Synthesis, C-N cleavage and photoluminescence of gold(III) isocyanide complexes

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Dedicated to Professor D. M. P. Mingos on the occasion of his 70th birthday. Happy Birthday Mike!

ABSTRACT: The synthesis and crystal structure of the gold(III) isocyanide complexes [(C^N^C)AuCN^{t}Bu]+X- (**1a**, X = $(C_6F_5)_3BOAc^F$; **1b**, X = PF6) are reported [(C^N^C) = 2,6-bis(4-$Bu^tC_6H_3)_2$pyridine; OAc^F = trifluoroacetate]. Compound **1a** slowly decomposes under C-N bond cleavage of the ^{t}BuNC ligand, to give (C^N^C)AuCNB$(C_6F_5)_3$ and ^{t}BuOAc^F, whereas [(C^N^C)AuCN^{t}Bu]PF_6 decomposes mainly to [(C^N^C)AuCN. On UV irradiation the complexes show photoluminescence, with (C^N^C)AuCN showing the most intense emission.

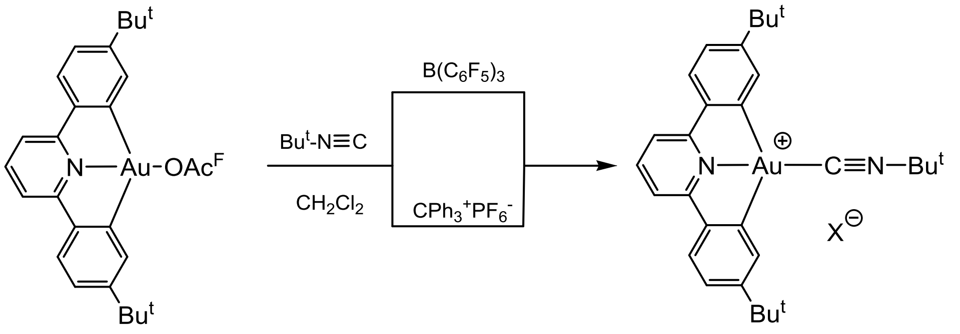
Keywords:
Gold,
Pincer complexes
Isocyanide
Cyanide
Photoemission

Introduction

Pincer ligands with C^N^C donors based on the 2,6-diphenylylpyridine dianion have proved to be a particularly robust platform for the exploration of gold(III) chemistry, not least due to the resistance of such (C^N^C)Au(III) complexes towards reduction to gold(I). Such complexes have led to numerous high-profile applications, notably as light-emitting materials [1 – 6], as well as anti-tumour agents [7 - 9]. These pincer ligands have also allowed the isolation of new key classes of Au(III) complexes, such as hydride and alkene complexes [(C^N^C) = 2,6-bis(4-$Bu^tC_6H_3)_2$pyridine] [10, 11]. As part of our interest in the bonding and reactivity of Au(III) complexes with donor ligands [12 - 14] we became interested in isocyanide compounds, and report here the synthesis, structures and reactivity of C^N^C gold *t*-butylisocyanide compounds [15].

Results and Discussion

The addition of ^{t}BuNC to a mixture of (C^N^C)AuOAc^F, and B(C_6F_5)$_3$ in dichloromethane afforded the expected adduct, [(C^N^C)AuCN^{t}Bu][(C_6F_5)$_3$BOAc^F] (**1a**), which was isolated as a yellow-green powder (Scheme 1). Similarly, the reaction of (C^N^C)AuOAc^F, ^{t}BuNC and [CPh$_3$]PF$_6$ gave [(C^N^C)AuCN^{t}Bu]PF$_6$ (**1b**) which, on recrystallization from dichloromethane/light petroleum, was isolated as yellow crystals suitable for X-ray diffraction (Figure 1). The IR stretching frequency of the ligated Bu^{t}NC was observed at 2271 cm^{-1}; the spectroscopic data for the cations in **1a** and **1b** are essentially identical.



