

Direct cycloauration of 2-anilinopyridine (Hanp) with tetrachloroaurate(III) and the X-ray crystal structure of $[\text{AuCl}_2(\text{anp})]$

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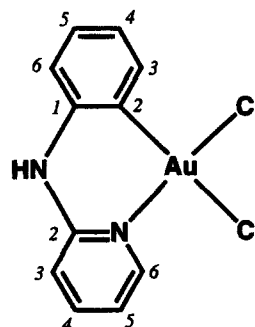
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Abstract—2-Anilinopyridine (Hanp) reacted with sodium tetrachloroaurate(III) in refluxing water directly to give cyclometallated $[\text{AuCl}_2(\text{anp})]$, which was characterized spectroscopically and its structure determined by X-ray analysis. The metallation reaction involved direct activation of an ortho C—H bond of the phenyl moiety and the deprotonated anionic ligand, anp, coordinated to Au through the pyridine-N and phenyl ortho-C atoms forming a six-membered chelate ring. Similarly cycloaurated complexes, $[\text{AuBr}_2(\text{anp})]$ and $[\text{AuCl}_2(\text{C—N})]$ (CN = tlp, map, and tpm), were also prepared and characterized (Htlp = 2-(*p*-toluidino)pyridine, Hmap = 2-(*N*-methylanilino)pyridine, and Htpm = 2-(*p*-toluidino)pyrimidine). © 1997 Elsevier Science Ltd

Keywords: cyclometallation; cycloauration; gold(III) complexes; 2-anilinopyridines; organogold(III) compounds.

Examples are abundant for cyclometallation reactions forming a five-membered chelate ring but comparatively few for the reaction forming a six-membered one [1,2]. Cyclopalladation has, from another point of view, been studied very widely, while only little has been investigated on cycloauration [3]. Cycloauration is, sometimes, difficult to be achieved with direct activation of a C—H bond and transmetallation reaction of organomercury compounds with appropriate gold compounds is hence frequently used [4]. In a previous paper [5] we have reported cyclopalladation of 2-anilinopyridine (abbreviated as Hanp) and some derivatives, and now extended our investigation to cycloauration. The direct cycloauration of Hanp and some derivatives forms a six-membered auraheterocycle with an Au—C bond (Scheme 1): the reaction is a rare example of direct cycloauration forming a six-membered chelate ring [6].



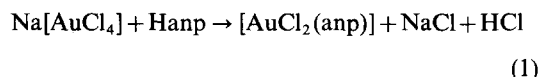
Scheme 1.

RESULTS AND DISCUSSION

Reaction of an aqueous solution of sodium tetrachloroaurate with an equimolar amount of Hanp at room temperature formed initially a dark brown sus-

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pension, which, upon reflux for a few hours, faded into light brownish yellow. The pH of the suspension fell eventually to *ca* 1.2 (checked with a pH test paper). The composition of the precipitate was confirmed to be $[\text{AuCl}_2(\text{anp})]$ by elemental analysis (eq. 1). Under similar



conditions $[\text{AuBr}_2(\text{anp})]$ (from Hanp and $\text{AuBr}_3 \cdot 2\text{H}_2\text{O}$) and $[\text{AuCl}_2(\text{C}-\text{N})]$ ($\text{C}-\text{N} = \text{tlp}$, map, and tpm; from Htlp, Hmap, and Htpm, respectively, with $\text{Na}[\text{AuCl}_4]$) were obtained {Htlp = 2-(*p*-toluidino)pyridine, Hmap = 2-(*N*-methylanilino)pyridine, Htpm = 2-(*p*-toluidino)pyrimidine}. Numbering of atoms is indicated in Scheme 1. $[\text{AuCl}_2(\text{anp})]$ easily reacted with Ptol_3 (tri-*p*-tolylphosphine) to give $[\text{AuCl}(\text{anp})(\text{Ptol}_3)]\text{Cl}$.

