DALTON
FULL PAPER

Synthesis, structure and metal compounds of a novel chromophoric cyanamide ligand

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The novel compound 2-cyanaminofluoren-9-one (HL) has been synthesized, and is readily deprotonated to form the corresponding cyanamide anion L^-. This has been isolated as the Tl^+L^- and $AsPh_4{}^+L^-$ salts. The UV/visible spectra of HL and $AsPh_4{}^+L^-$ show the same amine to carbonyl charge transfer transition seen in other aminofluorenones, although at longer wavelengths. The compound $AsPh_4{}^+L^-$ undergoes the reversible one electron reduction typical of fluorenones, whilst HL undergoes an irreversible reduction. The crystal structure of $AsPh_4{}^+L^-$ was determined and related to the solvatochromic behaviour of the L^- anion. Some simple EHMO calculations have been carried out on the L^- anion of $AsPh_4{}^+L^-$, which show the cyanamide based HOMO and carbonyl based LUMO involved in the aforementioned CT transition. The thallium salt Tl^+L^- has also been used as a transmetallating agent in reaction with trimethyltin chloride to produce the corresponding tin cyanamide complex $[SnMe_3L]$, and in reaction with (triphenylphosphine)gold chloride to produce the first reported gold cyanamide compound $[AuL(PPh_3)]$, whose crystal structure has been determined.

There has been a great deal of interest in the last decade in the chemistry of compounds containing highly conjugated carbon chains, both in organic and organometallic systems, because of their potential utility in the synthesis of molecular wires[1] and other nanoelectronic devices,[2] and as likely monomers for the preparation of novel polymers related to polyacetylene.[3] Work here in Cambridge has focused on the chemistry of transition metal–acetylide systems,[4] and recently has concentrated in particular on compounds containing highly conjugated organic groups as spacers.[5] This is designed to lower the HOMO–LUMO gap of the compounds by having a ligand with a low lying LUMO between the metal centres, since research has shown that the LUMO in such compounds is confined to this ligand.[6]

Wishing to explore other conjugated systems, and bearing in mind the promising results obtained with conjugated spacer groups, recently I have investigated the chemistry of metal–cyanamide compounds. Cyanamides are pseudo-halide nitrogen ligands that are readily co-ordinated to metals; their chemistry has not been extensively investigated, although there has been some work by Crutchley and co-workers[7] in Canada over the past ten years. I report here the synthesis and characterisation of a new fluorenone–cyanamide compound and show that it forms stable (triphenylphosphine)gold(I) and trimethyltin derivatives.

Results and discussion

The novel compound 2-cyanaminofluoren-9-one (HL) is readily synthesized from 2-aminofluoren-9-one by an adaptation of the literature procedure.[8] As is normally the case for aryl cyanamides, the amine proton of this ligand is acidic and a stable cyanamide anion is formed through deprotonation with triethylamine. This has been isolated as the thallium(I) and tetraphenylarsonium salts. The former of these is soluble only in highly polar solvents such as DMF, but the latter is soluble in common organic solvents such as dichloromethane, acetonitrile and ethanol.

The neutral compound HL is orange, whereas the anion L^- is an intense purple. The UV/visible spectra of these compounds are presented in Fig. 1; the solution used to record the spectrum of the anion L^- was prepared by adding two drops of diisopropylamine to that used to record the spectrum of HL, so the concentration is the same in both cases. Both spectra consist of four bands, three of which have intensities that vary considerably more than their wavelengths (Table 1). The fourth band does, however, move considerably to longer wavelengths

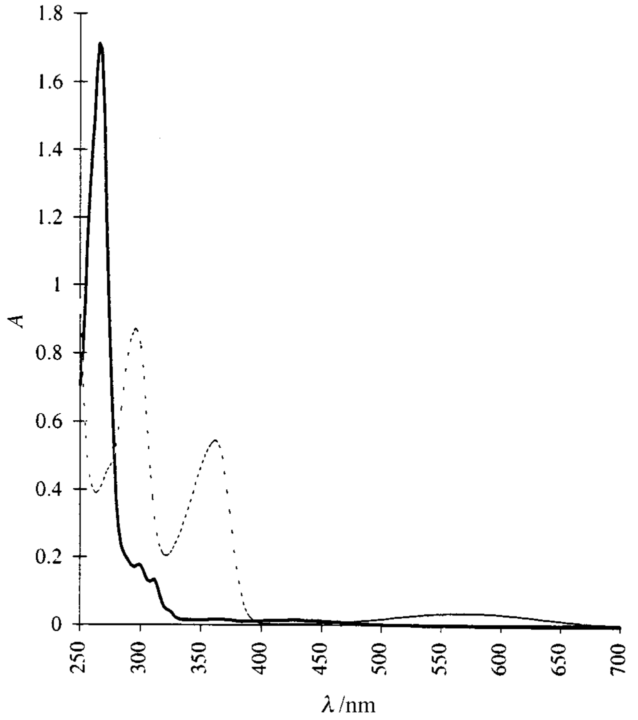
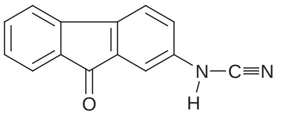
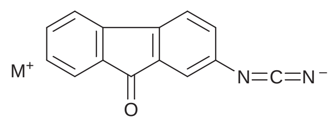


Fig. 1 The UV/visible spectra of HL (——) and the L^- anion (- - -) in acetonitrile.



