡CH (R = Ph, ferrocenyl, *p*-ferrocenylphenyl) at room temperature in a basic medium. All the new compounds generally displayed good solubility in polar organic solvents and their identities were completely elucidated by various spectroscopic methods. The X-ray crystal structures of these acetylide-functionalised compounds represent the first structurally characterised examples of such alkynylmercury(II) complexes and confirmed that the alkynylmercury(II) moiety is directed to the *ortho* position of the *N*-phenyl ring of the Schiff bases. In one instance, the crystal structure reveals that a loose 1D polymeric aggregate is formed for the first time through a combination of weak intermolecular Hg···Hg and Hg···$\eta^2$-C≡C interactions to afford an infinite zigzag chain of Hg atoms supported by acetylide linkages. All the complexes in this study were found to exhibit rich luminescence and solution redox behaviour and correlation of these data with the theoretical calculations by the density functional theory was made.

## Introduction

The synthesis, structure and luminescence properties of transition metal complexes of alkynyl ligands have attracted enormous attention in the past two decades.[1] Metal alkynyls are common for many transition metals, particularly those of groups 8−11, and their chemistry has been developed extensively.[1,2] The interest in the study of mono-, di- and polynuclear gold(I) σ-acetylide complexes stems not only from their rich photochemistry but also from the observation of weak intermolecular d$^{10}$-d$^{10}$ Au···Au interactions which can play important roles in materials science and crystal engineering.[3] In many cases, it is the combination of the complementary intermolecular forces of aurophilic interactions, hydrogen bonding, π−π stacking and other non-covalent interactions that determines the solid-state luminescent properties of these materials. In contrast to the large body of work on alkynylgold(I) compounds, the chemistry of group 12 metal alkynyls, especially d$^{10}$ alkynylmercury(II) compounds, has not been so thoroughly investigated, and related research work on the isoelectronic mercury(II) system is still in its infancy.[4] Although mercury(II) acetylides were reported as early as the 1920s, they are limited to those of simple alkyl- and arylmercury derivatives.[5] Indeed, mono- and dialkynylmercury complexes have been shown to be useful in the analysis of toxic mercury(II) species[6] and to be valuable building blocks for the synthesis of luminescent metal-organic polymers and supramolecular aggregates.[4]

Very recently, a comprehensive program was launched in our laboratory to develop the chemistry of alkynylmercury complexes. We have reported a new class of bis(alkynyl)mercury(II) complexes incorporating a series of aromatic groups.[4d,4e] These molecules were shown to display a rich photophysical behaviour and interesting structural properties. The crystal structures of [MeHgC≡CRC≡CHgMe] (R = thiophene-2,5-diyl, [2,2′]-bithiophene-5,5′-diyl) reveal the formation of a loose polymeric structure in each case through weak intermolecular non-covalent Hg···Hg interactions.[4e] The solid-state aggregation of [Hg(C≡CR)$_2$] (R = Ph, SiMe$_3$) has been discussed by Nicholson et al. in which both mercuriophilic and Hg-$\eta^2$-C$_2$ interactions appear to contribute to the supramolecular aggregation process.[4b] π-Coordination of some transition metal ions to bis-alkynylmercury complexes has also been explored recently in which some compounds reveal weak anion···cation interactions and the structure of {[Hg(C≡CTol)$_2$Ag][BF$_4$]}$_n$ shows a polymeric skeleton comprised of helices cross-linked by C−H···π in-

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[a] Department of Chemistry, Hong Kong Baptist University
Waterloo Road, Kowloon Tong, Hong Kong SAR, P.R. China
Fax: (internat.) +852-3411-7348
E-mail: rwywong@hkbu.edu.hk
[b] Department of Chemistry, Zhongshan University
Guangzhou 510275, P.R. China
[c] Department of Chemistry, The Hong Kong University of Science and Technology,
Clearwater Bay, Hong Kong SAR, P.R. China

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teractions.[4a] In the pursuit of unsymmetrical diorganomercurials bearing an alkynyl ligand, we set out a strategy to synthesise some σ-acetylide complexes of orthomercuriated Schiff bases.[7] Perusal of the literature suggested that there were no examples of such kinds of alkynylmercury(II) compounds and their structures and luminescence behaviour have not been described before. We present here the synthesis and structural characterisation of the first σ-alkynyl complexes of orthomercuriated Schiff bases of substituted benzylideneanilines and anthracenylmethyleneanilines. The luminescence and electrochemical properties of these complexes have been examined.

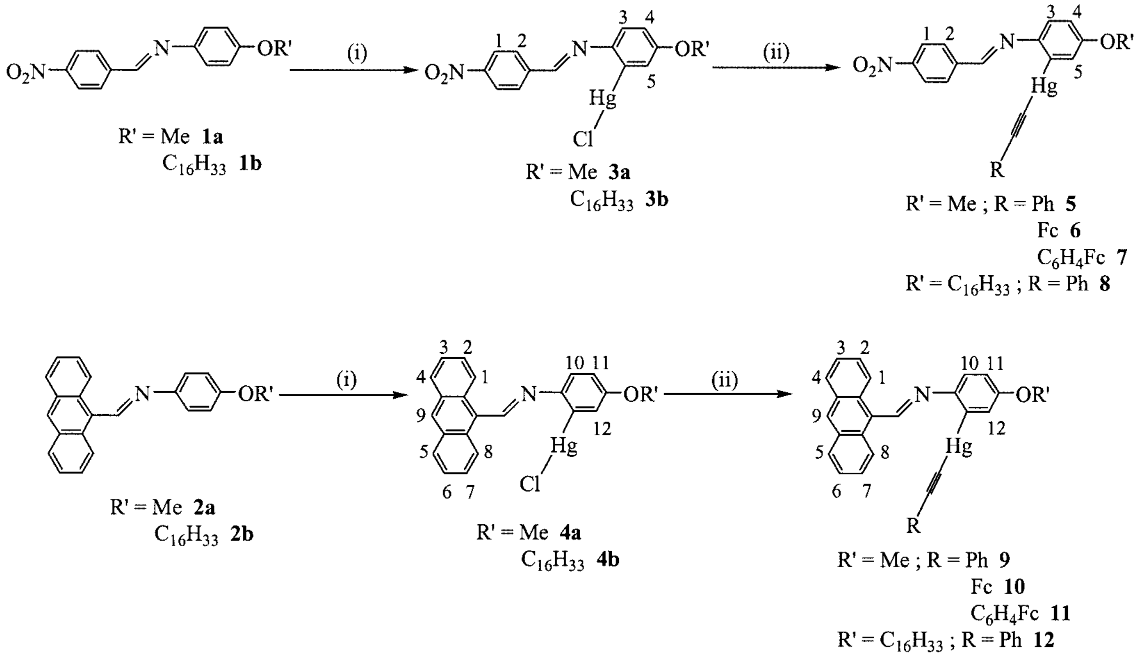
## Results and Discussion

### Syntheses and Spectroscopic Properties

Condensation reactions of *p*-nitrobenzaldehyde and 9-anthraldehyde with the respective *para*-substituted anilines readily afforded the Schiff bases **1a**, **1b**, **2a** and **2b** in high yields.[7b] The mercuric chloride precursors of the corresponding Schiff bases (**3a**, **3b**, **4a** and **4b**) were prepared by in situ reaction of the Schiff bases with one molar equivalent of mercuric acetate in dry MeOH under reflux for 4 h, followed by the addition of lithium chloride (Scheme 1). The products were precipitated from the reaction mixture and isolated in very good overall yields.

The general alkynylation routes leading to new compounds **5−12** are shown in Scheme 1. Based on the classical dehydrohalogenation method,[3h,4d,4e] room temperature reactions of the orthomercuriated derivatives with a slight excess of the terminal alkynes RC≡CH (R = Ph, Fc, *p*-$FcC_6H_4$, where Fc = ferrocenyl) in THF in the presence of NaOMe in MeOH furnished compounds **5−12** in 82−87% yields. Pure samples of these products were obtained after extraction of the crude compounds with hot $CHCl_3$ followed by subsequent recrystallisation from $CH_2Cl_2$/hexane. Compounds **5−12** were isolated as air-stable yellow to yellow-brown solids. They exhibit fairly good solubility in chlorinated solvents such as $CH_2Cl_2$ and $CHCl_3$ and the solubility of the complex is enhanced by increasing the chain length of the alkoxy group from MeO to $C_{16}H_{33}O$. They were satisfactorily characterised by elemental analyses, IR, MS, $^1H$ and $^{13}C$ NMR spectroscopy.

