

Synthesis and structure of stable chiral Au^I complexes with *N,N'*-diaryl-*n*-naphthamidinium-*N'*-[2,3,4,5-tetra(methoxycarbonyl)cyclopentadien-1-yl] ylides

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Novel *N*-amidine-functionalized cyclopentadiene gold(I) complexes [C₅(CO₂Me)₄{ArNC(–C₁₀H₇)NAr}]Au(PPh₃) have been prepared, and their stable chiral structure with the Au–N bond [2.091(6) Å] and the additional coordination Au⋯-system of the cyclopentadiene ring has been proved by X-ray crystallography and NMR spectroscopy.

In recent years, syntheses and studies of *N*-functionalized cyclopentadiene (Cp) ligands and their metal complexes have become a rapidly developing direction of cyclopentadiene chemistry.^{1–4} These complexes exhibit bidentate coordination of the Cp unit and the *N*-side-arm to a metal centre resulting in a diversity in their structure and reactivity. Chiral *N*-functionalized Cp ligands create a more rigidly coordinated chiral pocket around a metal by intramolecular coordination that makes these complexes very attractive for using as catalysts in metal-mediated asymmetric syntheses.^{4,5} Among effective *N*-functionalities are substituted aminoethyl and pyridyl side chains.^{1–4} Recently, we have synthesised novel chiral naphthamidinium-cyclopentadien-*N*-ylides sterically fitted for the formation of metal complexes capable of bidentate coordination of the metal centre to both the amidine and the Cp fragments.⁶

Here we report on the synthesis of chiral *N*-[(triphenylphosphine)gold(I)]-*N,N'*-diaryl-*n*-naphthamidinium-*N'*-[2,3,4,5-tetra(methoxycarbonyl)cyclopentadien-1-yl] ylides **2**, based on non-symmetrical *N*-amidine-functionalized Cp ligands, and the investigation into their structure by X-ray analysis and ¹H and ¹³C NMR spectroscopy. Compounds **2** were prepared in 90–92% yields by the treatment of *N*-methoxycarbonyl-*N,N'*-triaryl-amidinium-*N'*-[2,3,4,5-tetra(methoxycarbonyl)cyclopentadien-1-yl] ylides **1** with a methanol solution of KOH, which resulted in elimination of an *N*-methoxycarbonyl group and subsequent addition of (Ph₃P)AuCl in acetonitrile[†] (Scheme 1).

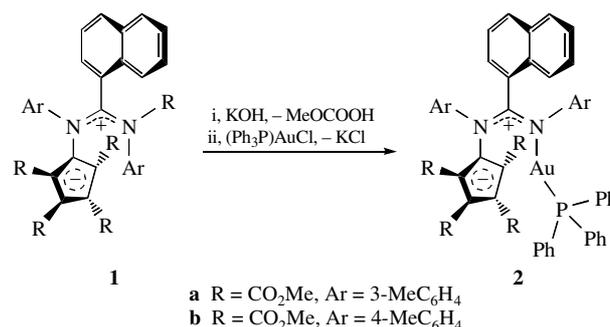
Complexes **2** are colourless crystals resistant to air and moisture and highly-soluble in most of organic solvents.

Figure 1(a) shows the structure of gold(I) complex **2a** in a crystal as proved by the X-ray diffraction study.[‡] The compound has a zwitterionic structure in which the Au atom is bound to the N(21) atom of the *Z*-amidine fragment. Polarization of the ligand manifests itself in the equalization of bond lengths in the five-membered Cp ring and the amidine moiety. The Au atom is linearly coordinated to the P and N(21) atoms, and the Au–P and Au–N(21) bond lengths are 2.221(2) and 2.091(6) Å. The plane of the amidine moiety is turned almost orthogonal to that of the Cp ring, and the Au atom is slightly brought out of the amidine plane thus approaching to the C(1) and C(5) atoms

[†] Compound **2**. Ylide **1**^{9,10} (5 mmol) was added to a solution of KOH (5 mmol) in methanol (80 ml). The mixture was stirred for 1 h at 40 °C. Then the solvent was evaporated *in vacuo*. The residue was dissolved in acetonitrile (50 ml), and a solution of Ph₃PAuCl in acetonitrile (50 ml) was added dropwise at 0 °C there. After 2 h precipitate KCl was separated, and the solvent was evaporated *in vacuo*. The residue was recrystallised from benzene–hexane (1:2). Yield 90–92%. Colourless crystals, mp 158–159 °C (**2a**), 164–165 °C (**2b**).