HL



M = Tl
M = Ph4As

Table 1 Wavelengths (in nm) and absorption coefficients (in parentheses, /10^3 M^{-1} cm^{-1}) in the UV/visible spectrum of HL and its anionic form L^-, and of its compounds

Compound	Solvent	Observed absorptions			
HL	CH_3CN	433 (0.27)	365 (0.28)	311 (4.12) 299 (5.59)	265 (4.16)
L^-	CH_3CN	568 (0.73)	361 (13.21)	296 (21.28)	274 (11.25)
$AsPh_4^+L^-$	CH_2Cl_2	578 (0.58)	364 (12.6)	300 (18.3)	272 (12.1)
[$SnMe_3L$]	CH_2Cl_2	452 (0.25)	333 (2.59) 321 (4.10)	283 (18.0)	269 (20.8)
[AuL(PPh_3)]	CH_2Cl_2	483 (0.49)	339 (0.80) 327 (0.89)	287 (2.03)	276 (1.94) 270 (1.94)

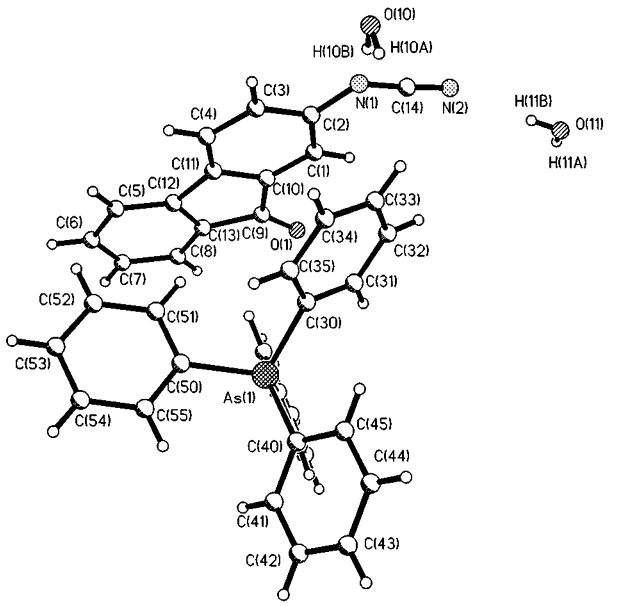


Fig. 2 The asymmetric unit of the crystal structure of $AsPh_4^+L^-$, showing the atom numbering scheme. One of the phenyl rings of the $[AsPh_4]^+$ cation, composed of C(20) to C(25), is obscured.

Table 2 Selected bond lengths (Å) and angles (°) for $AsPh_4^+L^-\cdot 2H_2O$

N(2)–C(14)	1.172(4)	C(14)–N(1)	1.295(3)
N(1)–C(2)	1.394(3)	C(1)–C(2)	1.406(4)
C(2)–C(3)	1.402(4)	C(3)–C(4)	1.392(4)
C(4)–C(11)	1.380(4)	C(5)–C(12)	1.382(3)
C(5)–C(6)	1.399(4)	C(6)–C(7)	1.375(4)
C(7)–C(8)	1.397(4)	C(8)–C(13)	1.373(4)
C(9)–O(1)	1.215(3)	C(9)–C(10)	1.485(3)
C(9)–C(13)	1.500(3)	C(10)–C(11)	1.400(3)
C(1)–C(10)	1.381(3)	C(11)–C(12)	1.484(4)
C(12)–C(13)	1.404(4)		
O(10)–H(10a)	0.91(4)	O(10)–H(10b)	0.79(4)
O(11)–H(11a)	0.93(4)	O(11)–H(11b)	0.73(3)
C(10)–C(1)–C(2)	119.2(2)	N(1)–C(2)–C(3)	118.3(2)
N(1)–C(2)–C(1)	123.7(2)	C(3)–C(2)–C(1)	118.0(2)
C(4)–C(3)–C(2)	122.4(2)	C(11)–C(4)–C(3)	119.0(2)
C(12)–C(5)–C(6)	117.8(3)	C(7)–C(6)–C(5)	122.1(3)
C(13)–C(8)–C(7)	118.3(3)	O(1)–C(9)–C(10)	127.9(2)
O(1)–C(9)–C(13)	126.9(2)	C(10)–C(9)–C(13)	105.1(2)
C(1)–C(10)–C(11)	122.2(2)	C(1)–C(10)–C(9)	128.5(2)
C(11)–C(10)–C(9)	109.3(2)	C(4)–C(11)–C(10)	119.2(2)
C(4)–C(11)–C(12)	132.4(2)	C(10)–C(11)–C(12)	108.4(2)
C(5)–C(12)–C(13)	120.0(3)	C(5)–C(12)–C(11)	131.5(3)
C(13)–C(12)–C(11)	108.5(2)	C(8)–C(13)–C(12)	121.8(2)
C(8)–C(13)–C(9)	129.5(2)	C(12)–C(13)–C(9)	108.7(2)
C(14)–N(1)–C(2)	117.2(2)	N(2)–C(14)–N(1)	176.3(3)
C(6)–C(7)–C(8)	120.0(3)		
H(10a)–O(10)–H(10b)	101(3)		
H(11a)–O(11)–H(11b)	101(3)		