All the spectroscopic data of new compounds are in agreement with their proposed structures. Each of the IR spectra of **5−12** displays a characteristic absorption band in the range 2137−2141 $cm^{-1}$ corresponding to the ν(C≡C) stretching modes. The $^1H$ NMR spectra of **1−12** all show features pertaining to the protons of the aromatic and other organic groups. The position of the mercury atom in **5−12** was determined by $^1H$ NMR spectroscopy. The four *C*-phenyl protons for each of **5−8** consists of a group of left-right symmetrical multiplet peaks in the aromatic region typical of a four-spin AA′BB′ system at lower field due to the electron-withdrawing effect of the $NO_2$ group. At higher field, the two doublets and a doublet of doublets which belong to the three-spin AMX system correspond to the three *N*-phenyl protons. Such spectral assignments show that mercuriation takes place at the *ortho* position of the *N*-phenyl ring rather than at the *ortho* position of the *C*-phenyl ring. The $^{13}C$ NMR spectra of the σ-acetylide complexes show two resonances for the sp carbon atoms of the C≡C units in which the chemical-shift values are virtually unaffected upon varying the substituents; assignment of these $^{13}C$ signals was made by analogy with other similar acetylide compounds.[4a,5c] In each case, we can detect the respective molecular ion peak $[M]^+$ or $[MH]^+$ in the FAB mass spectra,



Scheme 1. Reagents and conditions: (i) $Hg(OAc)_2$ followed by LiCl; (ii) RC ≡ CH, NaOH/MeOH

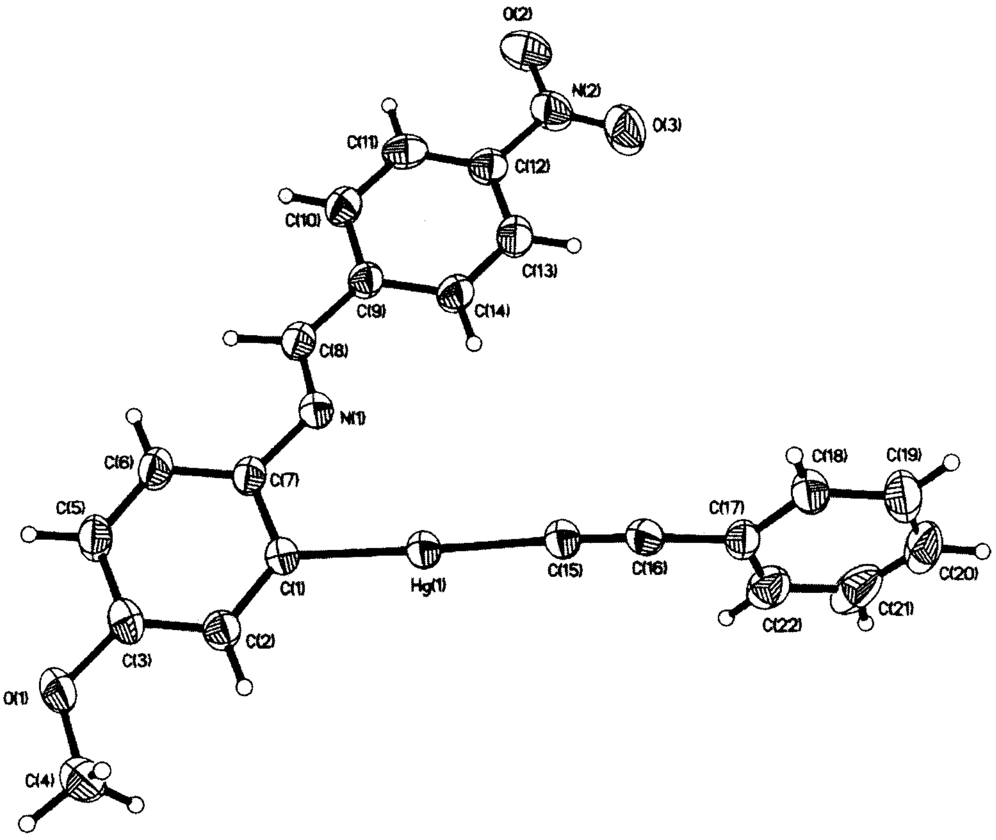


Figure 1. Molecular structure of **5**, with thermal ellipsoids shown at the 25% probability level

and for **5**−**12** we also observe the peaks corresponding to the detachment of the HgC≡CR groups.

## Crystal-Structure Analysis

The molecular structures of complexes **5** (Figure 1), **6** (Figure 2), **7** (Figure 3), **9** (Figure 4), and **10** (Figure 5) are shown, and selected structural parameters are listed in Table 1. In each case, the crystal structure shows an unsymmetrical diorganomercurial species in which the $Hg^{II}$ centre is σ bonded to an alkynyl ligand as well as an *ortho*-carbon atom of the *N*-phenyl ring of the corresponding Schiff base. The geometry about the Hg atom in each case is very similar, with the $Hg^{II}$ centre being two-coordinate and essentially linear [$C(sp^2)-Hg-C(sp)$ 177.6(4)−179.3(4)°]. The Hg−C(sp) bonds are similar in length to those in other $Hg^{II}$ acetylide compounds.[4,8] The near linearity of the Hg−C≡C fragment is confirmed from the Hg(1)−C(sp)−C(sp) angles [170.2(6)−178.5(13)°] and the slight deviations from 180° for **5** and **6** are consistent with the presence of short intermolecular interactions (vide infra). The C≡C bond lengths span the narrow range of 1.162(16)−1.196(9) Å, typical of other known $Hg^{II}$ acetylides.[8] The Hg···N nonbonded contacts, which range from 2.860 to 3.126 Å, and the $Hg(1)-C(sp^2)-C(sp^2)$ bond angles [112.3(4)−118.2(9)°], which are less than 120°, suggest the opportunity for a secondary N→Hg intramolecular interaction with a four-membered ring. The presence of such weak Hg···N contacts can be justified based on the currently acceptable van der Waals radius of each element.[9] The present structural investigations corroborate the proposed reaction mechanism, in which the mercuriation at the *ortho* position of the *N*-phenyl ring was facilitated by the imino moiety upon formation of a coordination complex with $Hg(OAc)_2$ in the first step, followed by a subsequent electrophilic substitution at the *ortho* position of the *N*-phenyl ring.[7b]

Examination of the crystal packing diagram for each compound reveals the involvement of various intermolecular contacts in their structures. Interestingly, there is a strong tendency for the molecules in **5** to aggregate, and the lattice structure of **5** is highlighted by the presence of extensive non-covalent Hg···Hg and Hg···$\eta^2$-C≡C interactive vectors, which link up the molecular units to form a loose polymeric structure. Such a polymeric aggregate shows a zigzag 1D chain of Hg atoms with an Hg···Hg interaction distance of ca. 3.959 Å between adjacent molecules; the average Hg−Hg−Hg bond angle is 135.9° (Figure 6). To the best of our knowledge, this represents the first structurally characterised example of a mercury(II) acetylide compound exhibiting infinite polymeric chains of Hg atoms, although it is known that crystals such as $Hg_3(AlCl_4)_2$ and $Hg_3AsF_6$ also contain zigzag mercury chains in their lattices.[4c,10] A similar chain-like structure supported by alkynyl ligands is also found for silver(I) in $[(Me_3P)AgC\equiv CR]_\infty$ (R = Ph, $SiMe_3$).[11] While the Hg···Hg contacts in **5** indicate that each of the individual interac-

