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Note

Synthesis and reactivity of the five-membered cycloaurated complexes of 2-phenylthiazole

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Abstract

2-Phenylthiazole (Hphtz) reacted with $H[AuCl_4]\cdot 4H_2O$ to give the salt $[H(Hphtz)][AuCl_4]$ (**1**), while the reaction of Hphtz with $Na[AuCl_4]\cdot 2H_2O$ or $AuCl_3\cdot 4H_2O$ afforded the adduct $[AuCl_3(Hphtz–N)]$ (**2**). When the adduct **2** was heated in 1,2-dichloroethane in the presence of $AgBF_4$, cycloauration took place to produce $[AuCl_2(phtz–C^1, N)]$ [phtz = 2-(2-thiazolyl)phenyl] (**3**). The reactivity of **3** towards Tl(acac) and PPh_3 was investigated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cyclometallation; Gold complexes; Thiazole complexes

1. Introduction

Cyclometallation by gold(III) i.e. cycloauration is believed to proceed through direct C–H bond activation of the heterosubstituted molecule. The first cycloauration was established in 1989 with 2-phenylpyridine by Constable and Leese [1]. However, in general this reaction is difficult to achieve and has not been widely explored. This is in sharp contrast to the well-established chemistry on the cyclometallation by Pd(II) or Pt(II) [2]. The cyclometallated complexes obtained so far by cycloauration can be classified into two categories. One is the complex having a terdentate N,N,C chelate derived from 2,9-diphenyl-1,10-phenanthroline [3], 4-(4-methoxyphenyl)-6-phenyl-2,2′-bipyridine [4], 6-benzyl-2,2′-bipyridine [5] or 6-*tert*-butyl-2,2′-bipyridine [5], and the other is the complex bearing a bidentate N,C chelate formed by 2-benzylpyridine [6,7], 2-benzoylpyridine [6], 2-anilinopyridine [8,9], 2-phenoxypyridine [8], 2-(phenylsulfanyl)pyridine [8], 2-(2-thienyl)-pyridine [10], 2-(3-thienyl) pyridine [10], 2-(alkylsulfanyl)pyridine [11] or papaverine [12]. However, all the above substrates, which give both types of cycloaurated complexes are definitely limited to the pyridine derivatives. Recently we have finally succeeded in the cycloauration of 1-ethyl-2-phenylimidazole, a ligand other than pyridine derivatives [13]. In this paper, we wish to report the cycloauration of 2-phenylthiazole, which is another example of cycloauration of a ligand other than pyridine derivatives.

2. Experimental

2.1. General procedures

The IR spectra were measured on a JASCO FT/IR-420 spectrophotometer and ^1H NMR spectra were recorded on a JEOL JNM-GX-270 spectrometer using tetramethylsilane as an internal standard. Melting points were determined on a Yanaco MP-500D micro melting-point apparatus and are uncorrected. Conductivity measurements were carried out at 25°C on a Toa Electronics CM-20E conductometer. 2-Phenylthiazole was prepared according to the literature [14]. Starting gold(III) compounds, $H[AuCl_4]\cdot 4H_2O$,

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$Na[AuCl_4]\cdot 2H_2O$ and $AuCl_3\cdot 4H_2O$ were purchased from Tanaka Kikinzoku Kogyo Co. Ltd. Other reagents were obtained commercially and used without purification.

2.2. Syntheses

2.2.1. [H(Hphtz)][AuCl$_4$] (1)

An ethanol solution (20 cm^3) of 2-phenylthiazole (Hphtz) (0.081 g, 0.502 mmol) was added to a solution of $H[AuCl_4]\cdot 4H_2O$ (0.100 g, 0.243 mmol) in the same solvent (20 cm^3). After the resulting yellow solution was stirred at room temperature (r.t.) for 1 day, it was concentrated and diluted with hexane to give yellow microcrystals of complex **1** (0.108 g, 89%), m.p. 176°C. *Anal.* Found: C, 21.71; H, 1.63; N, 2.83. Calc. for $C_9H_8AuCl_4NS$: C, 21.58; H, 1.61; N, 2.80%. IR (KBr, cm^{-1}): 355 (Au–Cl). Λ_M (1.0×10^{-3} mol dm^{-3}, acetone): 163 S cm^2 mol^{-1}.