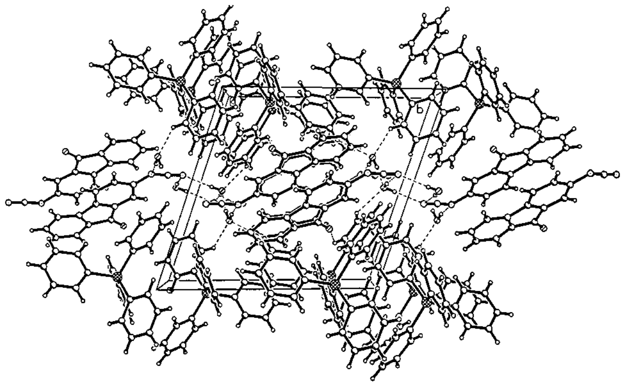


Fig. 3 A view down the *c* axis of the crystal structure of $AsPh_4^+L^-$, showing the hydrogen bonding (dotted lines) and graphitic packing present.

on deprotonation; it is also highly solvatochromic, shifting to 518 nm ($\varepsilon = 502$ dm^3 mol^{-1} cm^{-1}) in ethanol, resulting in a solution that is pink rather than purple. In common with similar bands seen in the spectra of other aminofluorenones, this is assigned to an intramolecular charge transfer from the cyanamide moiety to the fluorenone π skeleton.[9]

The electrochemistry of $AsPh_4^+L^-$ is straightforward; the cyclic voltammogram shows a single reversible one electron reduction at −1.42 V *vs.* Ag–AgCl. This is in common with the electrochemistry of other 2-substituted fluorenone derivatives.[10] In contrast, the cyclic voltammogram of HL is more complicated, showing an irreversible oxidation at +0.52 V and an irreversible reduction at −1.15 V. The oxidation is linked to the reduction, in that if the reduction is not performed the oxidation is not seen in the spectrum.

Slow evaporation of a water–ethanol solution of $AsPh_4^+L^-$ resulted in purple crystals that were found to be suitable for X-ray diffraction, and the resulting crystal structure is shown in Fig. 2. The salt crystallises in the triclinic space group $P\bar{1}$, with two molecules of water of crystallisation in the asymmetric unit. The L^- ion is essentially planar, as expected given the nature of the fluorenone unit and the tendency of cyanamide moieties to lie parallel to aromatic rings,[11] with the largest deviation from the plane of the fluorenone moiety being 0.15 Å for the atom O(1). The cyanamide N=C=N group is pointing slightly below the plane of the rest of the ion so that the terminal nitrogen atom N(2) is 0.25 Å from the plane. The angle at C(14) in the N=C=N group is 176.3(3)°, while the angle to the aromatic ring C(2)–N(1)–C(14) is 117.2(2)°. The fluorenone carbon–cyanamide nitrogen distance C(2)–N(1) of 1.394(3) Å is within the range of previously observed distances for this kind of ligand.[11] Selected bond lengths and angles are presented in Table 2.

The crystal packing diagram of $AsPh_4^+L^-$ (Fig. 3) reveals graphitic packing between adjacent $[AsPh_4]^+$ cations and between adjacent L^- anions, both showing the expected offset of rings. The former have neighbouring phenyl rings (related by the symmetry operation $-x$, $1 - y$, $1 - z$) at a distance of 3.74 Å, and the latter have the phenyl rings of neighbouring L^- moieties (related by $-x - 1$, $1 - y$, $-z$) at 3.60 Å. These L^- species are reversed with respect to each other, so the