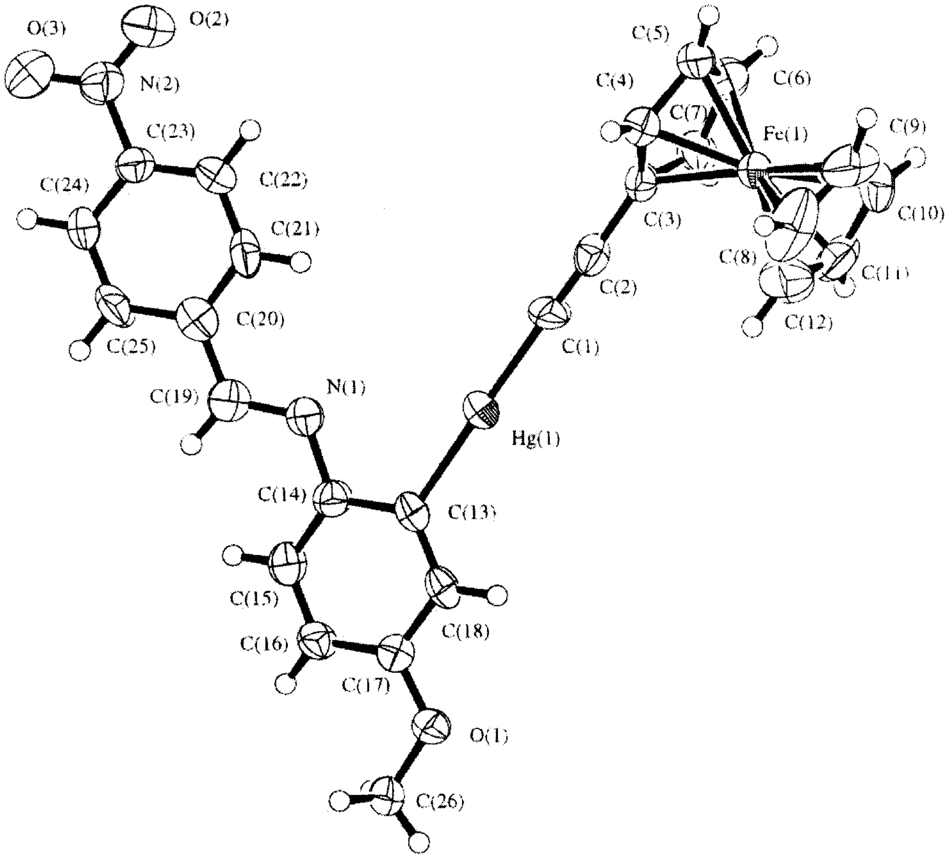


Figure 2. Molecular structure of **6**, with thermal ellipsoids shown at the 25% probability level

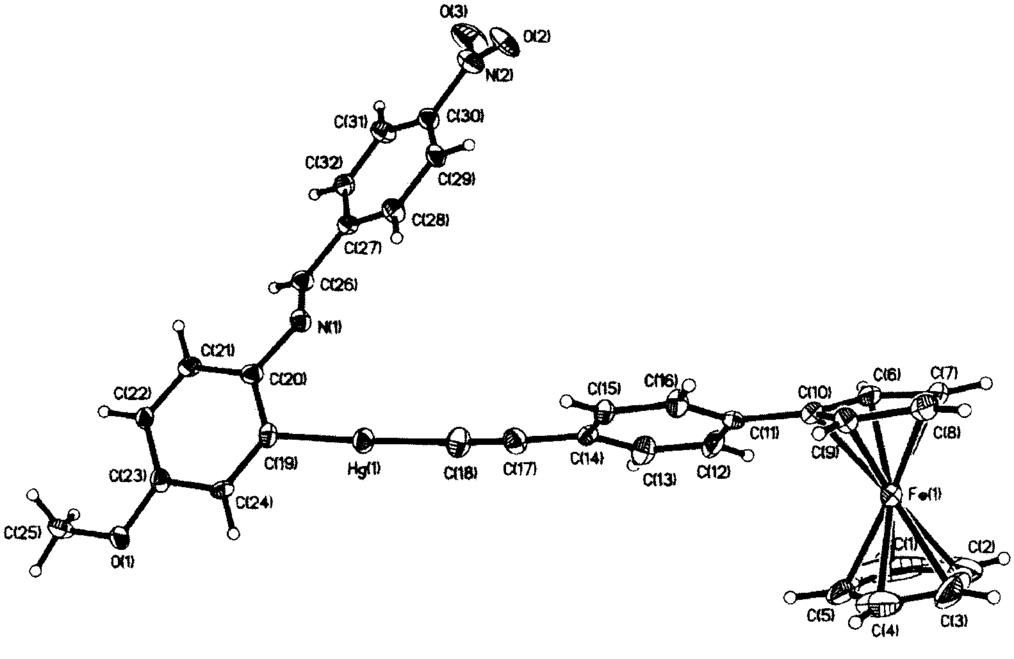


Figure 3. Molecular structure of **7**, with thermal ellipsoids shown at the 25% probability level

tions is relatively weak, it is the large number of them that play a supramolecular role and generate a significant driving force for solid-state aggregation. We believe that such mercuriophilic forces are more than just van der Waals interactions in these chemical systems. The intermolecular distances from the Hg atom to $C_\alpha$ [Hg(1)···C(15)] and $C_\beta$ [Hg(1)···C(16)] are 3.398 and 3.783 Å, respectively, which compare well with the values quoted for $[Hg(C{\equiv}CR)_2]$ (R = Ph, $SiMe_3$)[4b] but are significantly longer than the intramolecular distances found in some heterometallic

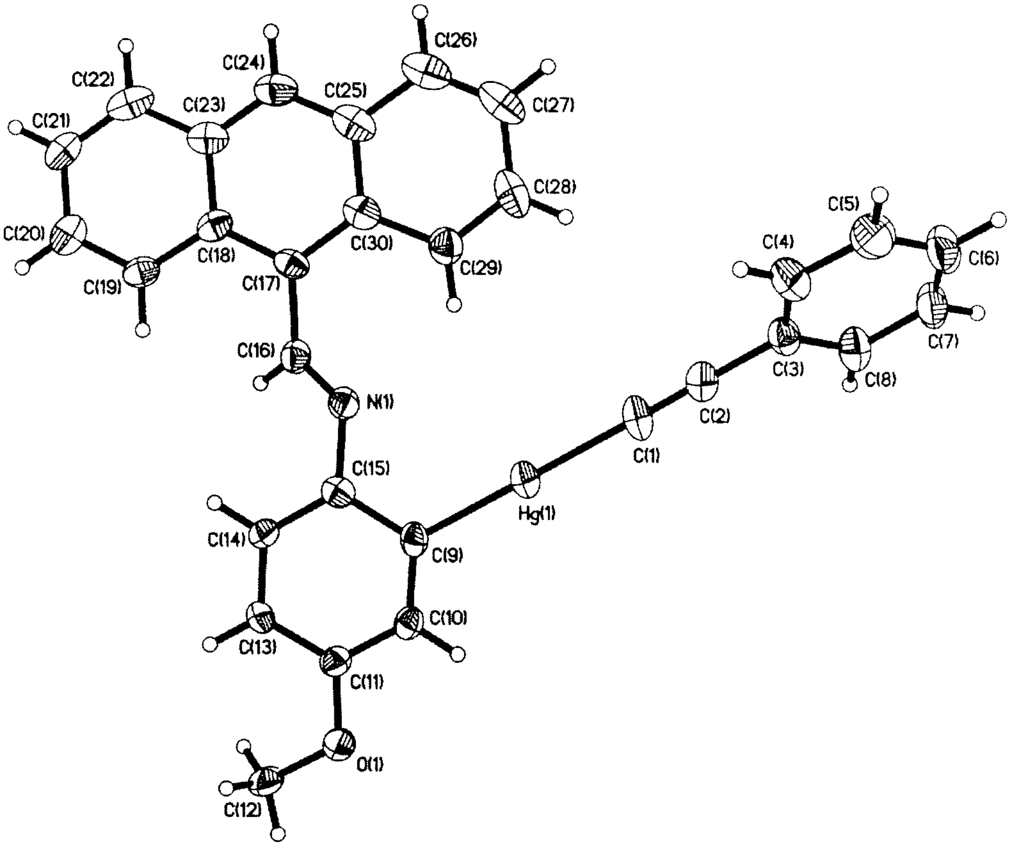


Figure 4. Molecular structure of **9**, with thermal ellipsoids shown at the 25% probability level

bis($\eta^2$-alkyne)mercury complexes.[4g][4h] While the closest intermolecular contacts in **6** are attributed to the hydrogen-bonding interactions [O(1)···H(15) 2.44 Å; O(2)···H(15) 2.72 Å), the weak mercuriophilic (4.21 Å) and Hg···$\eta^2$-C≡C attractions [Hg(1)···C(1) 3.41 Å; Hg(1)···C(2) 3.57 Å) also contribute to the overall intermolecular packing. The van der Waals radius of mercury has been the subject of much debate and a value of up to 2.2 Å has been proposed recently,[4c,7a,9] which is conceived to be a better estimate than the value quoted by Bondi in 1964.[12] In light of this, the observed Hg···Hg separations which are similar to the values of 3.71−4.25 Å for [Hg(C≡CR)$_2$] (R = Ph, SiMe$_3$)[4b] are towards the upper limit of those accepted as representing metallophilic interactions and are consistent with other previous interpretations.[4e,4f] For **7**, **9** and **10**, the Hg···Hg and Hg···C≡C interactions become unimportant and the nearest intermolecular contacts involve the Hg centre, the methoxy oxygen atom and a hydrogen atom from the aromatic rings. These contacts arise from Hg(1)···H(25) (3.372 Å), Hg(1)···O(1) (3.698 Å) and O(2)···H(32) (2.376 Å) interactions for **7**, whereas each molecular unit of **9** is linked to two adjacent units through short Hg(1)···O(1) contacts (3.084 Å). Presumably because of the greater steric bulk of both anthryl and ferrocenyl rings, there are no other significant short contacts for **10** other than the Hg(1)···H(25) interactions (2.921 Å). None of these five structures show close π−π stacking of the arene rings in the solid state.