2.2.2. [AuCl$_3$(Hphtz–N)] (2)

Method (a). An acetonitrile solution (5 cm^3) of 2-phenylthiazole (0.432 g, 2.68 mmol) was added to an aqueous solution (7.5 cm^3) of $Na[AuCl_4]\cdot 4H_2O$ (0.504 g, 1.16 mmol) at r.t. After 10 min, the precipitated solids were filtered off and recrystallized from CH_2Cl_2–diethyl ether to give an orange powder of complex **2** (0.453 g, 84%), m.p. 157°C. *Anal.* Found: C, 23.43; H, 1.45; N, 3.04. Calc. for $C_9H_7AuCl_3NS$: C, 23.27; H, 1.52; N, 3.02%. IR (KBr, cm^{-1}): 368 (Au–Cl). Λ_M (1.0×10^{-3} mol dm^{-3}, acetone): 4.0 S cm^2 mol^{-1}.

Method (b). An acetonitrile solution (6 cm^3) of 2-phenylthiazole (0.219 g, 1.36 mmol) was added to an aqueous solution (17%, 30 cm^3) of $AuCl_3\cdot 4H_2O$ (0.505 g, 1.35 mmol) at r.t. After stirring for 16 h, the precipitates were filtered off and recrystallized from dichloromethane and diethyl ether to give **2** (0.537 g, 86%).

Method (c). An aqueous acetonitrile suspension (17%, 30 cm^3) of the salt **1** (0.050 g, 0.099 mmol) was stirred at r.t. for 16 h. The suspension was filtered off, and the yellow filter cake was washed with water and a small volume of ethanol to give complex **2** (0.022 g, 48%).

2.2.3. [AuCl$_2$(phtz–C^1,N)] (3)

[phtz = 2-(2-thiazolyl)phenyl]

1,2-Dichloroethane solution (10 cm^3) of silver(I) tetrafluoroborate (0.139 g, 0.714 mmol) was added to **2** (0.318 g, 0.684 mmol) in the same solvent (40 cm^3). This mixture was refluxed for 13 h and then evaporated to dryness. The residue was extracted with acetonitrile (100 cm^3) and the extract was concentrated and diluted with diethyl ether to afford complex **3** (0.193 g, 66%) as pale yellowish white microcrystals, m.p. 231°C (dec.). *Anal.* Found: C, 25.40; H, 1.42; N, 3.31. Calc. for $C_9H_6AuCl_2NS$: C, 25.25; H, 1.41; N, 3.27%. IR (KBr, cm^{-1}): 364, 310 (Au–Cl). Λ_M (1.0×10^{-3} mol dm^{-3}, acetone): 0.1 S cm^2 mol^{-1}.

2.2.4. [AuCl(phtz–C^1,N)(acac–C^3)] (4)

A dichloromethane solution (15 cm^3) of Tl(acac) (0.038 g, 0.124 mmol) was added to a suspension of **3** (0.050 g, 0.117 mmol) in the same solvent (15 cm^3). The resulting mixture was stirred for 13 h at r.t. under shielding from the light and then filtered. The filtrate was concentrated and diluted with hexane to give white microcrystalline solids of complex **4** (0.047 g, 82%), m.p. 176°C (dec.). *Anal.* Found: C, 34.15; H, 2.67; N, 2.83. Calc. for $C_{14}H_{13}AuClNO_2S$: C, 34.20; H, 2.66; N, 2.85%. IR (KBr, cm^{-1}): 1684 (C=O), 315 (Au–Cl). Λ_M (1.0×10^{-3} mol dm^{-3}, acetone): 0.6 S cm^2 mol^{-1}.