Hmap is very different in reactivity towards $[\text{AuCl}_4]^-$ and $[\text{PdCl}_4]^{2-}$, although Hanp was similarly cyclometallated with the two chlorometalates; Hmap was cycloaurated with $[\text{AuCl}_4]^-$ but not cyclopalladated [5] with $[\text{PdCl}_4]^{2-}$ under the respective conditions where Hanp was cyclometallated with the two ions. The replacement of the hydrogen on the anilino-N atom with a methyl group changes decisively the reactivity towards cyclometallation. Steric and/or electronic effects may be expected but the origin is not definite so far. Both *p*-tolyl 2-pyridyl ether and *p*-tolyl 2-pyridyl sulfide are not directly cyclometallated with the two chlorometalates [5] similarly. In the two pyridine derivatives the NH group of Hanp is replaced with an ether-O and a sulfide-S atom and the formation of a similar six-membered metallacycle would be expected upon cyclometallation.

The ^1H NMR spectrum of $[\text{AuCl}_2(\text{anp})]$ in $\text{dms}-d_6$ (dimethylsulfoxide- d_6) indicates that one proton is removed from the phenyl ring of the ligand and the ^1H signals of the aromatic rings of free Hanp (with an intensity of 9 H) change to eight discrete signals: four doublets and four triplets each with an intensity of 1 H. The signal of the N-H group of free Hanp remains as a broad singlet at 10.8 ppm. The two doublets at 8.85 and 7.60 ppm are, respectively, assigned to H(6) (py) and H(3) (ph) (py implies a pyridine ring, pm a pyrimidine ring, and ph a phenyl ring) because the two signals shift significantly to lower fields in the spectrum of $[\text{AuBr}_2(\text{anp})]$ while the others shift slightly; H(6) (py) and H(3) (ph) are situated near the halogens [7] and the replacement should strongly affect the chemical shifts of the two.

A unique singlet (with an intensity 1 H) at 7.40 ppm of $[\text{AuCl}_2(\text{tlp})]$ and that at 7.39 of $[\text{AuCl}_2(\text{tpm})]$ suggests the presence of an isolated (non coupled) proton on an aromatic ring and are assigned to an *ortho*-H [ph H(3)] to a metallated site. The two complexes show methyl and N-H signals as expected, indicating the two groups leaved intact. Upon warming a $\text{dms}-d_6$ solution of $[\text{AuCl}_2(\text{tpm})]$, two doublets

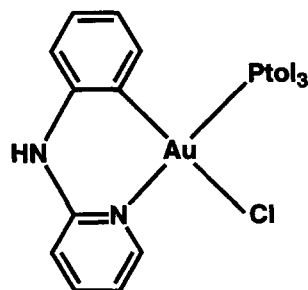
of doublets at 9.10 and 8.84 ppm became broad and at 390 K eventually coalesced to a broad singlet at 8.96 ppm accompanied by a change of a doublet of doublets at 7.21 ppm (at room temperature) to a triplet at 7.14 ppm. The remaining signals assigned to the phneyl ring are not broadened upon warming. Exchange between free and coordinated N atoms of the pyrimidine ring takes place and hence the protons adjacent to the N atoms result in equivalence at high temperature.

In the ^{13}C NMR (non-decoupled and completely ^1H decoupled) spectrum of $[\text{AuCl}_2(\text{anp})]$ the unique, weak signal at 122.1 ppm (due to a *tert*-carbon atom) is assigned to the aurated carbon atom [C(2)] and shifts to 124.6 ppm in that of $[\text{AuBr}_2(\text{anp})]$. The ^{13}C chemical shifts of the other carbon atoms are rather similar between the two complexes and 11 signals are observed as expected from the fact that all the carbon atoms are inequivalent. In the spectra of $[\text{AuCl}_2(\text{tlp})]$ and $[\text{AuCl}(\text{tpm})]$ the unique signals, respectively, at 122.1 and 121.7 ppm are likewise assigned to the aurated C-2.

The IR spectra show that the N-H group is left intact and the coordination of halogens is supported by the presence of $\nu(\text{Au}-\text{X})$: 357 and 284 cm^{-1} for $[\text{AuCl}_2(\text{anp})]$ and 200 and 182 cm^{-1} for $[\text{AuBr}_2(\text{anp})]$. These facts are consistent with Scheme 1. The IR spectra also bear out the presence of an *ortho* disubstituted benzene ring; the bands at 748 and 696 cm^{-1} of free Hanp were replaced with that at 752 cm^{-1} of $[\text{AuCl}_2(\text{anp})]$, a characteristic band of four adjacent hydrogens on a benzene ring [8]. This is also the case for $[\text{AuCl}_2(\text{map})]$ (699 and 767 cm^{-1} for Hmap and 758 cm^{-1} for $[\text{AuCl}_2(\text{map})]$).