## Absorption and Luminescence Properties

The electronic absorption and emission data of our compounds are given in Table 2. In general, these orthomercuriated complexes absorb strongly in the range 383−413 nm. The dependence of the solution absorption spectra on the nature of the original Schiff bases suggests that the transitions are mainly π−π* ligand-centred, and the apparent insensitivity of the low-energy absorption bands towards the ancillary groups R on the mercury centre (cf. **5**, **6** and **7**) precludes a metal-centred origin for these transitions.[4e] We also note that the lowest-energy absorption features show slight bathochromic shifts when the alkynylmercury(II) fragments are introduced at the *ortho* position of the Schiff bases (cf. **2a** and **9**), reflecting a certain degree of through-metal π-delocalisation due to metal-to-ligand back-donation to the π*(C≡CR) orbital. Hence, the electronic absorption spectra are probably dominated by intraligand π−π* transitions, but possibly mixed with a small contribution from the metal in the HOMO and the LUMO.[13] The π,π* character of the electronic states involved is consistent with the molecular orbital calculations. Figure 7 depicts the contour plots of the HOMOs and LUMOs for **2a**, **9** and **10**, showing the common bonding features in the frontier region. The HOMOs and LUMOs for the three complexes resemble each other and correspond to the π and π* orbitals of the conjugated organic unit. The substituents HgC≡CPh in **9** and HgC≡CFc in **10** only af-

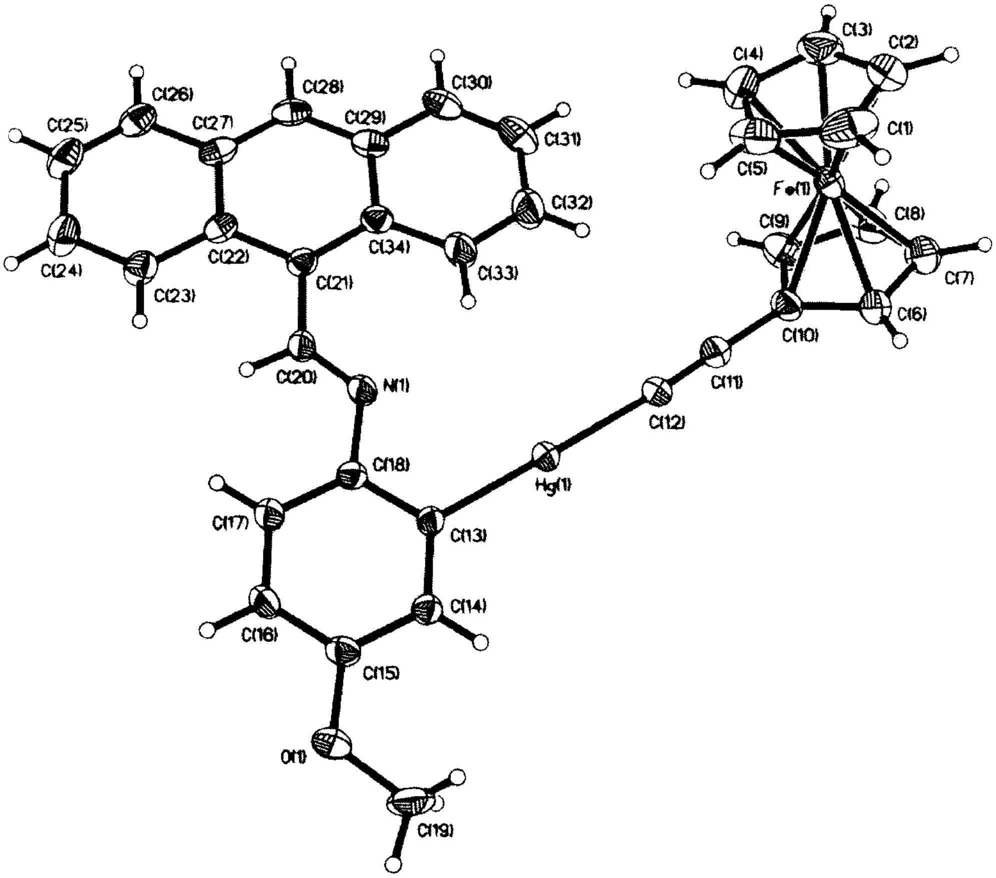


Figure 5. Molecular structure of **10**, with thermal ellipsoids shown at the 25% probability level

Table 1. Selected bond lengths (Å) and angles (°) for **5**, **6**, **7**, **9** and **10**

| | **5** | **6** | **7** | **9** | **10** |
|---|---|---|---|---|---|
| Hg(1)−C($sp^2$) | 2.057(6) | 2.08(1) | 2.081(8) | 2.061(11) | 2.054(3) |
| Hg(1)−C(sp) | 2.016(7) | 2.02(1) | 2.023(9) | 2.047(12) | 2.045(4) |
| C(sp)−C(sp) | 1.196(9) | 1.18(1) | 1.182(11) | 1.162(16) | 1.169(5) |
| C(imine)−N(1) | 1.258(9) | 1.28(1) | 1.254(10) | 1.257(14) | 1.196(5) |
| Fe(1)−ring(Cp) | | 1.6408 | 1.6509 | | 1.6523 |
| Fe(1)−ring($C_5H_4$) | | 1.6375 | 1.6416 | | 1.6564 |
| Hg(1)···N(1) | 2.860 | 3.049 | 3.041 | 3.126 | 2.999 |
| C($sp^2$)−Hg(1)−C(sp) | 178.3(3) | 179.3(4) | 177.6(4) | 179.0(5) | 178.83(15) |
| Hg(1)−C(sp)−C(sp) | 170.2(6) | 173(1) | 177.7(9) | 178.5(13) | 175.5(4) |
| C($sp^2$)−N(1)−C($sp^2$) | 123.2(6) | 120(1) | 120.1(7) | 119.1(9) | 123.2(4) |
| Hg(1)−C($sp^2$)−C($sp^2$) | 112.3(4) | 117.4(8) | 116.0(6) | 118.2(9) | 117.6(2) |
| C($sp^2$)−C($sp^2$)−N(1)[a] | 115.2(5) | 115.7(10) | 118.4(7) | 118.6(10) | 115.6(3) |

[a] $sp^2$ carbon atoms of the *N*-phenyl ring.

fect the energies of those orbitals above the LUMO and below the HOMO. The second LUMO for both **9** and **10** has significant contribution from the Hg's empty p orbitals. The presence of the ferrocenyl group in **10** introduces the two Fe($d_\delta$) orbitals as the second and third HOMOs (we define the δ-type d orbital by viewing the orbitals along the Ct−Fe−Ct direction where Ct is the centre of each cyclopentadienyl ring). The order of calculated HOMO−LUMO gaps **2a** (3.40 eV) > **10** (3.33 eV) > **9** (3.17 eV) is in line with our experimental observations.

Complexes **5**−**12** were found to exhibit luminescence in the solid state at 290 and 11 K (Table 2). There is little change in the emission spectra upon variation of the excitation wavelength, indicating that a single emissive state or multiple states in equilibrium is (are) responsible for the observed emission. The emission energy is dependent on the nature of the structure of the Schiff bases (Figure 8), but does not vary much with respect to the identity of R′. The striking similarity of the emission peak shapes of these σ-alkynyl complexes and those of their parent Schiff bases