2.2.5. [AuCl$_2$(phtz–C^1)(PPh$_3$)] (5)

A solution of PPh_3 (0.031 g, 0.118 mmol) in dichloromethane (15 cm^3) was added to a suspension of **3** (0.050 g, 0.117 mmol) in acetone (10 cm^3). The resulting suspension was stirred for 11 h. Then the suspension was filtered off and the filter cake was washed with acetone to give pale yellowish white solids of **5** (0.068 g, 84%), m.p. 131°C. *Anal.* Found: C, 46.97; H, 3.07; N, 2.03. Calc. for $C_{27}H_{21}AuCl_2NPS$: C, 47.14; H, 3.11; N, 2.01%. IR (KBr, cm^{-1}): 319, 300 (Au–Cl). Λ_M (5.0×10^{-4} mol dm^{-3}, acetone): 5.0 S cm^2 mol^{-1}.

2.2.6. [AuCl(phtz–C^1)(PPh$_3$)$_2$]BF$_4$ (6)

Method (a). To a suspension of **3** (0.050 g, 0.117 mmol) in acetone (10 cm^3), an acetone solution (10 cm^3) of PPh_3 (0.063 g, 0.241 mmol) and then $NaBF_4$ (0.064 g, 0.586 mmol) were added. The resulting suspension was heated at 60°C for 1 day, and then evaporated to dryness. The residue was extracted with dichloromethane, and the extract was concentrated and diluted with diethyl ether to give **6** as pale yellow white microcrystals (0.110 g, 94%), m.p. 181°C. *Anal.* Found: C, 53.83; H, 3.61; N, 1.40. Calc. for $C_{45}H_{36}AuBClF_4NP_2S$: C, 53.83; H, 3.61; N, 1.40%. IR (KBr, cm^{-1}): 312 (Au–Cl), 1068 (BF_4^-). Λ_M (1.0×10^{-3} mol dm^{-3}, acetone): 166 S cm^2 mol^{-1}.

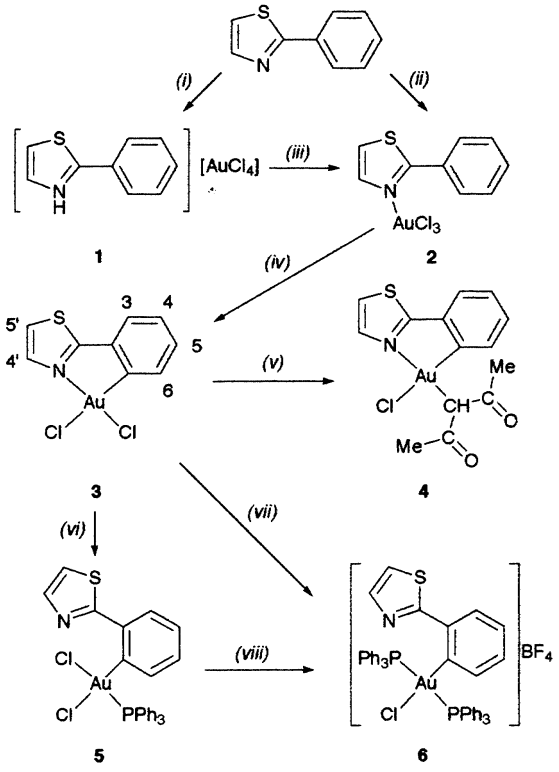
Method (b). An acetone solution (10 cm^3) of PPh_3 (0.016 g, 0.062 mmol) and then solid $NaBF_4$ (0.033 g, 0.294 mmol) were successively added to a suspension of **5** (0.040 g, 0.059 mmol) in acetone (8 cm^3). After the resulting mixture was heated at 60°C for 2 days, the volatile materials were evaporated off. The residue was extracted with dichloromethane, and the extract was concentrated and diluted with diethyl ether to give **6** as pale yellow powder (0.043 g, 72%).

3. Results and discussion

The reaction procedures in this study are summarized in Scheme 1. The ^{1}H NMR spectral data of the new compounds are listed in Table 1.