1a, X = Ac^{F}OB(C_6F_5)$_3$
1b, X = PF$_6$

Scheme 1 Synthesis of (C^N^C)Au isocyanide complexes

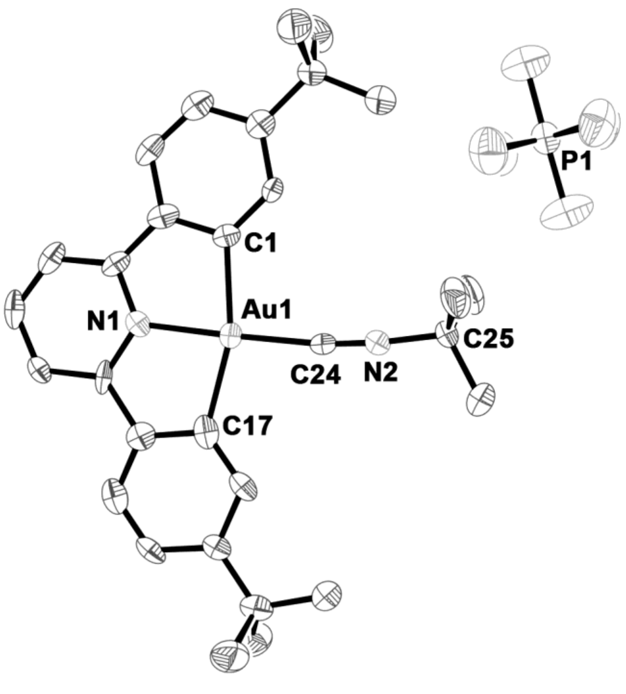


Figure 1. Structure of [(C^N^C)AuCN^{t}Bu]PF$_6$·CH$_2$Cl$_2$ (**1b**·CH$_2$Cl$_2$). Selected bond distances (Å) and angles (°): Au-C(24) 1.964(12), C(24)-N(2) 1.141(13), N(1)-Au 1.994(9); Au-C(24)-N(2) 173.4(10).

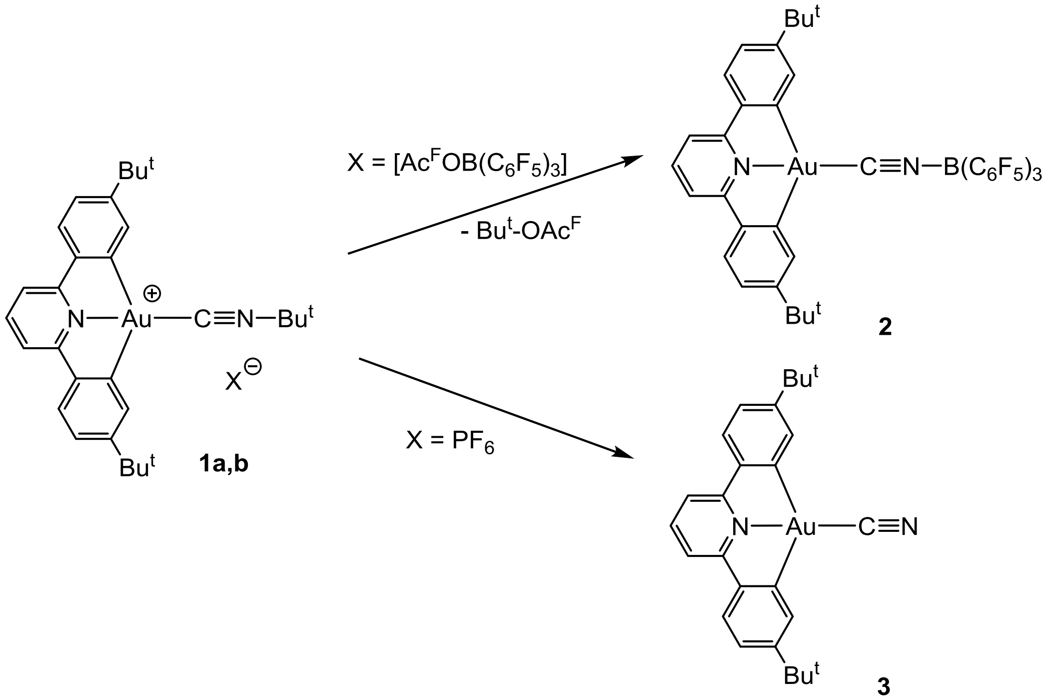
Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and solvent molecules are omitted.