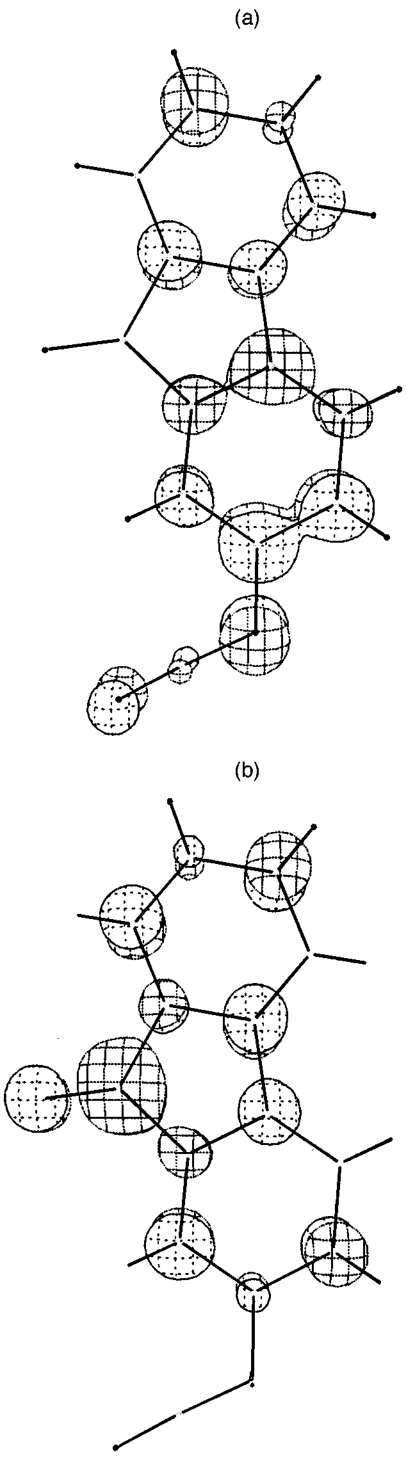


Fig. 4 The HOMO (a) and LUMO (b) of the L$^-$ anionic part of AsPh$_4$$^+L^-$.

C(1)C(2)C(3)C(4)C(11)C(10) ring of one lies over the C(5)C(6)C(7)C(8)C(13)C(12) ring of the other. There is also extensive hydrogen bonding present within the lattice. The water molecule H(11a)O(11)H(11b) acts as a hydrogen bond donor, having hydrogen atom H(11b) interacting with the terminal nitrogen atom N(2) of the nearest cyanamide groups (at 2.08 Å), and hydrogen atom H(11a) interacting with the same atom in a neighbouring unit cell (related by the symmetry operation $-x-1$, $2-y$, $-z$) in a bridging fashion. For the water molecule H(10a)O(10)H(10b) only H(10a) is hydrogen bonding to the nearest cyanamide group, to the amine nitrogen N(1) at 1.974 Å. The atom H(10b) acts as a hydrogen bond donor interacting with the oxygen atom O(11) of the water of crystallisation in a neighbouring asymmetric unit (related by $-x-1$, $2-y$, $1-z$). The oxygen atom O(10) also acts as a hydrogen bond acceptor unit to the hydrogen atoms H(52) (at 2.514 Å) and H(41) (at 2.364 Å) of two of the phenyl rings of two adjacent [AsPh$_4$]$^+$ cations (related by $-x-1$, $1-y$, $1-z$ and $x-1$, y, z respectively). The other water oxygen atom O(11) is also interacting with one of the phenyl rings of a [AsPh$_4$]$^+$ cation (H(34), related by $-x-1$, $2-y$, $1-z$, at 2.572 Å). The result of all this hydrogen bonding is to produce a geometry around both O(10) and O(11) that is approximately tetrahedral. Finally, the carbonyl oxygen O(1) acts as a hydrogen bond acceptor with atom H(35) of a [AsPh$_4$]$^+$ cation (related by x, $y-1$, $z-1$), 2.420 Å away.

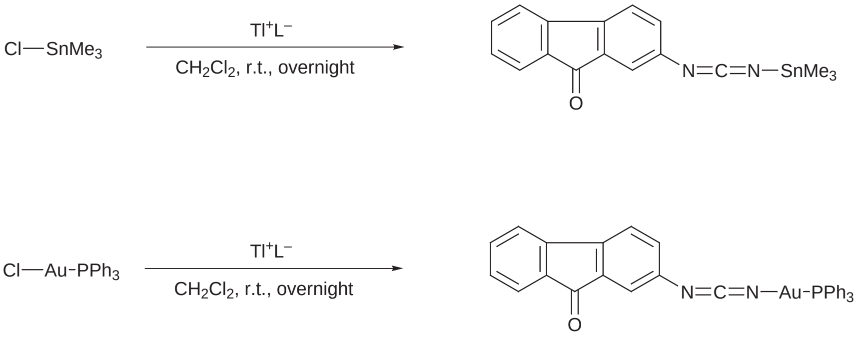
Simple EHMO calculations have been performed upon the L$^-$ anion shown in Fig. 2, using the crystallographic data as an input for the CACAO program.[12] The resulting MOs support the idea of a cyanamide to carbonyl charge transfer being responsible for the longest wavelength band seen in the UV/visible spectrum of AsPh$_4$$^+L^-$. The HOMO is of π symmetry, and is shown in Fig. 4(a); it contains a contribution from the π_{nb} orbital of the cyanamide group that is perpendicular to the plane,[13] but none from the carbonyl. The LUMO (Fig. 4(b)) is also of π symmetry. In contrast to the HOMO, it contains no contribution from the cyanamide part of the anion, but has a large component from the carbonyl group. This provides strong support for assigning the longest wavelength UV/visible band to a cyanamide to carbonyl π–π* charge transfer.