2-Phenylthiazole (Hphtz) reacted with $H[AuCl_4]\cdot 4H_2O$ in ethanol to give the salt $[H(Hphtz)][AuCl_4]$, whereas the reaction of Hphtz with $Na[AuCl_4]\cdot 2H_2O$ or $AuCl_3\cdot 4H_2O$ in aqueous acetonitrile afforded the adduct $[AuCl_3(Hphtz–N)]$ (**2**). The adduct **2** was also obtained from the salt **1** in aqueous acetonitrile. Such the conversion has already been found in the similar salts of 2-phenoxy- and 2-(phenylsulfanyl)-pyridine [8], and 1-ethyl-2-phenylimidazole [13]. In the far-IR spectrum, the adduct **2** showed only one strong band at 368 cm^{-1}, attributable to the overlapping ν(Au–Cl) frequency *trans* to the thiazole–nitrogen and chloro ligand [15]. The absence of the characteristic band owing to ν(Au–Cl) frequency of the band *trans* to sulfur (which appears around 310 cm^{-1}) [16], excludes the possibility of thiazole–sulfur coordination.

When the adduct **2** was heated in 1,2-dichloroethane in the presence $AgBF_4$, coordinated 2-phenylthiazole in **2** cyclometallated with the central gold(III) to give $[AuCl_2(phtz–C^1, N)]$ [phtz = 2-(2-thiazolyl)phenyl] (**3**) in 66% yield. While the ^{1}H NMR spectrum of adduct **2** exhibited seven protons in the aromatic region, that of **3** showed only six and well-separated aromatic protons (Table 1). This fact indicated that metallation occurred on the 2-phenylthiazole moiety in **3**. It has been known that gold(III) species sometimes attack carbon atoms in the heterocycles of 1-phenylpyrazole [17], 2-(2-thienyl)pyridine [10] and 6-(2-thienyl)-2,2′-bipyridine [18] to produce aurated heterocycles. However, the ^{1}H–^{1}H COSY spectrum of **3** revealed that two thiazole-ring protons $H^{4'}$ and $H^{5'}$ appeared at δ 8.38 (d) and 8.19 (d) as an AB pattern. Moreover, in the far-IR spectrum two strong bands due to the stretching mode of Au–Cl bond *trans* to nitrogen and carbon atoms were observed at 364 and 310 cm^{-1}, respectively. These results and the elemental analysis confirmed the five-membered cycloaurated structure of 2-phenythiazole in **3** as shown in Scheme 1.



Scheme 1. (i) $H[AuCl_4]\cdot 4H_2O$; (ii) $Na[AuCl_4]\cdot 2H_2O$ or $AuCl_3\cdot 4H_2O$; (iii) aqueous CH_3CN (17%); (iv) $AgBF_4$; (v) T1(acac); (vi) PPh_3; (vii) $2PPh_3$, $NaBF_4$; (viii) PPh_3, $NaBF_4$.

The cycloaurated complex **3** reacted with thallium(I) acetylacetonate to give $[AuCl(phtz–C^1, N)(acac–C^3)]$ (**4**). In the ^{1}H NMR spectrum of **4**, besides the signals due to the cycloaurated 2-phenylthiazole moiety, both methyl and methine protons of the acac ligand appeared as singlets at δ 2.44 and 4.58, respectively. As far as the IR spectrum of **4** is concerned, ν(C=O) frequency of the acac ligand appeared as only one band at 1684 cm^{-1} and a ν(Au–Cl) frequency *trans* to carbon atom was observed at 315 cm^{-1}. On the basis of these data, together with the conductivity measurement (Λ_M 0.6 S cm^2 mol^{-1}), complex **4** was assigned to the four-coordinate neutral complex where the acac ligand is metallated at C^3 as illustrated in Scheme 1.

