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Cycloaurated derivatives of 2-phenylpyridine

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Abstract

The reaction of 2-phenylpyridine (HL^1) with $H[AuCl_4]$ or $Na[AuCl_4]$ under a variety of conditions leads to the formation of the square-planar *N*-bonded complex $[Au(HL^1)Cl_3]$. Warming this in MeCN results in a 'roll-over' cyclometallation to yield $[AuL^1Cl_2]$; this complex may also be prepared by the transmetallation of $[\{HgL^1Cl\}_n]$ with $[AuCl_4]^-$. No evidence was obtained for the formation of cationic cyclometallated complexes of the type $[Au(L^1)_2]^+$ or $[Au(bipy)L^1]^+$.

Introduction

There has been considerable recent interest in the cyclometallated bonding mode, which combines the electronic influences of a carbon-donor ligand with the stability of a chelate coordination compound [1–3]. We have been particularly interested in the chemistry of cyclometallated derivatives of 2-phenylpyridine (HL^1) and other ligands that may be regarded as chelating *C,N*-donor analogues of 2,2′-bipyridine (bipy) [4–6]. The photophysical properties of cyclometallated derivatives of 2-phenylpyridine and related ligands have proved to be of particular interest [7], and have prompted us to investigate methods for the systematic synthesis of such compounds. In the course of these investigations, we became aware that cycloauration of 2-phenylpyridine had not been demonstrated, although numerous organometallic derivatives of gold in various oxidation states are well known [8]. In this paper, we report the preparation of cycloaurated complexes of 2-phenylpyridine by direct auration and by gold-mercury exchange reactions.

Results and discussion

The formation of cycloaurated complexes by direct reaction of a ligand with a gold compound is relatively uncommon, although we have demonstrated that the potentially terdentate ligand 6-(2″-thienyl)-2,2′-bipyridine (HL^2) undergoes ready metallation upon reaction with $[AuCl_4]^-$ [6]. The reaction of HL^1 with either

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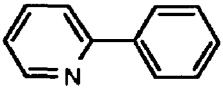
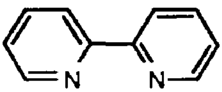
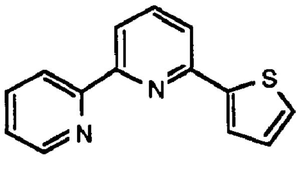
H[AuCl$_4$] or Na[AuCl$_4$] leads to [Au(HL^1)Cl$_3$] in near-quantitative yield. The formulation of the complex as [Au(HL^1)Cl$_3$] was supported by microanalytical data. The infrared spectrum exhibits a single, intense Au–Cl stretching mode at 369 cm^{-1}, which is directly comparable to ν(Au–Cl) 363–366 cm^{-1} in [Au(py)Cl$_3$] [9].



HL^1



bipy



HL^2

This is support for the formulation with a simple *N*-bonded 2-phenylpyridine ligand. The spectrum also exhibits strong absorptions at 1602, 1477, 788, 763, 741 and 700 cm^{-1}, which are characteristic of *N*-bonded 2-phenylpyridine complexes [10]. The ^{1}H NMR spectrum of a solution of [Au(HL^1)Cl$_3$] in CD$_3$COCD$_3$ (see experimental) exhibits 9 resonances in accord with the proposed structure.