For **2a**: ¹H NMR (300 MHz, CDCl₃) δ: 1.79 (s, 3H, Me), 1.89 (s, 3H, Me), 3.11 (s, 3H, OMe), 3.47 (s, 3H, OMe), 3.72 (s, 3H, OMe), 3.85 (s, 3H, OMe), 6.47–8.35 (m, 15H, Ar).

For **2b**: ¹H NMR (300 MHz, C₆D₆) δ: 1.63 (s, 3H, Me), 1.70 (s, 3H, Me), 3.25 (s, 3H, OMe), 3.52 (s, 3H, OMe), 3.88 (s, 3H, OMe), 3.92 (s, 3H, OMe), 6.32–8.89 (m, 15H, Ar).



Scheme 1

of the five-membered ring at distances of 2.938 and 3.116 Å respectively [Figure 1(b)]. The short Au⋯C(1) and Au⋯C(5) distances and a high deviation of the P–Au–N angle [P–Au–N(21) is 158.6(2)°] from 180° point to the additional coordination of the π -bonds of the Cp unit by Au^I. The secondary bonding interactions Au⋯-system have been discovered for gold(I) compounds of the general type R–Au–L, where R is an organic radical, and L is a phosphine ligand.^{8,11,12} Note that the earlier described Au^I complexes of cyclopentadienes possess the structure intermediate between the ¹- and ³-types with the gold atom π -bonded to the Cp ring and with two additional coordinative bonds with the adjacent ring carbons ('slip distortion'); the P–Au–C angles [178.6° in C₅Ph₄HAuPPh₃, 169.7° in C₅(CO₂Me)₅AuPPh₃ and 176.7° in C₅Bz₅AuPPh₃] are deflected from the linear two-coordination.^{13–16} In the thioamide complex (C₁₃H₁₁N₂OS)AuPPh₃, the P–Au–S angle is 172.1°, and the Au⋯N distance is 2.574 Å.⁸ For compound **2a**, the deviation of the P–Au–N(21) angle from linearity is maximal. This is due to the geometry of the ligand with a rigid conjugated amidine skeleton. In the sterically hindered *Z*-amidine moiety, tolyl groups are quasi-orthogonal to the amidine plane

[‡] Crystal data. C₅₆H₄₈AuN₂O₈, *M* = 1104.90, rhombohedral, space group *R*3, *a* = 38.118(6), *b* = 38.118(6), *c* = 9.302(2) Å, α = 90.0°, β = 90.0°, γ = 120.0°, *V* = 11704(4) Å³, *Z* = 9, *d*_{calc} = 1.411 g cm^{–3}. The X-ray diffraction experiment was carried on a Bruker SMART diffractometer with a CCD detector [*T* = 293(2) K, graphite-monochromated MoK radiation, λ = 0.71069 Å, $\theta/2\theta$ scan technique, 2° < 2θ < 44°]. The structure was solved by the heavy atom technique. Reflections collected: 16027, independent reflections: 6305 [*R*(int) = 0.0913], refinement method: full-matrix least-squares, data/restraints/parameters: 6300/241/614, goodness-of-fit on *F*²: 1.134, final *R* indices *I* > 2 σ (*I*): *R*₁ 0.0701, *wR*₂ 0.1396; *R* indices (all data): *R*₁ 0.0889, *wR*₂ 0.1597, *f*_{max} = 0.874 e/Å³. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement in the riding motion approximation. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, 1999, issue 1. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/39.