Complex **3** reacted with an equimolar amount of PPh_3 to give $[AuCl_2(phtz–C^1)(PPh_3)]$ (**5**). In the far-IR spectrum of **5**, two bands characteristic of ν(Au–Cl) frequencies *trans* to PPh_3 and *trans* to phenylene carbon were observed at 319 and 300 cm^{-1}, respectively. The molar conductivity (Λ_M 5.0 S cm^2 mol^{-1}) showed that **5** is a neutral complex. These facts clearly showed that with an equimolar amount of PPh_3 the C–N chelate ring in **5** easily opens. Such the easy opening of the chelate ring was also found in the five-membered cycloaurated complexes $[AuCl_2(C–N)]$ (C–N denotes cycometallated ligand) derived from azobenzene [19] and 4-butyl-*N*-(2,3,4-trimethoxybenzylidene)aniline [15], whereas the chelate rings formed from 2-(2-thienyl)- and 2-(3-thienyl)-pyridine, 1-ethyl-2-phenylimidazole and *N*,*N*-dimethylbenzylamine remained unchanged affording cationic species $[AuCl(C–N)(PPh_3)]^+$ [10,13,19]. The cyclometallated ring finally opened when **3** was treated with two molar equivalents of PPh_3. Thus in the presence of $NaBF_4$ $[AuCl(phtz–C^1)(PPh_3)_2]BF_4$ (**6**) was obtained. The Au–Cl stretching band at 312 cm^{-1} indicated the *trans* arrangement of the carbon and the chloride atoms.

In conclusion, here we have showed the second example of the cycloauration of a ligand other than pyridine derivatives.

Table 1
^{1}H NMR spectral data of the new complexes [a]

Complex	Thiazolyl moiety [b]	Phenyl moiety	Others
1	7.80 (d, 1H, $H^{5'}$) [c] 7.95–8.0 (c, 1H, $H^{4'}$) [d]	7.55–7.5 (c, 3H, *m*, *p*-Ph) 7.95–8.0 (c, 2H, *o*-Ph) [d]	
2	7.79 (d, 1H, $H^{5'}$) [e] 8.07 (d, 1H, $H^{4'}$) [e]	7.6–7.75 (c, 3H, *m*, *p*-Ph) 7.95–8.0 (c, 2H, *o*-Ph) [d]	
3	8.19 (d, 1H, $H^{5'}$) [c] 8.38 (d, 1H, $H^{4'}$) [c]	7.39 (dt, 1H, H^4) [f,g] 7.47 (dt, 1H, H^5) [f,g] 7.76 (d, 1H, H^3) [f] 7.89 (dd, 1H, H^6) [f,g]	
4	7.54 (d, 1H, $H^{5'}$) [e] 8.40 (d, 1H, $H^{4'}$) [e]	7.35–7.45 (c, 2H, H^4, H^5) 7.62 (dd, 1H, H^3) [g,h] 7.80 (dd, 1H, H^6) [g,h]	2.44 (s, 6H, acac–Me) 4.58 (s, 1H, acac–CH)
5	7.80 (d, 1H, $H^{5'}$) [c] 8.19 (d, 1H, $H^{4'}$) [c]	7.0–7.05 (c, 2H, H^4, H^5) 7.3–7.35 (c, 2H, H^3, H^6)	7.4–7.65 (c, 15H, PPh_3)
6	7.87 (d, 1H, $H^{5'}$) [c] 8.49 (d, 1H, $H^{4'}$) [c]	6.8–6.85 (m, 1H, H^5) 6.9–7.0 (c, 2H, H^3 and H^4) 7.2–7.25 (m, 1H, H^6)	7.35–7.65 (c, 30H, PPh_3)

[a] Measured in DMSO-d_6 except for **2** and **4** ($CDCl_3$) at 270 MHz and at 23°C; δ in ppm with respect to $SiMe_4$; s, singlet; d, doublet; dd, double doublet; dt, double triplet; m, multiplet; c, complex.

[b] Lower field resonance was tentatively assigned to $H^{4'}$ in consideration of the ^{1}H NMR data of thiazole or 2-aminothiazole [20]. ^{1}H NMR data of free 2-phenylthiazole in $CDCl_3$ are as follows; δ 7.33 [d, $H^{5'}$, $^3J(HH) = 3.4$ Hz], 7.4–7.5 [c, *m*, *p*-H's of Ph], 7.87 [d, $H^{4'}$, $^3J(HH) = 3.4$ Hz], 7.95–8.0 [c *o*-H's of Ph].