Table 1 compares the spectroscopic and geometric parameters of $\mathbf{1}^+$ with those of a number of representative gold ^{t}BuNC complex types. Both the gold(I) and gold(III) isocyanide complexes show C-N stretching modes well above the value of 2135 cm^{-1} for free ^{t}BuNC. The vibrational frequencies are not very sensitive to the nature of the ligand in *trans* position; there is however a marked difference between Au(I) and Au(III)-CNR compounds, with the latter occurring at higher frequency, by some 30 - 40 cm^{-1}.

Table 1. Comparison of ν(CN) frequencies and geometric parameters of gold CNBu^t complexes.

Complex	IR [cm^{-1}]	r(C≡N)	R(Au-C)	Ref.
[(C^N^C)AuCN^{t}Bu]$^+$ $\mathbf{1}^+$	2271	1.141(13)	1.964(12)	This work
^{t}BuNCAuBr$_3$	2282	1.127(12)	1.991(10)	15c
^{t}BuNCAuBr	2235	1.13(1)	1.939(8)	16
[Au(CN^{t}Bu)$_2$]AuI$_2$·(I$_2$)	2234	1.145(11)	1.980(1)	15c
[(SIDipp)Au(CN^{t}Bu)][SbF$_6$]	2244	1.144(5)	1.986(4)	17

Complex **1a** is stable at room temperature; however, over a period of 72 h in dichloromethane solution the slow conversion to a follow-on product was observed, which was identified as the isocyanoborate (C^N^C)Au-CN-B(C_6F_5)$_3$ (**2**). This compound is evidently formed by an unusual C-N bond cleavage reaction involving ^{t}Bu-transfer, with ^{t}BuOAc^{F} as the by-product. The identity of **2** was confirmed by X-ray diffraction (Figure 2). To confirm the identity of the product, complex **2** was also independently prepared from (C^N^C)AuCN and B(C_6F_5)$_3$ (Scheme 2). The structure shows that the Au-C(cyanide) as well as the C≡N distances in **2** are essentially identical to the corresponding bond lengths in the ^{t}BuNC precursor **1**.



Scheme 2. Decomposition reactions of Au(III) isocyanide complexes.

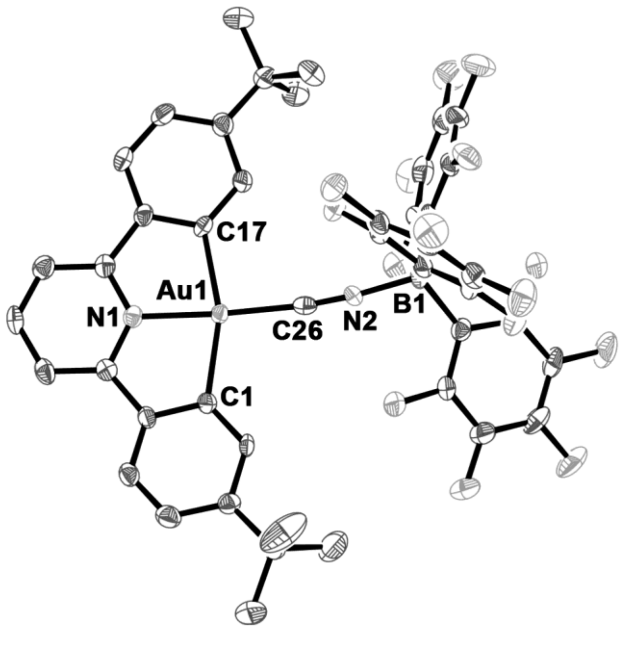


Figure 2. Structure of (C^N^C)Au-CN-B$(C_6F_5)_3$·0.5CH_2Cl_2 (**2**·0.5CH_2Cl_2). Selected bond distances (Å) and angles (°): Au-C(26) 1.964(7), C(26)-N(2) 1.138(8), N(2)-B 1.593(9), N(1)-Au 1.988(5); Au-C(26)-N(2) 172.9(6). Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and solvent molecules are omitted.