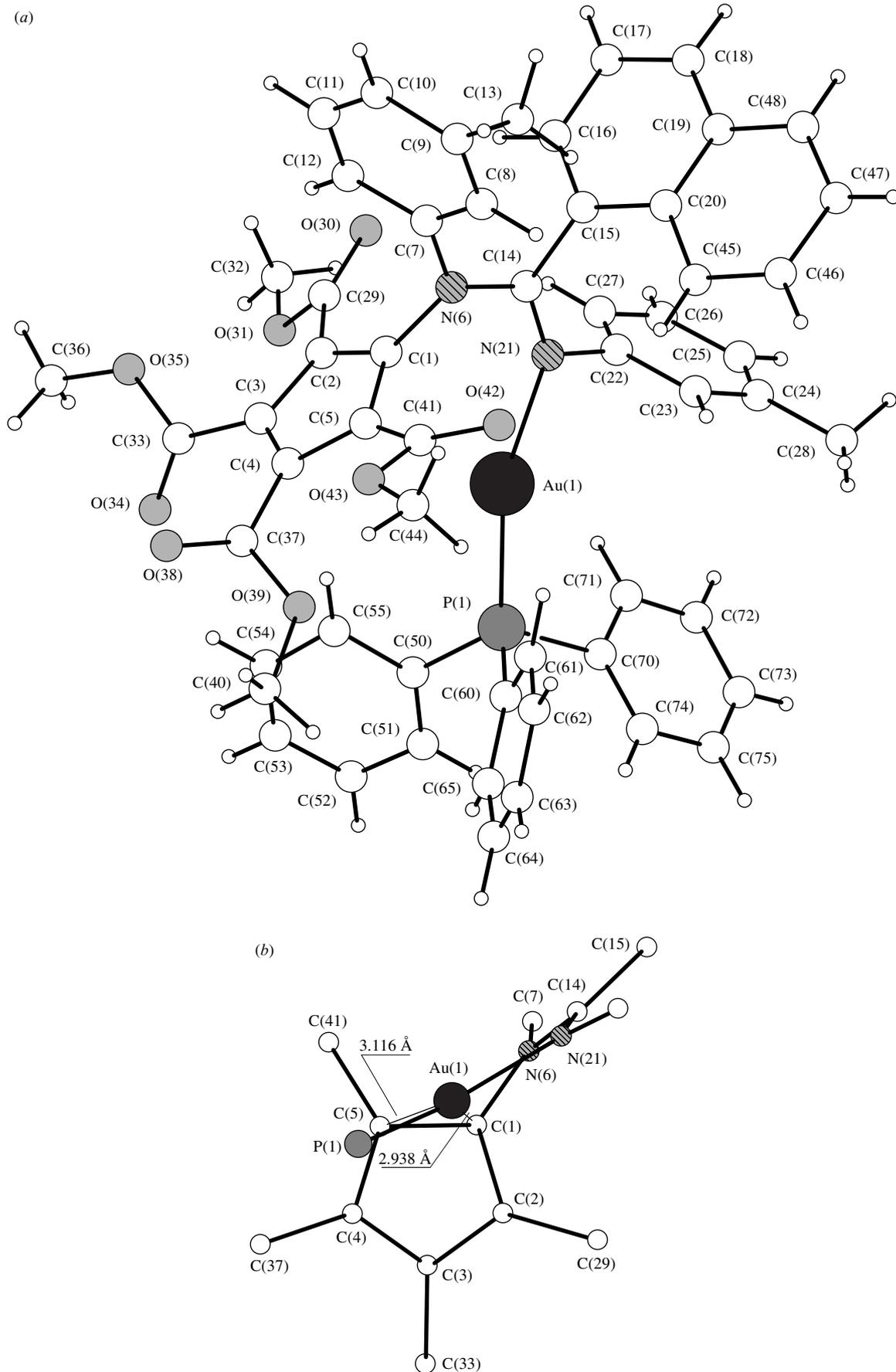


Figure 1 (a) The molecular structure of compound **2a**. Selected bond lengths (Å): C(1)–C(2) 1.399(14), C(2)–C(3) 1.387(12), C(3)–C(4) 1.398(12), C(4)–C(5) 1.381(12), C(1)–C(5) 1.455(11), N(6)–C(14) 1.335(12), N(21)–C(14) 1.322(10), N(6)–C(1) 1.403(11); torsion angles (°): C(14)–N(6)–C(1)–C(2) 81.9(13), N(6)–C(14)–N(21)–Au 16.56(13), C(14)–N(6)–C(7)–C(8) 58.8(9), C(14)–N(21)–C(22)–C(27) 79.1(9). (b) Projection of the molecule **2a**, which shows the coordination of the gold atom to the Cp ring.