In the ^1H NMR spectrum of $[\text{AuCl}(\text{anp})(\text{Ptol}_3)]\text{Cl}$ the remarkable shielding of H(3) (ph) signal (at 6.62 ppm) should be caused by the aromatic ring current [7] of Ptol_3 coordinated at the *cis* position to the aurated carbon atom [ph C(2)]. The signal of H(6) (py) did not shift so remarkably. Observation of no detectable $^{13}\text{C}-^{31}\text{P}$ coupling for the aurated carbon atom [ph C(2)] and low energy $\nu(\text{Au}-\text{Cl})$ (311 cm^{-1}) in the IR spectrum [9] are consistent with a *cis* (C, P) and *trans*-(C, Cl) geometry (Scheme 2).

The crystallographic data of $[\text{AuCl}_2(\text{anp})]$ (Table



II
Scheme 2.

1) showed spontaneous resolution of the complex recrystallized from acetonitrile, the space group being $P2_12_1$. The square planar structure is depicted in Fig. 1 together with atom labelling, and the selected bond lengths and angles are given in Table 2. Significant difference is found in bond lengths between Au–Cl(1), 2.277(7) and Au–Cl(2), 2.339(7) Å, reflecting the trans influence of the *trans*-bonding N and C atoms, respectively. The six-membered chelate ring is not planar and the two atoms, Au [0.82(3) Å] and N(2) [0.36(3) Å], are out of the plane defined by N(1), C(5), C(7), and C(6) atoms, the ring adopting a boat conformation. The two aromatic rings incline relative to the coordination plane defined by Au, Cl(1), Cl(2), N(1), and C(6) atoms, and the pyridine ring makes an angle of 40.7(7)° with the plane and the phenyl ring an angle of 38.0(7)°, relieving unfavorable approach of H{C(1)} and Cl(2) (the distance is calculated to be 2.74 Å) and of H{C(11)} and Cl(1) (2.65 Å), respectively. The overall structure is similar to that reported recently [6] for cycloaurated $[\text{AuCl}_2\{2-(2-\text{C}_6\text{H}_4(\text{C}(\text{CH}_3)_2)\text{C}_5\text{NH}_4\})]$.

Table 1. Crystallographic data and experimental details for $[\text{AuCl}_2(\text{anp})]$

Compound	$[\text{AuCl}_2(\text{anp})]$
Formula	$\text{C}_{11}\text{H}_9\text{N}_2\text{AuCl}_2$
Fw	437.08
Crystal system	orthorhombic
Space group	$P2_12_1$ (No. 19)
<i>a</i> (Å)	8.057(1)
<i>b</i> (Å)	18.498(3)
<i>c</i> (Å)	7.766(1)
<i>Z</i>	4
<i>V</i> (Å ³)	1157.4(3)
$\mu(\text{Mo-K}\alpha)$ (cm ⁻¹)	131.26
Transm factor	0.754–1.000
Crystal color	orange
Crystal habit	prismatic
Crystal size (mm ³)	0.15 × 0.25 × 0.35
<i>d</i> _{calc} (g/cm ³)	2.51
<i>F</i> (000)	808
Diffractionmeter	Rigaku AFC7R
$\lambda(\text{Mo-K}\alpha)$, Å	0.71069
<i>T</i> (K)	298
Scan range (°)	1.732 + 0.30tan θ
Scan mode	ω -2 θ
Scan speed (°/min)	8
2 θ _{max} (°)	60
Reflections measd	0 ≤ <i>h</i> ≤ 11 0 ≤ <i>k</i> ≤ 26 0 ≤ <i>l</i> ≤ 11
No. of reflections measd	1944
No. of reflections obsd [<i>I</i> (<i>F</i>) > 3 σ (<i>I</i> (<i>F</i>))]	1810
No. of parameters refined	145
<i>R</i>	0.080
<i>R</i> _w	0.096

$$R = \sum \|F_o\| - |F_c| / \sum \|F_o\|$$

$$R_w = [\sum w \|F_o\| - |F_c|^2 / \sum w |F_o|^2]^{1/2}$$

$$w = [\sigma^2(F_o) + \{0.015(F_o)\}^2]^{-1}$$

EXPERIMENTAL

Measurements

¹H and ¹³C NMR spectra were recorded on a Bruker AMX 400 Spectrometer with tetramethylsilane as an internal standard. IR spectra were measured on Perkin–Elmer System 2000 FTIR Spectrometer and the nujol mull method was employed.