Although direct cycloauration is not usually successful, the transmetallation of other organometallics (frequently lithium, magnesium or mercury(II) species) has been found to be useful for the preparation of cyclometallated gold(III) complexes. It is significant that [Au(HL^1)Cl$_3$] was the only product from the reaction of HL^1 with [AuCl$_4$]$^-$, even when the reactions were allowed to proceed for 24 h at reflux. Only after > 100 h under reflux is there any evidence for the direct formation of [AuL^{1}Cl$_2$]. We have previously demonstrated that the complex [{HgL^{1}Cl}$_n$], which is readily prepared by direct reaction of HL^1 with mercury(II) acetate followed by metathesis with LiCl, is a useful intermediate for the preparation of cyclometallated transition metal complexes containing L^1 [6,11]. The reaction of [{HgL^{1}Cl}$_n$] with H[AuCl$_4$] in MeCN resulted in the formation of a pale yellow solution, from which feathery needles of a complex slowly deposited. The same product was obtained from the reaction of [{HgL^{1}Cl}$_n$] with Na[AuCl$_4$]. Elemental analysis suggested an empirical formula [AuL^{1}Cl$_2$], and the mass spectrum exhibited highest mass peaks at *m/z* 421, 423, 425 ([AuL^{1}Cl$_2$]$^+$). Fragmentation ions were observed at *m/z* 386, 388 ([AuL^{1}Cl]$^+$) and *m/z* 351 ([AuL^1]$^+$); all peaks exhibited the correct isotopomer distributions. The infrared spectrum of the complex exhibits a weak absorption at 363 cm^{-1} which may be an Au–Cl stretching modes, although we do not observe this stretch in the spectrum of [AuL^{3}Cl$_2$]. The spectrum also exhibits strong ligand modes at 1607, 1491, 1445, 786, 766, 729 and 412 cm^{-1}. The absorption at 412 cm^{-1} is diagnostic of a cyclometallated *C,N*-bonded 2-phenylpyridine [4–6,10]. The ^{1}H NMR spectrum of the complex is shown in Fig. 1, and clearly shows the presence of only 8 aromatic protons. The assignments were made on the basis of a double quantum filtered phase sensitive COSY experiment. There is an ambiguity in the direction of assignment of the ABCD pattern associated with the cyclometallated phenyl ring. The formation of the cyclic complex by transmetallation with the organomercury(II) compound is expected [5,8]. The direct formation of cycloaurated complexes by reaction with suitable ligands is extremely rare, although we recently demonstrated that gold(III) complexes of HL^2 undergo a ready transformation from an *N*-bonded to *C,N*-bonded mode.

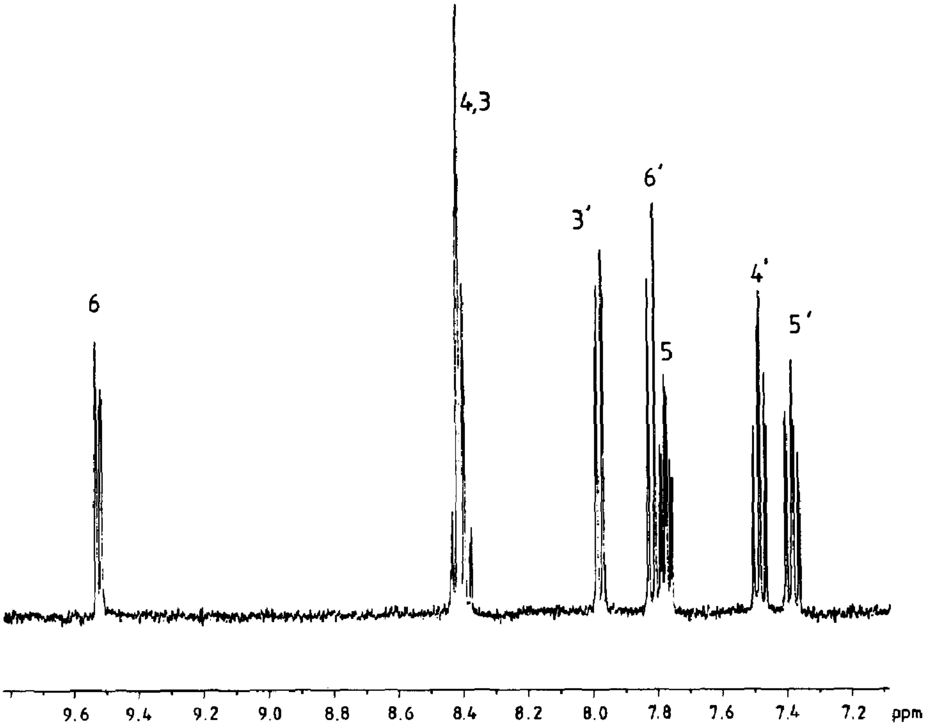


Fig. 1. ^{1}H NMR spectrum of the complex [AuL^1Cl_2].

Although the direct reaction of HL^1 with $[AuCl_4]^-$ leads to [$Au(HL^1)Cl_3$] only, warming [$Au(HL^1)Cl_3$] in MeCN results in conversion to [AuL^1Cl_2]. The complex so obtained is identical in all respects to that obtained from the transmetallation reactions. This case of the change from the *N*-bonded to *C,N*-bonded mode provides a simple route to the metallated complexes, and is clearly related to the 'roll-over' processes of platinum complexes of HL^2 [12].