The crystal structure of AsPh$_4$$^+L^-$ and the MO calculations provide a good explanation for the observed solvatochromism of the low energy charge transfer band. The structure determination shows that it is the cyanamide group rather than the carbonyl that interacts most strongly with the polar solvent, and the MO calculations show that this group forms part of the HOMO. Thus, the lower of the two states involved in the transition is more stabilised by polar solvents, and so the transition moves to higher energies (and thus shorter wavelengths) as the solvent polarity increases.[14]

Metal complexes

The thallium complex Tl$^+$L$^-$ behaves as a transmetallating agent on reaction with trimethyltin chloride and (triphenylphosphine)gold chloride, eliminating thallium chloride and allowing attachment of the L$^-$ ion to the metal as a ligand (Scheme 1). The red-orange trimethyltin–cyanamide [SnMe$_3$L] has been characterised by standard spectroscopic and analytical methods. The IR spectrum shows a broad ν(N=C=N) stretch with a maximum at 2108 cm^{-1}, very similar to that of AsPh$_4$$^+L^-$ at 2104 cm^{-1}, and a shoulder at 2150 cm^{-1}. This is surprising since there is normally a large change of this frequency upon co-ordination of a cyanamide ligand to a metal, as has been observed for the gold–cyanamide compound [AuL(PPh$_3$)]; here, ν(N=C=N) appears at 2159 cm^{-1}, with a shoulder at 2123 cm^{-1}.

Slow evaporation of a saturated acetone solution of [AuL(PPh$_3$)] resulted in orange crystals that were suitable for X-ray diffraction; the resulting crystal structure is shown in Fig. 5, and selected bond lengths and angles are given in Table 3. The gold–nitrogen bond length Au(1)–N(2) is 2.017 Å, and the only bond distance in the co-ordinated L moiety that is significantly different from that of the "free" ligand in the crystal structure of AsPh$_4$$^+L^-$ is C(14)–N(1), which is slightly shorter at 1.257(9) Å. Similarly, the bond angles within the co-ordinated and unco-ordinated L ligands are very similar. As for AsPh$_4$$^+L^-$, there are intermolecular interactions within the crystal lattice; O(1) is at 2.49 Å from H(41a) of a neighbouring triphenylphosphine group (related by $-x$, $-y$, $-z+2$), and N(2) is at 2.577 Å from H(23a) of another triphenylphosphine ligand (related by x, $y-1$, z). There are also two hydrogen atoms H(6a) (related by $x, y, z-1$) and H(3a) (related by $-x-1$, $-y-1$, $-z+2$) that are at 3.058 Å from Au(1), but which do not appear to have any directional interactions with it. The geometry of the bonding



Scheme 1 Synthesis and structure of metal complexes.

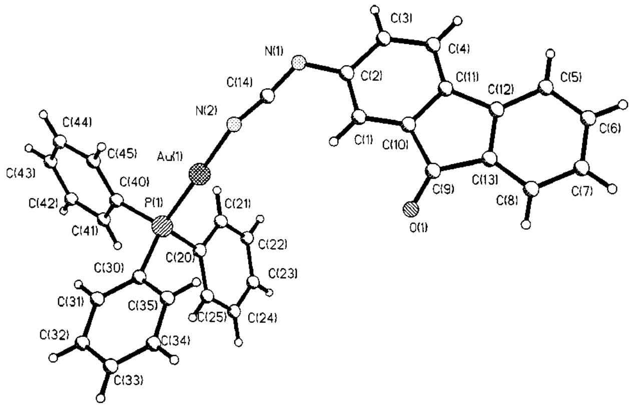


Fig. 5 The crystal structure of [AuL(PPh$_3$)].