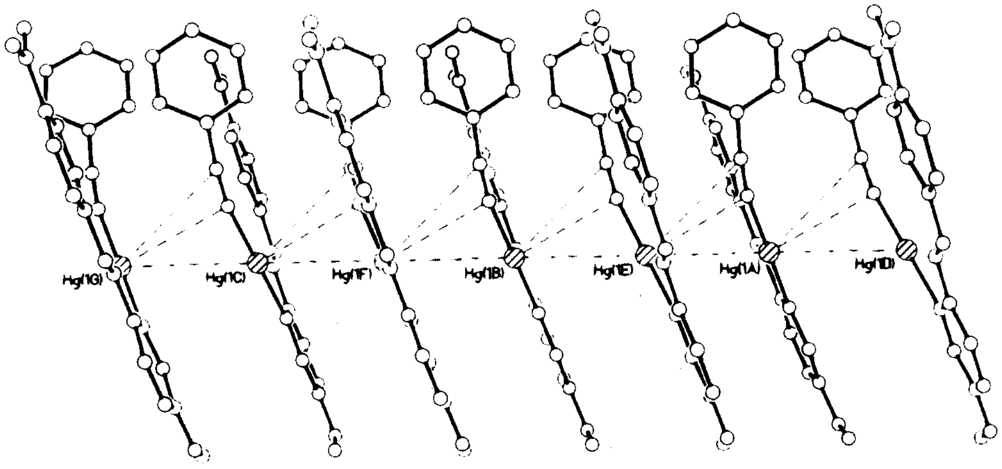


Figure 6. Crystal packing diagram for **5** showing the polymeric chain of Hg atoms aggregated through Hg···Hg and Hg···$\eta^2$-C≡C intermolecular contacts; all hydrogen atoms are omitted for clarity

and organomercuric chlorides are suggestive of a ligand-dominated emissive state, and the lowest emissive states in these complexes can tentatively be assigned as metal-perturbed intraligand $\pi-\pi^*$ transitions. The emission energies of the complexes in the solid state at 11 K roughly follow the order **9** > **5**, **10** > **6** and **12** > **8**, which is in agreement with the electron-withdrawing ability of the nitro group in the latter which tends to reduce the HOMO−LUMO gap. However, compounds **7** and **11** were found to be weakly emissive both in solution and as solids, and the appearance of the low-energy emission bands as broad shoulders or weak peaks makes it difficult for one to determine their exact maxima for comparative studies. In most cases, the marked red shift in the emission wavelengths for the solid-state spectra is a manifestation of the formation of aggregates in the ground state due to the presence of intermolecular interactions in the solid lattice, which is not present in solution (vide supra).[3b,13]

### Electrochemistry

Table 3 collects the electrochemical data for our complexes in $CH_2Cl_2$. Each of the cyclic voltammograms of **5**−**12** essentially shows an irreversible oxidation wave (+0.77 to +1.11 V) which is suggested to arise from Schiff-base ligand-centred oxidation since the potentials within the same ligand class are found to have similar values. For the $NO_2$-substituted Schiff bases and their organomercury complexes, we observe one quasi-reversible reduction couple which can be attributed to reduction of the nitro moiety; these $E_{1/2}$ values (−1.41 to −1.45 V) are almost invariant of the structures. For each of **6**, **7**, **10** and **11**, the cyclic voltammogram is also characterised by one quasi-reversible oxidation wave due to the ferrocenyl electrophore that is present. The ferrocenyl oxidation potential is less anodic for **7** (+0.07 V) and **11** (+0.06 V) than for **6** (+0.13 V) and **10** (+0.10 V) because of the greater degree of electron delocalisation along the metal-capped ethynyl bridges with an additional $C_6H_4$ unit which would increase the ease of oxidation.

## Concluding Remarks

This report has demonstrated that orthomercuriated Schiff bases are useful precursors to afford a range of luminescent diorganomercurial σ-alkynyl compounds. Structural characterisations of complexes **5**, **6**, **7**, **9** and **10** are particularly interesting and constitute the first examples of this type. The results also provide further evidence for the existence of N→Hg intramolecular coordination and the fact that the initial mercuriation step occurs at the *ortho* position of the *N*-phenyl ring instead of the *C*-phenyl ring. Depending on the geometric and steric properties of the end groups anchored on the alkynyl unit and the type of Schiff base employed, we were able to build up polymeric mercury(II) acetylide systems in the solid state aggregated through Hg···Hg and Hg···$\eta^2$-C≡C secondary interactions. Such a supramolecular aggregation process is best favoured for orthomercuriated molecules with the least steric bulk, such as **5**. The absorption and emission properties of **5**−**12** are dominated by mildly mercury-perturbed organic $\pi-\pi^*$ transitions, which are consistent with the results obtained from theoretical calculations. A comparison of the *p*-nitrophenyl and 9-anthryl substituents illustrates that the emission maximum is bathochromically shifted in the presence of the electron-accepting $NO_2$ group in the former case.

## Experimental Section

**General Procedures:** All reactions were conducted under an atmosphere of dry nitrogen with the use of standard Schlenk techniques. Solvents for preparative work were dried and distilled before use. IR spectra were obtained using a Nicolet FTIR-550 spectrometer. NMR spectra were recorded on a JEOL JNM-EX 270 or a Varian Inova 400 MHz FT NMR spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan-SSQ 710 spectrometer. Electronic absorption spectra were measured with a HP 8453 UV/Vis spectrometer. For emission spectral measurements, the 325 nm line of a He-Cd laser was used as an excitation source. The luminescence spectra were analysed by a 0.25 m focal length

Table 2. Photophysical data of orthomercuriated complexes

| Complex | Absorption[b] $\lambda_{max}$/nm ($\varepsilon$/$10^4$ $\text{M}^{-1}\cdot\text{cm}^{-1}$) | Emission[a] | |
|---|---|---|---|
| | | Medium (*T*/K) | $\lambda_{em}$ (nm) |
| **1a** | 261 (1.4), 383 (1.6) | $CH_2Cl_2$ (290) | 478 |
| | | solid (290) | 575 |
| | | solid (11) | 600 |
| **1b** | 267 (2.8), 384 (2.8) | $CH_2Cl_2$ (290) | 470 |
| | | solid (290) | 570 |
| | | solid (11) | 595 |
| **2a** | 252 (3.8), 400 (1.4) | $CH_2Cl_2$ (290) | 467 |
| | | solid (290) | 565 |
| | | solid (11) | 560 |
| **2b** | 254 (3.9), 405 (1.9) | $CH_2Cl_2$ (290) | 470 |
| | | solid (290) | 555 |
| | | solid (11) | 560 |
| **3a** | 267 (1.4), 383 (1.6) | $CH_2Cl_2$ (290) | 455 |
| | | solid (290) | 601 |
| | | solid (11) | 623 |
| **3b** | 268 (1.2), 385 (1.3) | $CH_2Cl_2$ (290) | 448, 465 sh, 534 sh |
| | | solid (290) | 568 |
| | | solid (11) | 555 |
| **4a** | 252 (3.4), 404 (1.1) | $CH_2Cl_2$ (290) | 440 |
| | | solid (290) | 550 |
| | | solid (11) | 533, 567 |
| **4b** | 254 (3.2), 308 (0.6), 410 (0.9) | $CH_2Cl_2$ (290) | 439, 468, 498 sh |
| | | solid (290) | 530 |
| | | solid (11) | 526, 561 |
| **5** | 253 (2.5), 387 (1.4) | $CH_2Cl_2$ (290) | 456 |
| | | solid (290) | 563 |
| | | solid (11) | 569, 610 |
| **6** | 277 (1.8), 387 (1.1) | $CH_2Cl_2$ (290) | 469 sh, 533 |
| | | solid (290) | 425 sh, 602 |
| | | solid (11) | 602 |
| **7** | 269 (2.6), 298 (2.4), 389 (1.2) | $CH_2Cl_2$ (290) | 452 vw |
| | | solid (290) | 434, 510 sh |
| | | solid (11) | 420, 436, 520 sh |
| **8** | 255 (3.2), 389 (1.6) | $CH_2Cl_2$ (290) | 461 |
| | | solid (290) | 556 |
| | | solid (11) | 558 |
| **9** | 248 (3.8), 307 (0.7), 410 (1.1) | $CH_2Cl_2$ (290) | 447 |
| | | solid (290) | 552 |
| | | solid (11) | 535, 570 |
| **10** | 274 (2.9), 406 (0.9) | $CH_2Cl_2$ (290) | 466 |
| | | solid (290) | 573 |
| | | solid (11) | 575 |
| **11** | 262 (5.0), 304 (2.2), 408 (0.7) | $CH_2Cl_2$ (290) | 465 vw |
| | | solid (290) | 435, 575 vw |
| | | solid (11) | 435, 578 vw |
| **12** | 248 (3.7), 310 (0.7), 413 (1.3) | $CH_2Cl_2$ (290) | 452 |
| | | solid (290) | 540 |
| | | solid (11) | 534, 571 |

[a] Excitation wavelength is 325 nm. sh = shoulder. vw = very weak. [b] All absorption spectra were recorded in $CH_2Cl_2$ at 290 K.