The PF_6^- salt **1b**, too showed limited stability in solution, and during the accumulation of the ^{13}C NMR spectrum slow decomposition could be observed. Recrystallization gave a product mixture from which the cyanide (C^N^C)AuCN (**3**) was identified as the major component; the P-containing by-products were not identified.

It appears therefore that these Au(III) *ᵗ*BuNC complexes undergo facile cleavage of the C-N bond in the presence of electrophiles. The decomposition or conversion of *ᵗ*BuNC complexes by reactions with electrophiles is of course not unknown; for example, it can lead to hydrolysis to afford the corresponding CO complex [18], while it is also the classical route to the synthesis of amino-carbyne complexes [19]. The formation of metal cyanides from *ᵗ*BuNC complexes has been observed in a number of thermolysis reactions, with hydrocarbons as the by-products [20]. The redox reactions of M(III)Cp_3 derivatives (M = Ti, Zr) with *ᵗ*BuNC also gave M(IV) cyanides as products, by an unknown mechanism [21]. The recent study by Jones on Ni(II)-CN*ᵗ*Bu pincer complexes [22] is probably most relevant to the present system, and while the C-N cleavage process does not appear to have been observed for Au(I) or Au(III) CN*ᵗ*Bu complexes, it seems most likely that the process follows a pathway similar to that outlined for the nickel compounds [22], i.e. with the intermediate formation of a CMe_3^+ cation which readily abstracts an anion. In our system Bu^tOAc^F was identified as a by-product.

Photophysical Properties. On irradiation with UV light (λ = 354 nm) the complexes **1**, **2** and **3** exhibit photoemission in the yellow-green region of the spectrum. A summary of the photophysical properties of the complexes can be found in Table 2, while illustrative examples are depicted in Figures 3 and 4.

Table 2. Photophysical properties of complexes **1b**, **2** and **3**.

Complex	Absorption / nm	$\lambda_{em}(\lambda_{ex})$ / nm	
	CH_2Cl_2	solid	CH_2Cl_2
[(C^N^C)AuCN*ᵗ*Bu][PF_6] **1b**	258, 313*sh*, 414, 436.	486, 516_{max}, 545, 579*sh* (300-400).	465_{max} (366); 470_{max}, 504 (414, 436).
(C^N^C)Au-CN-B$(C_6F_5)_3$ **2**	257, 313*sh*, 407, 426.	469, 502_{max}, 535, 570*sh* (300-400).	457_{max} (360); 465_{max}, 485 (407, 426).
(C^N^C)Au-CN **3**	254, 311*sh*, 398, 418.	460, 491_{max}, 527, 555, 595*sh* (300-400).	454, 490, 518 (398, 418).