Table 1 ^{13}C NMR (75.47 MHz, δ/ppm) data for compounds **1**–**3** at 298 K.^a

Compound	Substituent at N	Solvent	C=O	NCN	C _{Ar} 'quaternary'	CH _{Ar}	C ¹ _{Cp ring}	C ^{2,5} _{Cp ring}	OMe	Me
1a	CO ₂ Me	CD ₂ Cl ₂	164.20, 165.37, 167.49, 167.50, 167.51	152.95	125.32, 127.78, 130.88, 133.46, 138.51, 139.36, 143.56	123.91, 124.93, 126.77, 127.25, 127.64, 128.27, 128.87, 129.30, 133.08, 137.39	120.01	107.11, 110.92, 118.20	50.85, 51.31, 51.61, 51.65, 56.23	20.98, 20.99
1b	CO ₂ Me	CD ₃ CN (342 K)	164.92, 166.19, 167.84, 167.94, 168.00	153.55	125.79, 128.31, 131.50, 133.49, 139.57, 140.27, 142.39	124.84, 125.55, 126.86, 127.61, 127.94, 129.19, 129.44, 129.80, 129.92, 133.92, 135.94	120.30	108.79, 111.08, 119.19	50.90, 51.31, 51.50, 51.54, 56.43	20.69, 20.88
2a	AuPPh ₃	CDCl ₃	165.55, 165.70, 166.93, 168.74	166.15	129.61, 130.56, 132.38, ^b 137.07, 137.34, 143.90, 148.32	123.09, 123.30, 124.28, 124.61, 125.58, 125.97, 126.38, 126.48, 126.69, 127.25, 128.03, 127.78, 128.94, 129.69, 130.83, 131.28, ^c 134.22, 134.41	121.80	107.20, 115.10, 116.10	50.56, 50.79, 51.03, 51.46	20.93, 20.94
2b	AuPPh ₃	C ₆ D ₆	166.03, 166.31, 166.33, 169.25	167.64	129.23, 131.12, 131.67, ^b 132.67, 133.02, 135.31, 142.25, 146.70	124.46, 125.58, 126.18, 126.33, 126.75, 128.26, 128.52, 128.73, 128.88, 129.86, 130.92, ^c 131.29, 134.50, 134.69	123.43	106.79, 114.95, 116.72	50.40, 50.67, 50.77, 51.32	20.48, 20.54
2b	AuPPh ₃	CD ₃ CN	166.09, 166.83, 167.27, 167.58	168.59	130.35, 131.37, 131.70, ^b 133.50, 134.88, 137.37, 143.17, 146.81	125.34, 126.41, 126.80, 127.02, 127.33, 128.16, 129.17, 129.48, 129.97, 130.13, 131.14, 132.66, ^c 135.01, 135.20	121.28	108.67, 113.73	51.18, 51.60, 51.76, 51.83	20.63, 20.72
2b	AuPPh ₃	CDCl ₃	165.50, 165.65, 166.14, 166.70	168.78	130.60, 130.93, 132.43, ^b 133.16, 135.29, 137.68, 141.66, 145.87	124.44, 125.54, 125.63, 125.75, 125.90, 126.70, 128.08, 128.29, 128.76, 128.92, 129.30, 131.27, ^c 134.25, 134.44	121.90	107.19, 113.77, 116.24	50.55, 50.79, 51.04, 51.47	20.65, 20.70
3	Na	C ₆ D ₆ (+1 equiv. 15-crown-5)	166.49, 166.50, 169.84, 170.15	159.48	131.83, 132.81, 133.25, 133.68, 137.90, 143.84, 148.90	123.01, 124.85, 125.66, 126.22, 127.00, 129.53, 129.98	118.42	110.07, 111.61, 117.24	50.44, 51.34	20.39, 20.51

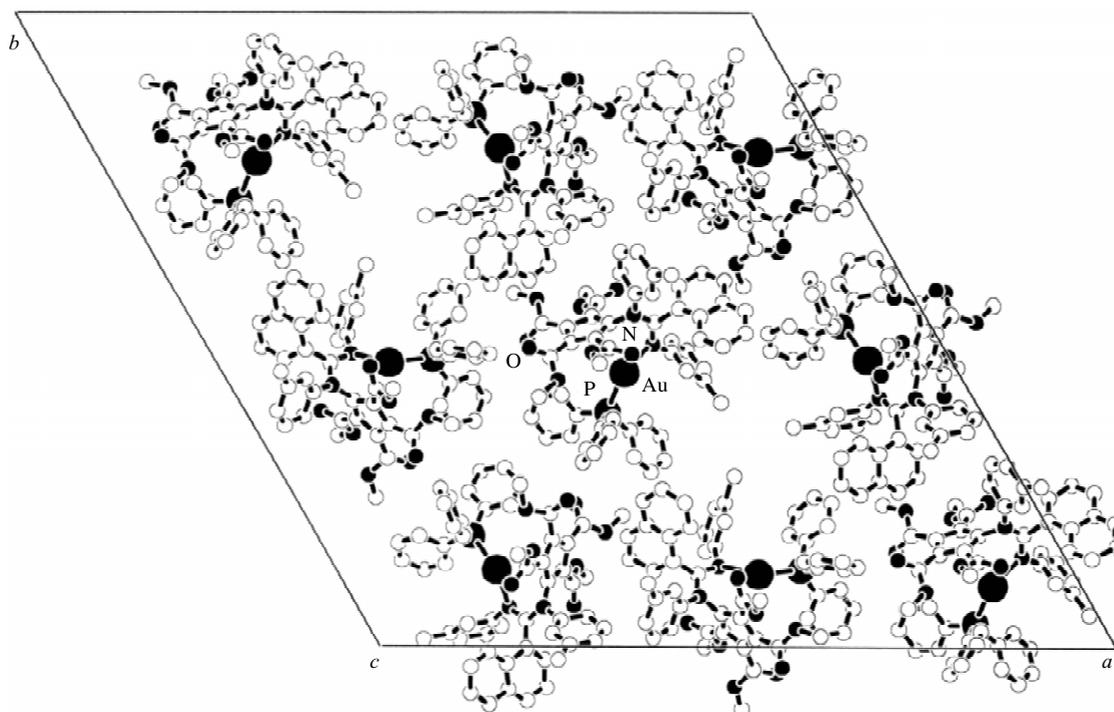
^aThe signals were assigned by the APT method. ^bd, *i*-Ph-P, $J(\text{PC})$ 8 Hz. ^cd, *o*-Ph-P, $J(\text{PC})$ 15 Hz.