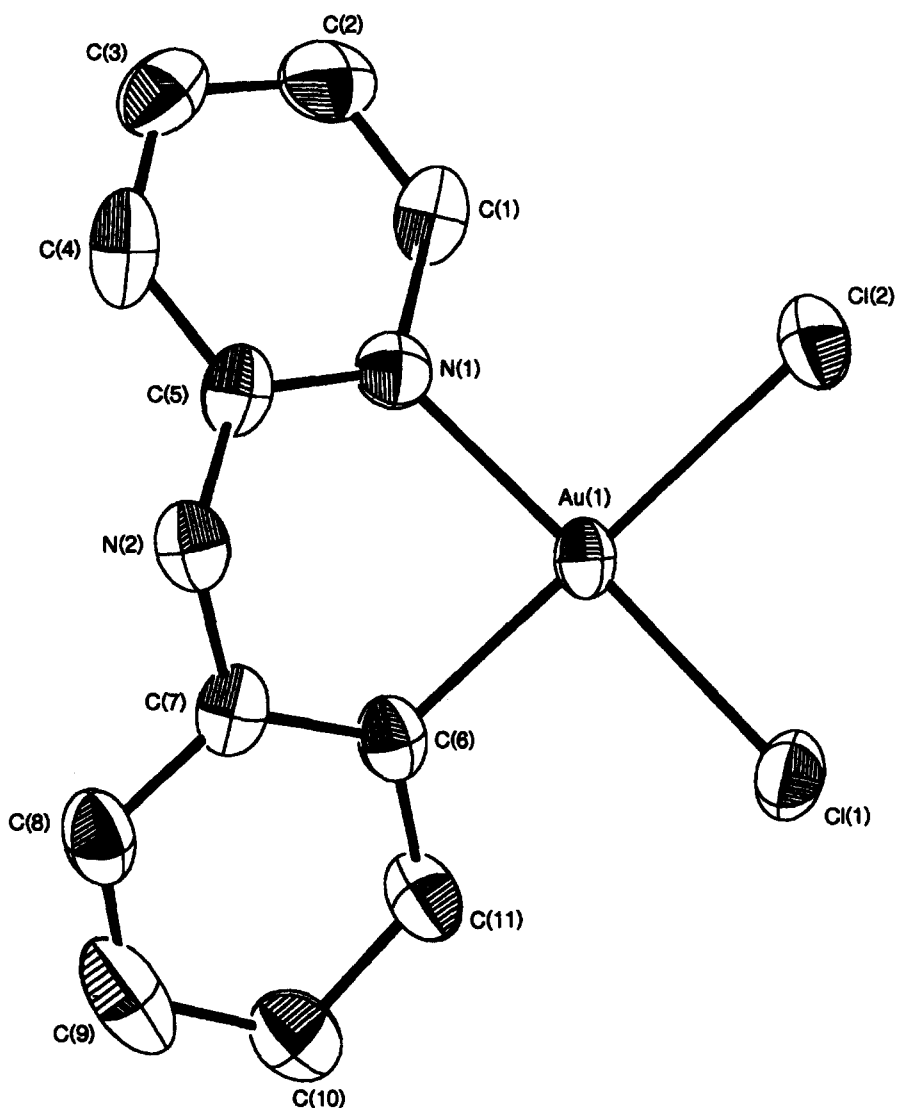
Preparation of the ligands

Hanp was commercially available (Aldrich), and Htlp and Hmap were prepared by the method in the literature [10]. For the preparation of Hmap, the reaction temperature was maintained at 180°C, not at reflux as reported in the literature [11]. The IR and ¹H NMR spectral data of the ligands were reported in a previous paper [5]. The ¹³C{¹H} NMR spectra (CDCl₃) were as follows: Hanp, 120.5 [ph C(2)], 122.8 [ph C(4)], 129.3 [ph C(3)], 140.6 [ph C(1)], 108.2 [py C(3)], 114.9 [py C(5)], 137.7 [py C(4)], 148.4 [py C(6)], 156.2 [py C(2)] ppm; Htlp, 20.8 (CH₃), 121.3 [ph C(2)], 129.8 [ph C(3)], 132.7 [ph C(4)], 137.9 [ph C(1)], 107.7 [py C(3)], 114.5 [py C(5)], 137.6 [py C(4)], 148.4 [py C(6)], 156.8 [py C(2)] ppm; Hmap, 34.8 (CH₃), 125.4 [ph C(4)], 126.3 [ph C(2)], 129.7 [ph C(3)], 146.8 [ph C(1)], 109.1 [py C(3)], 113.1 [py C(5)], 136.5 [py C(4)], 147.7 [py C(6)], 158.8 [py C(2)] ppm.

Htpm was prepared by the method reported [10] for Htlp and recrystallized from ethanol. Yield 29%. M.p. 129–130°C. Calcd. for C₁₁H₁₁N₃: C, 71.3; H, 6.0; N, 22.7%. Found, C, 71.2; H, 5.8; N, 22.7%. IR: $\nu(\text{N—H})$, 3257, 3172 cm⁻¹. ¹H NMR (CDCl₃): 2.31 (CH₃), 7.14d [ph H(3)], 7.47d [ph H(2)], 6.64t [pm H(4)], 8.38d [pm H(3)], 8.34 (NH). ¹³C NMR: 20.8 (CH₃), 120.3 [ph C(2)], 129.4 [ph C(3)], 132.5 [ph C(4)], 136.8 [ph C(1)], 112.0 [pm C(4)], 158.0 [pm C(3)], 160.5 [pm C(1)] ppm.

Preparation of the complexes