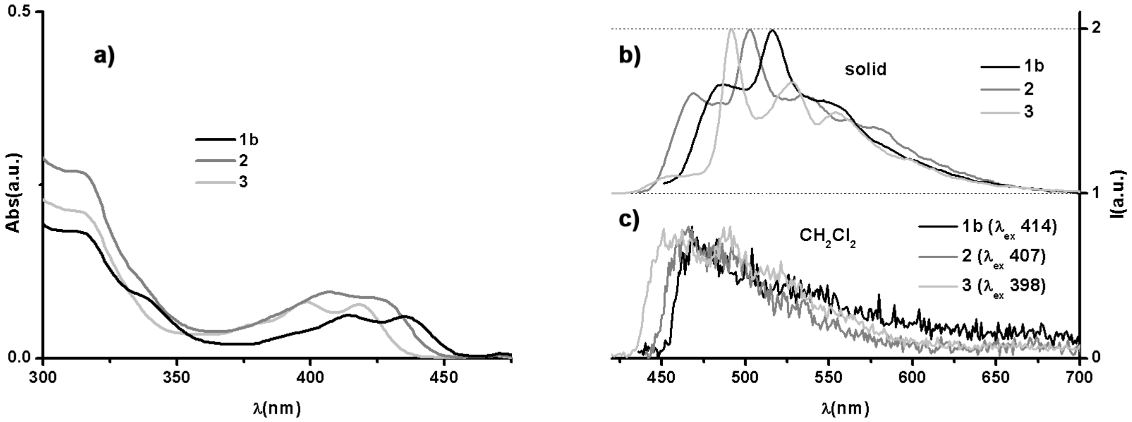


Figure 3. (**a**) Low energy region of the UV-Vis electronic spectra for complexes **1b**, **2** and **3** in CH_2Cl_2 solution. (**b**) Emission spectra of complexes **1b**, **2** and **3** in the solid state at 298 K. (**c**) Emission spectra of complexes **1b**, **2** and **3** in CH_2Cl_2 solution under excitation at the lower energy absorption band.

The low-energy absorption bands (398–436 nm) observed in the UV-Vis spectra of all complexes in CH_2Cl_2 solution have been typically assigned [1, 2] as a metal-perturbed intra-ligand (IL) π–π* transitions of the C^N^C ligand. In the solid state all complexes display yellow-green emission, which is particularly intense for the cyanide complex **3**. This finding is in line with strong emission observed by Che et al. on Au(III) acetylide and cyanide complexes with dissymmetric C^N^C ligands [23]. As was pointed out in previous studies on related systems [1 – 8], the emission most probably involves population of a ligand-based triplet state, as indicated also by the vibrational fine structure of the emission band. Both the lowest energy absorption in DCM solution and the emission in the solid state follow the energy sequence (**3** > **2** > **1b**). This trend is attributed, on the basis to previous studies [23], to the decrease of the donor strength (CN > CN-B(C_6F_5)$_3$ > CN^{t}Bu) of the ancillary ligand with concomitant relative stabilization of the lowest unoccupied molecular orbital. The emission bands in CH_2Cl_2 solution reproduce well those observed in the solid state, when the solution of each complex is excited at the corresponding low-energy absorptions for each complex. However, complexes **1b** and **2**, when excited with high energy light (λ_{ex}366 and 360 nm, respectively, see Figure 4) also exhibit a remarkably intense higher energy asymmetric emission.

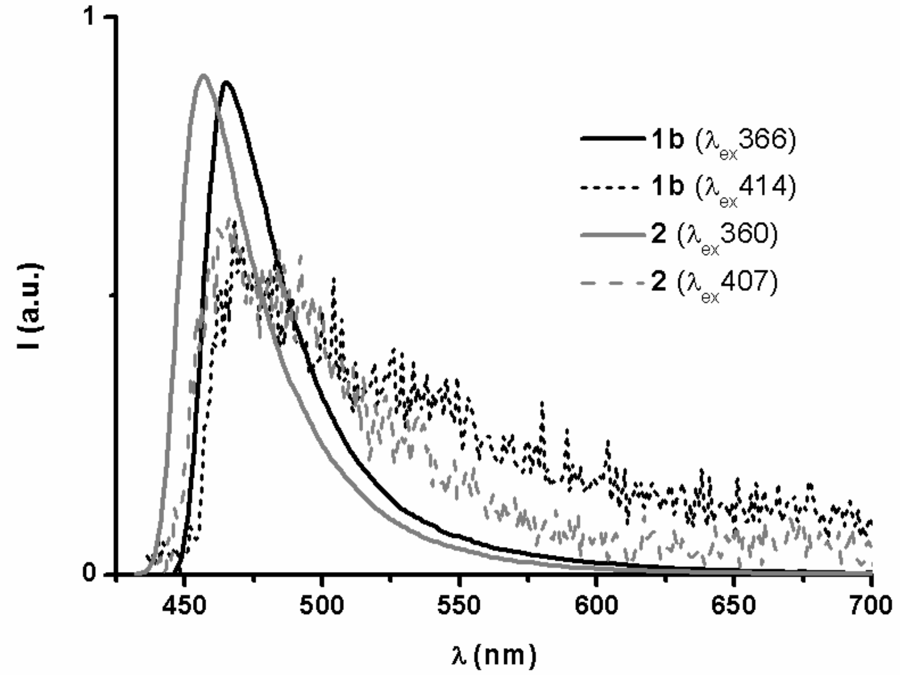


Figure 4. Emission spectra of complexes **1b** and **2** in CH_2Cl_2 solution when excited by UV light of different energies