[Figure 1(a)]. However, even in this conformation, the bulky 1-naphthyl group cannot be placed in the amidine plane and is turned relative to that [torsion angle N(6)–C(14)–C(15)–C(16) is 76.0(8)°] thus providing for the chirality of ylide complex **2a**.

The non-centrosymmetric space group of crystalline **2a** was determined by X-ray structure analysis.[‡] The unit-cell contents (Figure 2) exhibits the stoichiometry [C₅(CO₂Me)₄(C₆H₄Me-3)-NC(-C₁₀H₇)N(C₆H₄Me-3)]Au(PPh₃); monomeric complex **2a** includes an asymmetric unit in the structure.

In contrast with the earlier described gold(I) Cp derivatives in solutions of which rapid migration of the AuPPh₃ group around the perimeter of the Cp ring has been observed,^{13,14} complexes **2** are stereochemically rigid according to the dynamic NMR spectral data.

In the ^{13}C NMR spectra of complexes **2** (Table 1), the carbon signals of the Cp ring appear in the δ region 123–107 ppm, which is characteristic of negatively charged atoms of the Cp ring, whereas in ¹-derivatives of pentamethoxycarbonylcyclo-

**Figure 2** Unit-cell contents of compound **2a**.

pentadienes, the δ values of sp^2 -hybridized Cp carbons are in the range 140–145 ppm, and those of sp^3 -hybridized Cp carbons, in the range 60–70 ppm.^{13,17} Signals due to the amidine carbon atom NCN of these compounds are observed at δ 166–169 ppm; these values are characteristic of positively charged carbon atoms. The downfield shift of these signals, as compared to those of the NCN atom in ylides **1** (δ 153–154 ppm), is caused by the AuPPh₃ group bound to the N(21) atom. The additional coordination of the gold atom to the π -system of the Cp ring in **2** is manifested by the downfield shift of the Cp ring atom C(1) signal (**2b**, C₆D₆, δ 123.43 ppm), as compared to that in sodium 1-[*N,N'*-di(*p*-tolyl)-*n*-naphthamidiny]-2,3,4,5-tetra(methoxycarbonyl)cyclopentadienide **3**, which forms an anion in the presence of 15-crown-5 (C₆D₆, δ 118.42 ppm) (Table 1). This structure of compounds **2** with the Au–N bond is retained in both non-polar and polar solvents.

The ¹H and ¹³C NMR spectra of compounds **2** demonstrate the absence of the C_s symmetry of the molecules. In the ¹H NMR spectra, four singlets in the 1:1:1:1 ratio are observed for the four methoxycarbonyl groups. In the ¹³C NMR spectra of **2**, the carbons of carbonyl and methoxy groups are magnetically nonequivalent giving rise to four signals in each case. Moreover, the C(2) and C(5) atoms of the Cp ring, adjacent to the amidine substituent, give two different signals (Table 1). By heating a [²H₈]toluene or [²H₄]o-dichlorobenzene solution of **2** to 110 or 150 °C, respectively, no changes in the ¹H and ¹³C NMR spectral patterns were observed. These data are indicative of the rigid chiral structure of compounds **2**.

The rigidity of the chiral structure of naphthamidinium-cyclopentadien-*N*-ylide gold(I) complexes **2** is caused by a high energy barrier for hindered rotation of the bulky 1-naphthyl substituent around the C(14)–C(15) bond in the sterically hindered *Z*-amidine unit whose structure is stabilised by additional coordination of the gold atom with the π -system of the Cp ring.

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