Table 3 Selected bond lengths (Å) and angles (°) for [AuL(PPh$_3$)]

N(2)–C(14)	1.195(9)	C(14)–N(1)	1.257(9)
N(1)–C(2)	1.401(8)	C(1)–C(2)	1.399(9)
C(2)–C(3)	1.395(9)	C(3)–C(4)	1.402(10)
C(4)–C(11)	1.386(9)	C(5)–C(12)	1.390(10)
C(5)–C(6)	1.411(12)	C(6)–C(7)	1.366(13)
C(7)–C(8)	1.387(12)	C(8)–C(13)	1.371(10)
C(9)–O(1)	1.211(8)	C(9)–C(10)	1.506(9)
C(9)–C(13)	1.482(10)	C(10)–C(11)	1.403(9)
C(1)–C(10)	1.372(9)	C(11)–C(12)	1.508(9)
C(12)–C(13)	1.379(10)	Au(1)–N(2)	2.017(6)
Au(1)–P(1)	2.2295(17)		
C(10)–C(1)–C(2)	118.7(6)	N(1)–C(2)–C(3)	118.2(6)
N(1)–C(2)–C(1)	122.7(6)	C(3)–C(2)–C(1)	119.1(6)
C(4)–C(3)–C(2)	122.7(6)	C(11)–C(4)–C(3)	117.0(6)
C(12)–C(5)–C(6)	117.0(8)	C(7)–C(6)–C(5)	121.4(8)
C(13)–C(8)–C(7)	118.4(8)	O(1)–C(9)–C(10)	126.0(7)
O(1)–C(9)–C(13)	128.4(7)	C(10)–C(9)–C(13)	105.6(6)
C(1)–C(10)–C(11)	121.9(6)	C(1)–C(10)–C(9)	129.3(6)
C(11)–C(10)–C(9)	108.7(6)	C(4)–C(11)–C(10)	120.5(6)
C(4)–C(11)–C(12)	132.2(6)	C(10)–C(11)–C(12)	107.2(6)
C(5)–C(12)–C(13)	120.8(7)	C(5)–C(12)–C(11)	129.9(7)
C(13)–C(12)–C(11)	109.3(6)	C(8)–C(13)–C(12)	121.6(7)
C(8)–C(13)–C(9)	129.3(7)	C(12)–C(13)–C(9)	109.2(6)
C(14)–N(1)–C(2)	119.4(6)	N(2)–C(14)–N(1)	173.3(7)
C(6)–C(7)–C(8)	120.8(7)	C(14)–N(2)–Au(1)	144.0(6)
N(2)–Au(1)–P(1)	178.47(19)		

between metal and cyanamide is similar to that seen in the structure of other neutral metal–cyanamide compounds.[11,15]

The UV/visible spectra of the complexes are similar to that of AsPh$_4$$^+L^-$, with the same number of bands but with a shift of these to shorter wavelengths (Table 1).

Experimental

General

Solvents were pre-dried and distilled from appropriate drying agents.[16] All chemicals were obtained from commercial sources and used as received, except for [AuCl(PPh$_3$)], which was prepared according to the literature procedure.[17] The ^{1}H NMR spectra were recorded on a Bruker DRX 400 spectrometer and referenced to solvent resonances, and the ^{31}P-{^{1}H} spectrum on a Bruker AC 250 and referenced to external trimethyl phosphite. Solution IR spectra were recorded in a NaCl cell, and Nujol spectra between NaCl plates, on a Perkin-Elmer 1710 Fourier-transform spectrometer. The EI and +FAB mass spectra were recorded on a Kratos MS890 mass spectrometer, and ES mass spectra on a Micromass Quattro LC machine. Electrochemistry was performed under an argon atmosphere using an Autolab PGSTAT20, with platinum working and auxiliary electrodes and a Ag–AgCl reference electrode, in a 0.5 M solution of [^{n}Bu$_4$N][BF$_4$] in CH$_2$Cl$_2$ at 250 mV s^{-1}. The UV/visible absorption spectra were obtained on a Perkin-Elmer λ9 spectrometer. Microanalyses were carried out in this Department.

Synthetic procedures

2-Aminofluoren-9-one.[18] This was synthesized by a modification of a literature procedure.[19] 2-Aminofluorene (1.52 g, 0.838 mmol) was dissolved in 20 cm^3 of pyridine, and 4 drops of Triton B (benzyltrimethylammonium hydroxide, 40% w/w solution in methanol) were added. The solution was heated to 80 °C and oxygen bubbled through it for 4 h. It was then cooled, acidified with a few drops of glacial acetic acid, and poured into a mixture of 100 cm^3 of water and 5 cm^3 of glacial acetic acid. The resulting precipitate was filtered out and recrystallised from hot absolute ethanol to give the desired product as red-brown crystals (1.1 g, 5.63 mmol, 67%), mp 160–161 °C (lit.,[18a] 159.5–161 °C) (C$_{13}$H$_9$NO requires C, 79.98; H, 4.65; N, 7.16. Found: C, 79.23; H, 4.80; N, 7.11%). IR (CH$_2$Cl$_2$): 1717s (ν(C=O)) and 3396s cm^{-1} (br) (ν(N–H)). ^{1}H NMR (CDCl$_3$): δ 3.87 [br s, 2 H, NH], 6.72 [dd, 1 H, ^3J(HH) = 8.01, arene CH], 6.96 [d, 1 H, ^4J(HH) = 2.09, arene CH], 7.14 [t, 1 H, ^3J(HH) = 7.66, arene CH], 7.27 [d, 1 H, ^3J(HH) = 7.84, arene CH], 7.32 [d, 1 H, ^3J(HH) = 7.32, arene CH], 7.39 [t, 1 H, ^3J(HH) = 7.38, arene CH] and 7.56 [d, 1 H, ^3J(HH) = 7.35 Hz, arene CH].