In summary, the tBuNC pincer complexes [(C^N^C)AuCN^{t}Bu]X (X = Ac^{F}OB(C_6F_5)$_3$, PF_6) show distinctly higher ν(CN) frequencies than those of a variety of Au(I) ^{t}BuNC complexes. They decompose slowly under electrophilic attack with C-N bond cleavage, to give –CNB(C_6F_5)$_3$ or –CN products. On excitation with UV light these compounds show photoemissions at decreasing energies in the sequence **3** > **2** > **1b**.

Experimental

General considerations. Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under dry nitrogen or a Saffron Scientific and MBraun glove box. Nitrogen was purified by passing through columns of supported P_2O_5, with moisture indicator, and activated 4 Å molecular sieves. Anhydrous solvents were freshly distilled from appropriate drying agents. (C^N^C)Au(OAc^F) [12], and B(C_6F_5)$_3$ [24] were prepared using literature methods. ^{1}H, ^{13}C{^{1}H} and ^{19}F spectra were recorded using a Bruker Avance DPX-300 spectrometer. CD_2Cl_2 and C_6D_6 were dried over CaH_2, degassed by three freeze-pump-thaw cycles and stored on 4 Å molecular sieves prior to use. ^{1}H NMR spectra (300.13 MHz) were referenced to the residual protons of the deuterated solvent used. ^{13}C{^{1}H} NMR spectra (75.47 MHz) were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. IR spectra were recorded using a Perkin Elmer Spectrum 65 FT-IR spectrometer with a diamond ATR attachment or using liquid cells with KBr plates. UV−visible absorption spectra were recorded using a Perkin-Elmer Lambda 35 UV/vis spectrometer. Excitation and emission spectra were measured in a (TCSPC) FluoroLog Horiba Jobin Yvon spectrofluorometer. The assignment of the signals for the C^N^C ligand framework is as shown in Figure 5.

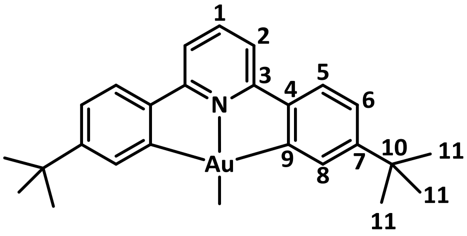


Figure 5. Numbering scheme of the C^N^C ligand.

Synthesis of $[(C\text{^}N\text{^}C)AuCN^{t}Bu][B(C_6F_5)_3OAc^F]$ 1a

(C^N^C)AuOAc^F (100 mg, 0.16 mmol) and $B(C_6F_5)_3$ (80.5 mg, 0.16 mmol) were charged into a Schlenk flask and cooled to –78°C. To this was added CH_2Cl_2 (30 mL) pre-cooled to –78 °C. The mixture was warmed to –30 °C and ^{t}BuCN (55 µL, 0.48 mmol) was injected. The mixture was kept at –30 °C for 5 min and then allowed to warm to room temperature. The volatiles were removed *in vacuo* and the yellow residue was washed with light petroleum (2 x 5 mL) to yield **1a** as a bright yellow-green powder (170 mg, 85%).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.03 (t, $J = 8$ Hz, 1H, H^1), 7.68 (d, $J = 2$ Hz, 2H, H^8), 7.62 (d, $J = 8$ Hz, 2H, H^5), 7.52 (d, $J = 8$ Hz, 2H, H^2), 7.45 (dd, $J = 8$, 2 Hz, 2H, H^6), 1.89 (s, 9H, $(CH_3)_3$CNC), 1.37 (s, 18H, H^{11}). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 166.15 (C^9), 165.91 (C^3), 157.32 (C^7), 145.61 (C^4), 145.16 (C^1), 132.84 (C^8), 126.51 (C^5), 126.03 (C^6), 118.00 (C^2), 35.49 (C^{10} + $(CH_3)_3C$NC), 30.73 (C^{11}), 29.55 $(CH_3)_3$CNC). ^{19}F NMR (282 MHz, C_6D_6) δ -76.96 (s, 3F, OAc^F), -135.08 (d, 6F, $J = 22.5$ Hz, *o*-C_6F_5), -161.47 (t, 3F, $J = 20.3$ Hz, *p*-C_6F_5), -166.38 to -166.56 (m, 6F, *m*-C_6F_5). IR (ATR) 2271 cm^{-1}. Anal. calcd. (found) for $C_{50}H_{36}AuBF_{18}N_2O_2$: C, 48.18 (48.08); H, 2.91 (2.85); N, 2.25 (2.30).