$[\text{AuCl}_2(\text{anp})]$: To an aqueous solution (30 cm³) of 398 mg (1 mmol) of Na[AuCl₄] · 2H₂O was added 170 mg (1 mmol) of Hanp and the mixture was stirred for 1 h at room temperature and for 3 h at refluxing temperature. After it was cooled to room temperature, the precipitate was filtered, washed with water, and dried in air. The product was dissolved in 250 cm³ of hot acetone and the filtered solution was concentrated to ca 25 cm³ to give a light brownish yellow precipitate, which was filtered, washed with a little acetone, and dried in air. Yield, 361 mg (82%). M.p. 248–249°C. Calcd for C₁₁H₉N₂Cl₂Au: C, 30.2; H, 2.1; N, 6.4%. Found, C, 30.4; H, 2.2; N, 6.4%. IR: $\nu(\text{N—H})$, 3295; $\pi(\text{C—H})$, 752; $\nu(\text{Au—Cl})$, 357, 284 cm⁻¹. ¹H NMR (dms-*d*₆): 7.06t, 7.30t [ph H(4,5)], 7.19d [ph H(6)], 7.60d [ph H(3)], 7.14t [py H(5)], 7.45d [py H(3)], 8.01t

Fig. 1. ORTEP drawing of $[\text{AuCl}_2(\text{anp})]$ and atom labelling scheme.Table 2. Selected bond distances (Å) and angles (°) for $[\text{AuCl}_2(\text{anp})]$

Au(1)—Cl(1)	2.277(7)	Au(1)—Cl(2)	2.399(7)
Au(1)—N(1)	2.05(2)	Au(1)—C(6)	2.01(2)
N(1)—C(5)	1.36(3)	N(2)—C(5)	1.34(3)
N(2)—C(7)	1.43(3)	C(6)—C(7)	1.38(3)
Cl(1)—Au(1)—Cl(2)	90.1(2)	Cl(1)—Au(1)—N(1)	176.1(6)
Cl(1)—Au(1)—C(6)	90.5(7)	Cl(2)—Au(1)—N(1)	92.0(6)
Cl(2)—Au(1)—C(6)	179.2(7)	N(1)—Au(1)—C(6)	87.3(9)
Au(1)—N(1)—C(5)	121(2)	N(1)—C(5)—N(2)	121(2)
C(5)—N(2)—C(7)	123(2)	N(2)—C(7)—C(6)	121(2)
C(7)—C(6)—Au(1)	119(2)		

[py H(4)], 8.85d [py H(6)], 10.76 (N—H) ppm. ^{13}C NMR ($\text{dms}\text{-}d_6$): 117.1 [ph C(6)], 122.1 [ph C(2)], 123.2, 128.8 [ph C(4,5)], 131.9 [ph C(1)], 133.6 [ph

C(3)], 114.8 [py C(3)], 115.7 [py C(5)], 141.7 [py C(4)], 148.4 [py C(6)], 148.5 [py C(2)] ppm.