2-Cyanaminofluoren-9-one (HL). Ammonium thiocyanate (0.565 g, 0.74 mmol) was refluxed under nitrogen in 30 cm^3 of acetone, and to this was added dropwise 0.86 cm^3 (1 equivalent) of benzoyl chloride, also in 30 cm^3 of acetone. This mixture was refluxed for 10 min, after which 1.45 g (0.74 mmol) of 2-aminofluoren-9-one in another 30 cm^3 of acetone were added slowly. After 1 h at reflux the solution was allowed to cool and poured into 200 cm^3 of distilled water. The resulting orange solid was filtered off, washed with copious amounts of water, and then redissolved in 200 cm^3 of 2 M sodium hydroxide solution. This solution was boiled for 5 min, then cooled to about 55 °C. Lead(II) acetate (2.81 g, 0.74 mmol) was added and stirred for 6 min. The resulting precipitate of lead sulfide was filtered off, and the filtrate cooled on ice. To the stirred solution was then added 10 cm^3 of glacial acetic acid, precipitating the desired product as an orange solid. This was recrystallised from a hot solution of 1 : 1 acetone–water to give 2-cyanaminofluoren-9-one as an orange solid (1.04 g, 0.47 mmol, 63%), mp 227 °C ($C_{14}H_8N_2O$ requires C, 76.35; H, 3.66; N, 12.72. Found: C, 76.35; H, 3.79; N, 12.69%). IR (Nujol mull): 3179m (ν(N–H)), 2235m, 2232 (sh) (ν(C≡N)) and 1715s cm^{-1} (ν(C=O)). ^1H NMR (CD_3CN): δ 7.17 [m, 2 H, arene CH], 7.30 [t, 1 H, ^3J(HH) = 7.49 Hz, arene CH] and 7.54–7.62 [m, 5 H, arene CH]. EI mass spectrum: *m*/*z* 220 (M^+).

Tl^+L^-. To a boiling solution of 0.91 g (4.13 mmol) of 2-cyanaminofluoren-9-one in 25 cm^3 of 1 : 1 acetone–water were added 1.49 g (5.6 mmol) of thallium(I) acetate in 25 cm^3 of the same solvent and 0.96 cm^3 of triethylamine. This was boiled for 1 min. Adding a little acetone to the hot solution dissolved all the solid material, and letting the resulting solution stand and cool overnight produced purple crystals of the desired product (1.24 g, 2.92 mmol, 70%), which were filtered off, washed with 1 : 1 acetone–water and dried under vacuum ($C_{14}H_7N_2OTl$ requires C, 39.70; H, 1.67; N, 4.64. Found: C, 39.69; H, 1.65; N, 4.55%). ^1H NMR (d_6-DMF): δ 6.80–7.42 [br m, 7 H, arene CH]. +FAB mass spectrum: *m*/*z* 205 (M^+).

$AsPh_4^+L^-$. To a solution of 0.074 g (0.336 mmol) of 2-cyanaminofluoren-9-one in 10 cm^3 of 2 M sodium hydroxide was added 0.15 g (0.35 mmol) of tetraphenylarsonium chloride. Dichloromethane (25 cm^3) was added to extract the product, and this organic layer was separated, dried over magnesium sulfate, filtered, and reduced to the minimum volume. The resulting solution was vigorously stirred and diethyl ether (100 ml) added to precipitate the product. This was filtered off, washed with diethyl ether and dried in air and *in vacuo*, to yield 0.184 g (0.314 mmol, 93%) of the product as a violet powder ($C_{38}H_{27}AsN_2O$ requires C, 75.74; H, 4.51; N, 4.64. Found: C, 74.57; H, 4.45; N, 4.55%). IR (CH_2Cl_2): 2104s (ν(N=C=N)) and 1711s cm^{-1} (ν(C=O)). ^1H NMR ($CDCl_3$): δ 6.91–6.97 [m, 3 H, arene CH], 7.02 [d, 1 H, ^3J(HH) = 7.4, arene CH], 7.15 [d, 1 H, ^3J(HH) = 7.4, arene CH], 7.26 [t, 1 H, ^3J(HH) = 5.5, arene CH], 7.35 [d, 1 H, ^3J(HH) = 7.26 Hz, arene CH] and 7.57–7.81 [m, 20 H, Ph_4As^+]. −ES mass spectrum: *m*/*z* 219 (L^-).