Synthesis $[(C\text{^}N\text{^}C)AuCN^{t}Bu][PF_6]$ 1b

(C^N^C)AuOAc^F (80 mg, 0.126 mmol) and $[Ph_3C][PF_6]$ (49 mg , 0.126 mmol) were charged into a Schlenk flask and cooled to –78°C. To this was added CH_2Cl_2 (30 mL) pre-cooled to –78 °C. The mixture was warmed to –30 °C and Bu^{t}NC (55 µL, 0.48 mmol) was injected. The mixture was kept at –30 °C for 5 min and then allowed to warm to room temperature. The solvent was removed *in vacuo* and the yellow residue was washed with light petroleum (3 x 5 mL) to yield **1b** as a bright yellow-green powder (77 mg , 80%). Single crystals of **1b** were obtained by layering a CH_2Cl_2 solution with light petroleum (1:1 *v*/*v*) and storing at room temperature.

The ^1H, $^{13}C\{^1H\}$ NMR spectra and IR spectra of **1b** and **1a** were essentially identical. ^{19}F NMR (282 MHz, C_6D_6) δ -76.24 (s). ^{31}P NMR (121 MHz, CD_2Cl_2) δ -144.44 (dt, *J* = 1421.3, 710.7 Hz) Anal calcd. (found) for $C_{31}H_{39}AuPF_6N_2$: C, 47.64 (47.50); H, 5.03 (4.87); N, 3.58 (3.68).

Synthesis of (C^N^C)AuCNB(C_6F_5)$_3$ 2

Method 1:

In a J-Young NMR tube, a sample of **1a** (40 mg, 0.032 mmol) was dissolved in CD_2Cl_2 (0.6 mL) and the mixture was warmed to 40 °C . After 48 h, full consumption of **1a** was established, together with the formation of (C^N^C)AuCNB(C_6F_5)$_3$ **2** and ^{t}BuOAc^F, as judged by the comparison with authentic samples.

The reaction was scaled up in a Schlenk flask. **1a** (150 mg, 0.12 mmol) was dissolved in CH_2Cl_2 (30 mL) and was warmed to 40 °C for 72 h. The solvent and ^{t}BuOAc^F were removed *in vacuo* to yield **2** as a yellow powder (105 mg, 81%). Single crystals were obtained by layering a CH_2Cl_2 solution of **2** with light petroleum (1:1 v/v) at room temperature.

Method 2:

A J-Young NMR tube was charged with (C^N^C)AuCN (**3**) (20 mg, 0.035 mmol) and B(C_6F_5)$_3$ (18 mg, 0.035 mmol) to which CD_2Cl_2 (0.6 mL) was added. The mixture was shaken and injected into an NMR spectrometer probe head indicating full instantaneous conversion of **3** into **2**.

^1H NMR (300 MHz, CD_2Cl_2) δ 7.90 (t, *J* = 8 Hz, 1H, H^1), 7.77 (d, *J* = 2 Hz, 2H, H^8), 7.49 (d, *J* = 8 Hz, 2H, H^5), 7.41 (d, *J* = 8.1 Hz, 2H, H^2), 7.34 (dd, *J* = 8, 2 Hz, 2H, H^6), 1.24 (s, 18H). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, RT) δ 166.18 (C^9), 165.82 (C^3), 157.43 (C^7), 145.47 (C^4), 144.11 (C^1), 134.17 (C^8), 125.82 (C^5), 124.90 (C^6), 117.14 (C^2), 35.19 (C^{10}), 30.39 (C^{11}).