double monochromator with a Peltier cooled photomultiplier tube and processed with a lock-in amplifier. For the low temperature experiments, samples were mounted in a closed-cycle cryostat (Oxford CC1104) in which the temperature can be adjusted from 10 to 330 K. Cyclic voltammetry experiments were performed with a Princeton Applied Research (PAR) model 273A potentiostat. A conventional three-electrode configuration consisting of a glassy-carbon working electrode, a Pt-wire counter electrode and a Ag/$AgNO_3$ reference electrode was used at a scan rate of 100 mV $s^{-1}$. The solvent in all measurements was deoxygenated $CH_2Cl_2$ and the supporting electrolyte was 0.1 M $[Bu_4N]PF_6$. Ferrocene was added as an internal standard after each set of measurements and all potentials reported were quoted with reference to the ferrocene-ferrocenium couple. Unless otherwise stated, all reagents were from commercial sources and used as received. The compounds **1a**,[7b] **3a**,[7b] ethynylferrocene[14] and *p*-ethynylphenylferrocene[15] were prepared according to the reported procedures. The synthesis of **3b**, **4a** and **4b** was described in the supplementary materials. Density functional calculations at the B3LYP level[16] were performed on **2a**, **9** and **10** on the basis of their experimentally determined geometries obtained from crystallographic data. The basis set used for C, O, N and H atoms was 6−31G,[17] while effective core potentials with a LanL2DZ basis set[18] were employed for Fe and Hg atoms. The Gaussian 98 program was used for the calculations.[19]

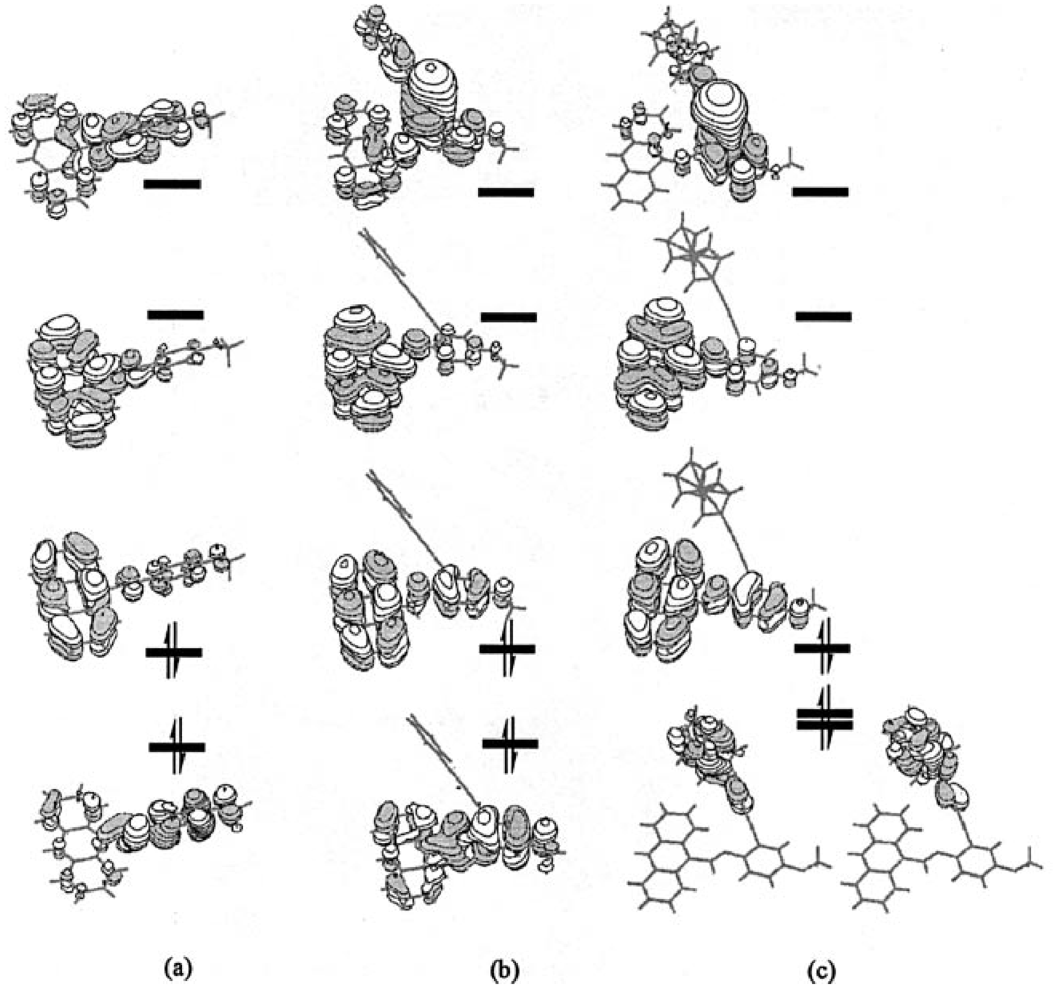


Figure 7. Spatial plots of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals for (a) **2a**, (b) **9** and (c) **10**

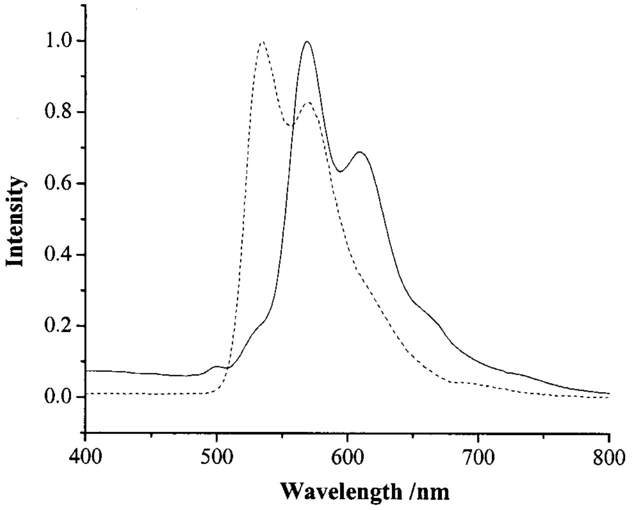


Figure 8. Solid-state emission spectra of **5** (solid line) and **9** (dashed line) at 11 K

***Caution!*** *Organomercurials are extremely toxic, and appropriate handling conditions should be used for their generation and disposal.*

**General Procedures for the Synthesis of σ-Alkynyl Complexes of Orthomercuriated Schiff Bases 5−12:** Basic MeOH was added dropwise to a mixture of each of the mercuric chloride derivatives (**3a**, **3b**, **4a** or **4b**, 0.10 mmol) and two molar equivalents of RC≡CH (R = Ph, Fc or $p$-$FcC_6H_4$) in THF. In a typical run, a 0.5 M solution of NaOH in MeOH (5 mL, 1.00 mmol) was added to the mixture of **3a** (49.1 mg, 0.10 mmol) and PhC≡CH (0.022 mL, 0.20 mmol) in THF (5 mL). The resulting mixture was stirred for 3 h at room temperature before all the volatile components were removed under reduced pressure. The residue was extracted with hot $CHCl_3$ and the yellow extract was then filtered through a thick layer of Celite. After evaporation of solvent, the crude product was recrystallised from $CH_2Cl_2$/hexane to afford an essentially pure yellow solid in high yield.

**Compound 5:** Yellow solid. Yield 86% (47.9 mg). IR (KBr): ν(CH=N) = 1621 and ν(C≡C) = 2141 cm$^{-1}$. $^1$H NMR ($CDCl_3$): δ = 3.85 (s, 3 H, Me), 6.88 (dd, $J_{H,H}$ = 2.7, 8.9 Hz, 1 H, $H_4$), 7.08 (d, $J_{H,H}$ = 2.7 Hz, 1 H, $H_5$), 7.32−7.35 (m, 3 H, Ph), 7.47 (d, $J_{H,H}$ = 8.9 Hz, 1 H, $H_3$), 7.51−7.54 (m, 2 H, Ph), 8.05 (d, $J_{H,H}$ = 8.8 Hz, 2 H, $H_2$), 8.32 (d, $J_{H,H}$ = 8.8 Hz, 2 H, $H_1$), 8.70 (s, 1 H, CH=N) ppm. $^{13}$C NMR ($CDCl_3$): δ = 55.58 (Me), 106.46, 115.03 (C≡C), 117.18, 122.16, 122.84, 124.00, 128.18, 128.24, 128.92, 131.94, 132.10, 141.68, 148.79, 148.84, 152.71, 159.24 (Ar), 162.54 (CH=N) ppm.