[c] $^3J(HH) = 3.5$ Hz.

[d] Overlapping to each other.

[e] $^3J(HH) = 4.0$ Hz.

[f] $^3J(HH) = 7.7$ Hz.

[g] $^3J(HH) = 1.5$ Hz.

[h] $^3J(HH) = 7.3$ Hz.

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References

[1] E.C. Constable, T.A. Leese, J. Organomet. Chem. 363 (1989) 419.
[2] (a) M.I. Bruce, Angew. Chem., Int. Ed. Engl. 16 (1977) 73;
(b) I. Omae, Chem. Rev. 79 (1979) 287;
(c) I. Omae, Coord. Chem. Rev. 32 (1980) 235;
(d) G.R. Newkome, W.E. Puckett, V.K. Gupta, G.E. Kiefer, Chem. Rev. 86 (1986) 451.
[3] C.W. Chan, W.T. Wong, C.M. Che, Inorg. Chem. 33 (1994) 1266.
[4] H.O Liu, T.C. Cheung, S.M. Peng, C.M. Che, J. Chem. Soc., Chem. Commun. (1995) 1787.
[5] M.A. Cinellu, A. Zucca, S. Stoccoro, G. Minghetti, M. Manassero, M. Sansoni, J. Chem. Soc., Dalton Trans. (1996) 4217.
[6] Y. Fuchita, H. Ieda, Y. Tsunemune, J. Kinoshita-Kawashima, H. Kawano, J. Chem. Soc., Dalton Trans. (1998) 791.
[7] M.A. Cinellu, A. Zucca, S. Stoccoro, G. Minghetti, M. Manassero, M. Sansoni, J. Chem. Soc., Dalton Trans. (1995) 2865.
[8] Y. Fuchita, H. Ieda, A. Kayama, J. Kinishita-Nagaoka, H. Kawano, S. Kameda, M. Mikuriya, J. Chem. Soc., Dalton Trans. (1998) 4095.
[9] M. Nonoyama, K. Nakajima, Polyhedron 16 (1997) 4039.
[10] Y. Fuchita, H. Ieda, S. Wada, S. Kameda, M Mikuriya, J. Chem. Soc., Dalton Trans. (1999) 4431.
[11] J. Vicente, M.T. Chicote, M.I. Lozano, S. Huertas, Organometallics 18 (1999) 753.
[12] M. Nonoyama, Synth. React. Inorg. Met.-Org. Chem. 29 (1999) 119.
[13] Y. Fuchita, H. Ieda, M Yasutake, J. Chem. Soc., Dalton Trans. (2000) 271.
[14] H. Erlenmeyer, C. Becker, E. Sorkin, H. Block, E. Suter, Helv. Chim. Acta 30 (1947) 2058.
[15] J. Vicente, M.D. Bermudez, F.J. Carrion, P.G. Jones, Chem. Ber. 129 (1996) 1301.
[16] (a) K.S. Liddle, C. Parkin, J. Chem. Soc., Chem. Commun. (1976) 26;
(b) D. Rasala, Bull. Soc. Chim. Fr. 129 (1992) 79;
(c) R.J. Puddephatt, in: G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, vol. 5, Pergamon, Oxford, 1987, p. 861.
[17] G. Minghetti, M.A. Cinellu, M.V. Pinna, S. Stoccoro, A. Zucca, M. Manessero, J. Organomet. Chem. 568 (1998) 225.
[18] (a) E.C. Constable, R.P.G. Henny, P.R. Raithby, L.R. Sousa, Angew. Chem. Int., Ed. Engl. 30 (1991) 1363;
(b) E.C. Constable, L.R. Sousa, J. Organomet. Chem. 427 (1992) 125.
[19] J. Vicente, M.T. Chicote, M.D. Bermudez, J. Organomet. Chem. 268 (1984) 191.
[20] N.S. Bhacca, D.P. Hollis, L.F. Johnson, E.A. Pier (Eds.), NMR Catalog, High Resolution NMR Spectra of Organic Compounds, vol. 2, The National Press, USA, 1963.