The complexes $[\text{AuBr}_2(\text{anp})]$ and $[\text{AuCl}_2(\text{C—N})]$

(C—N = tlp, map, and tpm) were similarly prepared from appropriate starting materials. [AuBr₂(anp)], yield 20%. M.p. 215–217°C. Calcd for C₁₁H₉N₂Br₂Au: C, 25.1; H, 1.8; N, 5.3%. Found, C, 24.8; H, 1.8; N, 5.3%. IR, $\nu(\text{N—H})$, 3320; $\pi(\text{C—H})$, 752; $\nu(\text{Au—Br})$, 200, 182 cm⁻¹. ¹H NMR (dms_o-d₆): 7.01t, 7.28t [ph H(4,5)], 7.19d [ph H(6)], 7.75d [ph H(3)], 7.13t [py H(5)], 7.45d [py H(3)], 8.01t [py H(4)], 8.94d [py H(6)], 10.64 (N—H) ppm. ¹³C NMR: 117.3 [ph C(6)], 124.4 [ph C(2)], 123.3, 128.7 [ph C(4,5)], 132.6 [ph C(1)], 135.7 [ph C(3)], 114.6 [py C(3)], 115.9 [py C(5)], 141.8 [py C(4)], 149.1 [py C(2)], 149.7 [py C(6)] ppm.

[AuCl₂(tlp)], yield 49%. M.p. 235°C (decomposition). Calcd for C₁₂H₁₁N₂Cl₂Au: C, 32.0; H, 2.5; N, 6.2%. Found, C, 32.1; H, 2.5; N, 6.3%. IR, $\nu(\text{N—H})$, 3291; $\nu(\text{Au—Cl})$, 354, 280 cm⁻¹. ¹H NMR (dms_o-d₆): 2.32s (CH₃), 7.06d, 7.11m* [ph H(5,6)], [py H(5)], 7.40s [ph H(3)], 7.42d [py H(3)], 7.97t [py H(4)], 8.80d [py H(6)], 10.67 (N—H) ppm. ¹³C NMR: 20.4 (CH₃), 116.7, 129.5 [ph C(5,6)], 133.5 [ph C(3)], 122.1 [ph C(2)], 129.6 [ph C(4)], 132.3 [ph C(1)], 114.7 [py C(3)], 115.4 [py C(5)], 141.5 [py C(4)], 148.3 [py C(6)], 148.6 [py C(2)] ppm.

[AuCl₂(map)], yield 35%. M.p. 210–212°C. Calcd for C₁₂H₁₁N₂Cl₂Au: C, 32.0; H, 2.5; N, 6.2%. Found, C, 32.0; H, 2.5; N, 6.0%. IR: $\pi(\text{C—H})$, 758; $\nu(\text{Au—Cl})$, 357, 295 cm⁻¹. ¹H NMR (dms_o-d₆): 3.62s (CH₃), 7.11t, 7.3–7.4m, 7.27t [ph H(4,5,6)], [py H(5)], 7.51d [ph H(3)], 7.63d [py H(3)], 8.18t [py H(4)], 8.90d [py H(6)]. ¹³C NMR: 37.5 (CH₃), 117.9, 124.4 [ph C(4,5)], 127.2 [ph C(2)], 128.7 [ph C(6)], 137.1 [ph C(1)], 114.9 [py C(3)], 117.5 [py C(5)], 143.0 [py C(4)], 149.7 [py C(6)], 151.3 [py C(2)] ppm.