Table 3. Redox data for orthomercuriated compounds and their organic precursors

| Compound | Oxidation[a] $E_{pa}$ ($E_{1/2}$)/V | Reduction[b] $E_{1/2}$/V |
|---|---|---|
| **1a** | +1.11 | −1.43 |
| **1b** | +1.07 | −1.41 |
| **2a** | +0.82 | |
| **2b** | +0.78 | |
| **3a** | +1.10 | −1.44 |
| **3b** | +1.08 | −1.42 |
| **4a** | [c] | |
| **4b** | +0.87 | |
| **5** | +1.11 | −1.42 |
| **6** | +1.09 (+0.13) | −1.41 |
| **7** | +1.04 (+0.07) | −1.42 |
| **8** | +1.04 | −1.45 |
| **9** | +1.07, +0.78 | |
| **10** | +0.79 (+0.10) | |
| **11** | +0.77 (+0.06) | |
| **12** | +1.07, +0.77 | |

[a] $E_{pa}$ refers to the anodic peak potential of the irreversible oxidation wave. $E_{1/2} = (E_{pa} + E_{pc})/2$ where $E_{pa}$ and $E_{pc}$ are the anodic and cathodic peak potentials of the quasi-reversible oxidation couple due to the ferrocenyl group, respectively. [b] $E_{1/2}$ refers to the half-wave potential of the quasi-reversible reduction wave. [c] Limited solubility.

FAB MS: *m*/*z* = 557 [M$^+$]. $C_{22}H_{16}HgN_2O_3$ (557): calcd. C 47.44, H 2.90, N 5.03; found C 47.15, H 2.83, N 4.99.

**Compound 6:** Brownish-yellow solid. Yield 81% (53.9 mg). IR (KBr): ν(CH=N) = 1617 and ν(C≡C) = 2137 cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ = 3.85 (s, 3 H, Me), 4.22 (t, $J_{H,H}$ = 1.8 Hz, 2 H, $C_5H_4$), 4.24 (s, 5 H, $C_5H_5$), 4.49 (t, $J_{H,H}$ = 1.8 Hz, 2 H, $C_5H_4$), 6.87 (dd, $J_{H,H}$ = 2.8, 8.9 Hz, 1 H, $H_4$), 7.07 (d, $J_{H,H}$ = 2.8 Hz, 1 H, $H_5$), 7.46 (d, $J_{H,H}$ = 8.9 Hz, 1 H, $H_3$), 8.06 (d, $J_{H,H}$ = 8.9 Hz, 2 H, $H_2$), 8.32 (d, $J_{H,H}$ = 8.9 Hz, 2 H, $H_1$), 8.69 (s, 1 H, CH=N) ppm. $^{13}$C NMR (CDCl$_3$): δ = 55.56 (Me), 64.67, 68.75, 70.18, 71.89 (Fc), 106.11, 115.03 (C≡C), 117.28, 122.33, 124.09, 128.34, 129.06, 141.84, 148.95, 149.07, 152.90, 159.38 (Ar), 162.82 (CH=N) ppm. FAB MS: *m*/*z* = 665 [M$^+$]. $C_{26}H_{20}FeHgN_2O_3$ (665): calcd. C 46.97, H 3.03, N 4.21; found C 46.88, H 2.81, N 4.09.

**Compound 7:** Yellow solid. Yield 84% (62.2 mg). IR (KBr): ν(CH=N) = 1618 and ν(C≡C) = 2137 cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ = 3.87 (s, 3 H, Me), 4.05 (s, 5 H, $C_5H_5$), 4.36 (t, $J_{H,H}$ = 1.8 Hz, 2 H, $C_5H_4$), 4.67 (t, $J_{H,H}$ = 1.8 Hz, 2 H, $C_5H_4$), 6.90 (dd, $J_{H,H}$ = 2.8, 8.8 Hz, 1 H, $H_4$), 7.10 (d, $J_{H,H}$ = 2.8 Hz, 1 H, $H_5$), 7.45 (s, 4 H, $C_6H_4$), 7.49 (d, $J_{H,H}$ = 8.8 Hz, 1 H, $H_3$), 8.08 (d, $J_{H,H}$ = 9.0 Hz, 2 H, $H_2$), 8.35 (d, $J_{H,H}$ = 9.0 Hz, 2 H, $H_1$), 8.72 (s, 1 H, CH=N) ppm. FAB MS: *m*/*z* = 740 [M$^+$]. $C_{32}H_{24}FeHgN_2O_3$ (740): calcd. C 51.87, H 3.26, N 3.78; found C 52.01, H 3.04, N 3.50.

**Compound 8:** Yellow solid. Yield 82% (63.0 mg). IR (KBr): ν(CH=N) = 1621 and ν(C≡C) = 2140 cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ = 0.87 (m, 3 H, Me), 1.25−1.55 [m, 26 H, $(CH_2)_{13}$], 1.80 (quint., $J_{H,H}$ = 6.8 Hz, 2 H, $OCH_2CH_2$), 3.99 (t, $J_{H,H}$ = 6.8 Hz, 2 H, $OCH_2$), 6.87 (dd, $J_{H,H}$ = 2.9, 8.9 Hz, 1 H, $H_4$), 7.06 (d, $J_{H,H}$ = 2.9 Hz, 1 H, $H_5$), 7.32−7.34 (m, 3 H, Ph), 7.46 (d, $J_{H,H}$ = 8.9 Hz, 1 H, $H_3$), 7.51−7.54 (m, 2 H, Ph), 8.05 (d, $J_{H,H}$ = 8.9 Hz, 2 H, $H_2$), 8.32 (d, $J_{H,H}$ = 8.9 Hz, 2 H, $H_1$), 8.70 (s, 1 H, CH=N) ppm. $^{13}$C NMR (CDCl$_3$): δ = 14.24, 22.75, 22.79, 26.12, 29.35, 29.44, 29.48, 29.67, 29.69, 29.74, 29.78, 31.66, 32.00, 68.38 ($C_{16}H_{33}$), 106.48, 115.65 (C≡C), 117.14, 122.70, 122.87, 124.02, 128.18, 128.27, 128.90, 132.10, 132.13, 141.74, 148.61, 148.78, 152.48, 158.91 (Ar), 162.56 (CH=N) ppm. FAB MS: *m*/*z* = 768 [M$^+$]. $C_{37}H_{46}HgN_2O_3$ (768): calcd. C 57.91, H 6.04, N 3.65; found C 57.72, H 5.88, N 3.39.

**Compound 9:** Yellow solid. Yield 88% (53.9 mg). IR (KBr): ν(CH=N) = 1624 and ν(C≡C) = 2141 cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ = 3.88 (s, 3 H, Me), 6.96 (dd, $J_{H,H}$ = 2.7, 8.9 Hz, 1 H, $H_{11}$), 7.11 (d, $J_{H,H}$ = 2.7 Hz, 1 H, $H_{12}$), 7.27−7.29 (m, 3 H, Ph), 7.42−7.53 (m, 4 H, $H_{2,3,6,7}$), 7.60 (d, $J_{H,H}$ = 8.9 Hz, 1 H, $H_{10}$), 7.64−7.67 (m, 2 H, Ph), 8.04 (d, $J_{H,H}$ = 8.4 Hz, 2 H, $H_{4,5}$), 8.54 (s, 1 H, CH=N), 8.87 (d, $J_{H,H}$ = 8.9 Hz, 2 H, $H_{1,8}$), 9.85 (s, 1 H, $H_9$) ppm. $^{13}$C NMR (CDCl$_3$): δ = 55.64 (Me), 106.08, 114.98 (C≡C), 117.35, 122.35, 123.10, 124.80, 125.29, 126.91, 127.22, 127.93, 128.13, 128.97, 130.54, 130.65, 131.24, 132.06, 132.84, 151.16, 156.22, 158.47 (Ar), 160.68 (CH=N) ppm. FAB MS: *m*/*z* = 613 [M$^+$]. $C_{30}H_{21}HgNO$ (613): calcd. C 58.87, H 3.46, N 2.29; found C 58.50, H 3.19, N 2.03.

**Compound 10:** Yellow-brown solid. Yield 82% (59.1 mg). IR (KBr): ν(CH=N) = 1622 and ν(C≡C) = 2140 cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ = 3.88 (s, 3 H, Me), 4.16−4.17 (m, 7 H, $C_5H_5$ + $C_5H_4$), 4.41 (t, $J_{H,H}$ = 1.9 Hz, 2 H, $C_5H_4$), 6.96 (dd, $J_{H,H}$ = 2.9, 8.6 Hz, 1 H, $H_{11}$), 7.10 (d, $J_{H,H}$ = 2.9 Hz, 1 H, $H_{12}$), 7.50−7.70 (m, 5 H, $H_{2,3,6,7,10}$), 8.05 (d, $J_{H,H}$ = 8.4 Hz, 2 H, $H_{4,5}$), 8.55 (s, 1 H, CH=N), 8.89 (d, $J_{H,H}$ = 8.9 Hz, 2 H, $H_{1,8}$), 9.86 (s, 1 H, $H_9$) ppm. $^{13}$C NMR (CDCl$_3$): δ = 55.61 (Me), 68.51, 70.06, 70.19, 71.75 (Fc), 105.55, 114.94 (C≡C), 117.42, 122.50, 124.94, 125.39, 127.07, 127.30, 129.09, 129.14, 130.63, 130.76, 131.36, 151.37, 156.32, 158.62 (Ar), 161.01 (CH=N) ppm. FAB MS: *m*/*z* = 721 [M$^+$]. $C_{34}H_{25}FeHgNO$ (721): calcd. C 56.72, H 3.50, N 1.95; found C 56.55, H 3.40, N 1.78.