[$SnMe_3L$]. Trimethyltin chloride (0.07 g, 0.35 mmol) and 0.16 g (0.37 mmol) of Tl^+L^- were stirred for 12 h in 10 cm^3 of dichloromethane. The resulting solution was filtered through Celite and refrigerated to give the desired product as orange crystals (0.06 g, 0.16 mmol, 41%) ($C_{17}H_{16}N_2OSn$ requires C, 53.31; H, 4.21; N, 7.31. Found: C, 53.06; H, 4.22; N, 6.98%). IR (CH_2Cl_2): 2150 (sh), 2108s (ν(N=C=N)) and 1718s cm^{-1} (ν(C=O)). ^1H NMR ($CDCl_3$): δ 0.63 [s, 9 H, ^2J(HSn) = 58.85, Me_3Sn], 7.00 [d, 1 H, ^3J(HH) = 7.9, arene CH], 7.19 [t, 1 H, ^3J(HH) = 7.2, arene CH], 7.33–7.42 [m, 3 H, arene CH] and 7.59 [d, 1 H, ^3J(HH) = 7.33 Hz, arene CH]. +FAB mass spectrum: *m*/*z* 384 (M^+).

[AuL(PPh_3)]. (Triphenylphosphine)gold chloride (0.18 g, 0.37 mmol) and 0.16 g (0.37 mmol) Tl^+L^- were stirred for 12 h in 10 cm^3 of dichloromethane. The resulting solution was filtered through Celite and evaporated to about 1 cm^3 in volume. Addition of an excess of hexane gave the required product as a red-orange solid (0.16 g, 0.24 mmol, 63%) ($C_{32}H_{22}AuN_2OP$ requires C, 56.65; H, 3.26; N, 4.13. Found: C, 56.54; H, 3.39; N, 3.93%). IR (CH_2Cl_2): 2159s, 2123 (sh) (ν(N=C=N)) and 1712s cm^{-1} (ν(C=O)). ^1H NMR ($CDCl_3$): δ 7.15 [t, 1 H, ^3J(HH) = 7.32 Hz, arene CH], 7.38 [m, 3 H, arene CH] and 7.53–7.59 [m, 17 H, arene CH]. ^{31}P NMR ($CDCl_3$): δ 31.65. +ES mass spectrum: *m*/*z* 721.1 (M + H^+ + MeCN).

Crystallography

Deep purple crystals of $AsPh_4^+L^-\cdot 2H_2O$ were obtained by slow evaporation of a saturated ethanol–water solution, and orange crystals of [AuL(PPh_3)] by slow evaporation of a saturated acetone solution. Suitable crystals were mounted using perfluoroether oil, and cooled to 180 K with an Oxford Cryostream apparatus. Geometric and intensity data were collected on a Rigaku AFC7R diffractometer, using the ω–2θ scan technique. Semiempirical absorption corrections based upon ψ scans were applied (TEXSAN).[20] The structure was solved by Patterson methods (SHELXS 97),[21] and subsequent Fourier-difference syntheses, and refined by full-matrix least squares on F^2 (SHELXL 97).[22] Details of crystal data, data collection and structure solution and refinement are summarised in Table 4. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all aromatic hydrogen atoms placed in idealised positions and allowed to ride on the relevant carbon atoms. The water hydrogen atoms of $AsPh_4^+L^-\cdot 2H_2O$ were located in the difference map and refined freely. A final electron density difference map showed no regions of significant electron density.

Table 4 Summary of crystal structure data for $AsPh_4^+L^-\cdot 2H_2O$ and [AuL(PPh_3)]

	$AsPh_4^+L^-\cdot 2H_2O$	[AuL(PPh_3)]
Empirical formula	$C_{38}H_{31}AsN_2O_3$	$C_{32}H_{22}AuN_2OP$
M	638.57	678.45
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	12.9059(3)	10.527(3)
b/Å	13.584(3)	11.852(3)
c/Å	9.2290(18)	12.330(3)
α/°	96.84(3)	99.59(2)
β/°	97.86(3)	107.35(2)
γ/°	107.43(3)	114.10(3)
U/Å^3	1507.0(5)	1264.8(6)
Z	2	2
μ(Mo-Kα)/mm^{-1}	1.170	5.908
T/K	180	180
No. reflections collected	9368	6086
No. independent reflections	6912	5800
Obs. reflections [$I > 2\sigma(I)$]	5464	4900
R_{int}	0.0353	0.0290
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0414, 0.0848	0.0420, 0.0981
all data	0.0633, 0.0930	0.0566, 0.1044

CCDC reference number 186/1456.

See http://www.rsc.org/suppdata/dt/1999/2059/ for crystallographic files in .cif format.

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