[AuCl₂(tpm)], yield 84%. M.p. 247°C (decomposition). Calcd for C₁₁H₁₀N₃Cl₂Au: C, 29.2; H, 2.2; N, 9.3%. Found, C, 29.2; H, 2.0; N, 9.3%. IR: $\nu(\text{N—H})$, 3317; $\nu(\text{Au—Cl})$, 357, 290 cm⁻¹. ¹H NMR (dms_o-d₆): 2.32 (CH₃), 7.11d, 7.16d [ph H(5,6)], 7.39s [ph H(3)], 7.21dd [pm H(4)], 8.84d, 9.10d [pm H(3,5)], 11.47 (N—H). ¹³C NMR: 20.5 (CH₃), 117.2, 129.6 [ph C(5,6)], 121.7 [ph C(2)], 130.3 [ph C(4)], 133.5 [ph C(3)], 133.6 [ph C(1)], 122.7 [pm C(4)], 150.7 [pm C(1)], 157.3, 163.1 [pm C(3,5)] ppm.

[AuCl₃(Hanp)]: the above procedure was applied without heating the reaction mixture to give a light brown powder, which was filtered, washed with water, and dried in air. Yield 401 mg (85%). M.p. 241–242°C. Calcd. for C₁₁H₁₀N₂Cl₃Au: C, 27.9; H, 2.1; N, 5.9%. Found, C, 28.6; H, 1.8; N, 6.1%. IR: $\nu(\text{N—H})$, 3332, 3298; $\nu(\text{Au—Cl})$, 354, 303, 294, 286 cm⁻¹. The ¹H NMR spectrum of a dms_o-d₆ solution of [AuCl₃(Hanp)] was identical to that of [AuCl₂(anp)].

[AuCl(anp)(Ptol₃)Cl]: To a suspension of 219 mg (0.5 mmol) of [AuCl₂(anp)] in 30 cm³ of dichloromethane was added 152 mg (0.5 mmol) of Ptol₃ and the mixture was stirred for 30 min. The filtered

solution was mixed with the same volume of n-hexane and concentrated to a small volume to precipitate a yellow powder. Yield 166 mg (47%). M.p. 167–169°C. Calcd for C₃₂H₃₀N₂Cl₂PAu: C, 51.8; H, 4.1; N, 3.8%. Found C, 51.8; H, 4.1; N, 3.9%. IR, $\nu(\text{N—H})$, 3152, 3121; $\nu(\text{Au—Cl})$, 311 cm⁻¹. ¹H NMR (CDCl₃): 6.21t, 6.97t [ph H(4,5)], 6.62d [ph H(3)], 7.91d [ph H(6)], 6.87t [py H(5)], 7.62dd [py H(4)], 8.32d [py H(3)], 8.66d [py H(6)], 12.03 [N—H], 2.43s, 7.28dd, 7.44dd (Ptol₃). ¹³C NMR: 120.3, 123.7, 128.6 [ph C(4,5,6)], 132.5 [ph C(3)], 130.9 [ph C(2)], 134.7 [ph C(1)], 115.9 [py C(5)], 116.8 [py C(3)], 140.4 [py C(4)], 146.5 [py C(6)], 151.3 [py C(2)], 21.7, 120.4, 130.1, 134.7, 144.4 (Ptol₃) ppm.

X-ray analysis

Crystallographic data and experimental details are given in Table 1. Upon recrystallization of [AuCl₂(anp)] from acetonitrile, single crystals were obtained. A crystal of [AuCl₂(anp)] with appropriate dimensions was cut out from a large sample and mounted on a glass fiber with epoxy resin. The unit cell parameters and the crystal orientation matrix were obtained by least-squares fit of 25 reflections with $22 < 2\theta < 25^\circ$. Three intensity control reflections measured every 150 reflections showed no significant variation in intensity. A Ψ -scan absorption correction was made. The structure was solved by direct methods (SHELXS-86) [12], and successive difference Fourier syntheses were used to locate all non-hydrogen atoms. The structure was refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms except for that attached to N(2) were placed at calculated positions with isotropic temperature factors equal to 1.2 B_{eq} for the attached atoms. Calculations were carried out using the Xtal 3.2 software [13].

Supplementary material—Complete tables of bond distances and angles, atomic coordinates, listing of anisotropic thermal parameters, and observed and calculated structure factors for [AuCl₂(anp)] are available from the authors on request.

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* The intensity of this signal is 2 H.

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