**Compound 11:** Yellow-brown solid. Yield 87% (69.3 mg). IR (KBr): ν(CH=N) = 1622 and ν(C≡C) 2138 cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ = 3.89 (s, 3 H, Me), 4.03 (s, 5 H, $C_5H_5$), 4.33 (t, $J_{H,H}$ = 1.6 Hz, 2 H, $C_5H_4$), 4.64 (t, $J_{H,H}$ = 1.6 Hz, 2 H, $C_5H_4$), 6.97 (dd, $J_{H,H}$ = 2.8, 8.8 Hz, 1 H, $H_{11}$), 7.13 (d, $J_{H,H}$ = 2.8 Hz, 1 H, $H_{12}$), 7.35−7.41 (m, 4 H, $H_{2,3,6,7}$), 7.50−7.54 (m, 2 H, $C_6H_4$), 7.61 (d, $J_{H,H}$ = 8.8 Hz, 1 H, $H_{10}$), 7.64−7.68 (m, 2 H, $C_6H_4$), 8.06 (d, $J_{H,H}$ = 8.0 Hz, 2 H, $H_{4,5}$), 8.56 (s, 1 H, CH=N), 8.89 (d, $J_{H,H}$ = 8.8 Hz, 2 H, $H_{1,8}$), 9.86 (s, 1 H, $H_9$) ppm. $^{13}$C NMR (CDCl$_3$): δ = 55.61 (Me), 66.48, 69.26, 69.41, 69.68 (Fc), 106.58, 115.03 (C≡C), 117.46, 120.24, 122.46, 124.92, 125.40, 125.74, 127.04, 127.34, 129.07, 130.65, 130.76, 131.35, 132.19, 132.88, 139.59, 151.35, 156.41, 158.62 (Ar), 160.90 (CH=N) ppm. FAB MS: *m*/*z* = 796 [M$^+$]. $C_{40}H_{29}FeHgNO$ (796): calcd. C 60.35, H 3.67, N 1.76; found C 60.02, H 3.43, N 1.59.

**Compound 12:** Yellow solid. Yield 80% (65.8 mg). IR (KBr): ν(CH=N) = 1624 and ν(C≡C) = 2141 cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ = 0.87 (m, 3 H, Me), 1.26−1.49 [m, 26 H, $(CH_2)_{13}$], 1.83 (quint., $J_{H,H}$ = 6.5 Hz, 2 H, $OCH_2CH_2$), 4.02 (t, $J_{H,H}$ = 6.5 Hz, 2 H, $OCH_2$), 6.96 (dd, $J_{H,H}$ = 2.8, 8.7 Hz, 1 H, $H_{11}$), 7.10 (d, $J_{H,H}$ = 2.8 Hz, 1 H, $H_{12}$), 7.27−7.29 (m, 3 H, Ph), 7.42−7.53 (m, 4 H, $H_{2,3,6,7}$), 7.58−7.68 (m, 3 H, $H_{10}$ + Ph), 8.04 (d, $J_{H,H}$ = 8.4 Hz, 2 H, $H_{4,5}$), 8.54 (s, 1 H, CH=N), 8.88 (d, $J_{H,H}$ = 8.9 Hz, 2 H, $H_{1,8}$), 9.86 (s, 1 H, $H_9$) ppm. $^{13}$C NMR (CDCl$_3$): δ = 14.23, 22.78, 26.16, 29.43, 29.45, 29.53, 29.69, 29.72, 29.74, 29.79, 32.00, 68.40 ($C_{16}H_{33}$), 106.08, 115.62 (C≡C), 117.27, 122.89, 123.15, 124.82, 125.26, 126.92, 127.18, 127.89, 128.11, 128.94, 130.46, 130.63, 131.23, 132.06, 133.06, 150.90, 155.99, 158.09 (Ar), 160.66 (CH=N) ppm. FAB MS: *m*/*z* = 823 [M$^+$]. $C_{45}H_{51}NHgO$ (823): calcd. C 65.71, H 6.25, N 1.70; found C 65.50, H 6.02, N 1.43.

**X-ray Crystallography:** Yellow to orange crystals of the compounds suitable for X-ray diffraction analyses were grown by slow evapor-

Table 4. Crystal data for complexes **5**, **6**, **7**, **9** and **10**

| | **5** | **6** | **7** | **9** | **10** |
|---|---|---|---|---|---|
| Empirical formula | $C_{22}H_{16}HgN_2O_3$ | $C_{26}H_{20}FeHgN_2O_3$ | $C_{32}H_{24}FeHgN_2O_3$ | $C_{30}H_{21}HgNO$ | $C_{34}H_{25}FeHgNO$ |
| Formula mass | 556.96 | 664.89 | 740.97 | 612.07 | 719.99 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Hexagonal | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/a$ | $P2_1/n$ | $P6_5$ | $P2_1/c$ |
| $a$ (Å) | 13.703(3) | 7.655(7) | 7.5643(6) | 26.103(2) | 15.2962(9) |
| $b$ (Å) | 19.968(4) | 21.831(5) | 34.412(3) | 26.103(2) | 12.7602(7) |
| $c$ (Å) | 7.3386(15) | 13.584(5) | 10.3974(8) | 5.9421(8) | 13.5800(8) |
| α (°) | 90 | 90 | 90 | 90 | 90 |
| β (°) | 104.96(3) | 100.78(5) | 104.827(2) | 90 | 95.6590(10) |
| γ (°) | 90 | 90 | 90 | 120 | 90 |
| $V$ (Å$^3$) | 1940.1(7) | 2230(1) | 2616.4(4) | 3506.3(7) | 2637.7(3) |
| $Z$ | 4 | 4 | 4 | 6 | 4 |
| μ (Mo-$K_\alpha$) (mm$^{-1}$) | 7.958 | 7.576 | 6.453 | 6.607 | 6.392 |
| $F$(000) | 1064 | 1280 | 1440 | 1776 | 1400 |
| $T$ (K) | 293 | 301 | 293 | 293 | 293 |
| Reflections collected | 11378 | 4343 | 15655 | 17552 | 14902 |
| Unique reflections | 4379 | 4028 | 6129 | 4068 | 5893 |
| $R_{\mathrm{int}}$ | 0.0296 | 0.0270 | 0.0827 | 0.1228 | 0.0253 |
| Observed reflections [$I > n\sigma(I)$] | 2787 ($n = 2.0$) | 2706 ($n = 1.5$) | 3056 ($n = 2.0$) | 3180 ($n = 2.0$) | 4672 ($n = 2.0$) |
| Final $R$ indices [$I > n\sigma(I)$][a] | $R1 = 0.0336$<br>$wR2 = 0.0740$ | $R = 0.047$<br>$R_w = 0.044$ | $R1 = 0.0489$<br>$wR2 = 0.0908$ | $R1 = 0.0510$<br>$wR2 = 0.1081$ | $R1 = 0.0284$<br>$wR2 = 0.0716$ |

[a] $R = R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$. $wR2 = [\Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w|F_o{}^2|^2]^{1/2}$.

ation of the solvents from their respective solutions in a hexane/$CH_2Cl_2$ mixture. Geometric and intensity data were collected using graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda = 0.71073$ Å) on a Rigaku AFC7R diffractometer (**6**) and Bruker AXS SMART CCD area-detector (for the rest). Absorption corrections based on the $\psi$-scan method[20] (**6**) or SADABS program[21] (for the other four compounds) were applied. The structure was solved by the direct methods (SIR92[22] for **6**, SHELXTL[23] for the rest) in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses. All non-hydrogen atoms were assigned with anisotropic displacement parameters. Hydrogen atoms were generated in their idealised positions and allowed to ride on the respective carbon atoms. Crystallographic data for the alkynylmercury complexes are collected in Table 4. For **2a**, the crystal and other experimental details are given in the Supporting Information.

CCDC-217511 to -217516 (for **2a**, **5**, **6**, **7**, **9** and **10**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EW, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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