^{19}F NMR (282 MHz, CD_2Cl_2, RT) δ -133.62 (dd, *J* = 23.3, 8.5 Hz, 6F, *o*-C_6F_5), -158.20 (t, *J* = 20.3 Hz, 3F, *p*-C_6F_5), -163.99 to -164.63 (m, 6F, *m*-C_6F_5). ^{11}B NMR (96 MHz, CD_2Cl_2) δ -12.09 (s). IR (ATR) 2251 cm^{-1}. Anal. calcd. (found) for $C_{45}H_{30}AuBF_{15}N_2$: C, 49.52 (49.35); H, 2.77 (2.89); N, 2.57 (2.59).

Synthesis of (C^N^C)AuCN (3)

Under an ambient atmosphere, (C^N^C)AuOAc^F (50 mg, 0.079 mmol) and KCN (7.8 mg, 0.119 mmol) were mixed in a flask and a mixture THF/H_2O (20/10 mL) was added. The mixture was stirred at room temperature for 3 hours and then more water (10 mL) added, what causes the precipitation of a yellow solid. This solid was filtered, washed with water and dried. Extraction with CH_2Cl_2 (20 mL), drying with $MgSO_4$, filtration and evaporation of the solvent following by drying afforded the analytical pure sample of (C^N^C)AuCN as a yellow powder (36.6 mg, 82%).

^{1}H NMR (300 MHz, CD_2Cl_2, RT) δ 8.01 (d, J = 2.0 Hz, 1H), 7.88 (t, J = 8.0 Hz, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.33 (dd, J = 8.2, 2.0 Hz, 1H), 1.37 (s, 9H). IR (ATR) ν(CN) = 2170 cm^{-1}. Anal. calcd. (found) for $C_{27}H_{30}AuN_2$: C, 55.96 (55.84); H, 5.22 (5.12); N, 4.83 (4.91).

X-Ray Crystallography.

Crystals of each sample were mounted in oil on glass fibres and fixed in the cold nitrogen stream on a diffractometer. Diffraction intensities were recorded at 140(2)K on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo-Kα radiation and graphite monochromator. Data were processed using the CrystAlisPro-CCD and –RED software [25].

The structures of all samples were determined by the direct methods routines in the SHELXS program and refined by full-matrix least-squares methods on F^2 in SHELXL [26]. Non-hydrogen atoms were generally refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions. No missed symmetry was reported by PLATON [27].

Refinement results are included in Table S1. Computer programs used in this analysis were run through WinGX [28]. Scattering factors for neutral atoms were taken from reference [29].

[(C^N^C)AuCN*t*Bu][PF$_6$]·CH$_2$Cl$_2$ (1b·CH$_2$Cl$_2$). Yellow block (0.2×0.1×0.1) grown by slow diffusion of petrol in a saturated solution of the crude in CH_2Cl_2. The asymmetric unit is formed by one half molecule of **1b**, being both the gold cation and the PF_6 situated on a symmetry plane, and one molecule of CH_2Cl_2. The A-alert generated by the check-cif is produced by the position of one hydrogen atom of the ^{t}Bu groups in the symmetry plane, causing an occupancy conflict.

(C^N^C)AuCNB(C$_6$F$_5$)$_3$·0.5CH$_2$Cl$_2$ (2·0.5CH$_2$Cl$_2$). Yellow block (0.1×0.05×0.05) obtained by slow diffusion of light petroleum ether in a solution of **2** in CH_2Cl_2. The asymmetric unit is formed by two molecules of **2** and one molecule of CH_2Cl_2. The complex crystallizes as a merohedric twin. This explains the A-alert generated due to the high positive residual density (2.25 and 2.57 eÅ^{-3}) on both gold centers.

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Appendix A. Supplementary material

CCDC 1043355 and 1043356 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table of Contents Entry

The gold(III) isocyanide pincer complex [C^N^C)Au-CN^{t}Bu][Ac^{F}OB(C_6F_5)$_3$] decomposes to cyanide products via C-N bond cleavage, to give complexes with enhanced photoemission.