Attempts to prepare salts of the complex $[Au(L^1)_2]^+$ by reaction of H[$AuCl_4$], Na[$AuCl_4$] or [AuL^1Cl_2] with an excess of [$\{HgL^1Cl\}_n$] in a variety of solvents were unsuccessful. In an attempt to prepare related cationic cyclometallated compounds, we have investigated the reactions of $[Au(bipy)Cl_2]^+$.

The complex [$Au(bipy)Cl_2$][$AuCl_4$] was prepared as a bright yellow solid by the reaction of 2,2'-bipyridine with H[$AuCl_4$] in aqueous acetonitrile (ν(Au–Cl) 362 cm^{-1}) [8]. The reaction of this complex with [$\{HgLCl\}_n$] in acetonitrile was slow, but the yellow colour was discharged during several hours, and an off-white solid separated from the solution. The ^{1}H NMR spectrum of this solid indicated that it was a mixture of $[Au(bipy)Cl_2]^+$ and [AuL^1Cl_2]; the organomercury(II) derivative clearly reacts with the $[AuCl_4]^-$ in preference to the $[Au(bipy)Cl_2]^+$ cation. However, even with an excess of [$\{HgLCl\}_n$] the only products were [$Au(bipy)Cl_2$]Cl and [AuL^1Cl_2].

Experimental

2-Phenylpyridine (Aldrich), H[$AuCl_4$] and Na[$AuCl_4$] (Johnson–Matthey) were used as supplied; [$\{HgL^1Cl\}_n$] was prepared by a published method [6,11]. Electronic spectra were recorded with a Pye–Unicam 8800 spectrophotometer; infrared spectra were recorded on a Perkin–Elmer 1710 FT or 983 spectrometer with the compound in compressed KBr pellets or as a in suspension in Nujol. Fast atom bombardment mass spectra were measured using a Kratos MS-50 spectrometer, and were loaded using acetonitrile as solvent with 3-nitrobenzyl alcohol as supporting matrix. NMR spectra were recorded on a Bruker WM250 or AM400 spectrometer.

Preparation of [Au(HL^1)Cl$_3$]. Method 1. A solution of 2-phenylpyridine (0.019 g, 0.12 mmol) in MeCN (3 cm^3) was added to a solution of H[AuCl$_4$] (0.034 g, 0.1 mmol) in water (3 cm^3); [Au(HL^1)Cl$_3$] immediately separated as a yellow solid. This was filtered off, washed well with water, and dried in vacuo to yield [Au(HL^1)Cl$_3$] (0.045 g, 98%) (Found: C, 28.6; H, 1.9; N, 3.0. C$_{11}$H$_9$NAuCl$_3$ calcd.: C, 28.8; H, 2.0; N, 3.0%; ^{1}H NMR (CD$_3$COCD$_3$): δ 9.29, 1H, d, J 5Hz, H^6; δ 8.47, 1H, td, J 7.8, 1.3 Hz, H^4; δ 8.08, 1H, dd, J 7.0, 1.3 Hz, H^3; δ 8.02, 1H, td, J 7.8, 7.0 Hz, H^5; δ 7.90, 3H).

Method 2. The above preparation was repeated but with EtOH (3 cm^3) in place of MeCN; [Au(HL^1)Cl$_3$] was obtained in 98% yield.

Method 3. The preparation described in method 1 was repeated except that the mixture of reactants was heated under reflux for 24 h; [Au(HL^1)Cl$_3$] was obtained in the same yield as before.

Method 4. A solution of 2-phenylpyridine (0.009 g, 0.06 mmol) in MeCN (1.5 cm^3) was added to a solution of Na[AuCl$_4$] (0.018 g, 0.05 mmol) in water (1.5 cm^3); [Au(HL^1)Cl$_3$] was immediately separated as a yellow solid (98%).

Method 5. The above preparation was repeated except that the mixture was heated under reflux for 24 h; the only isolated product was [Au(HL^1)Cl$_3$].

Method 6. The above preparation was repeated with EtOH (1.5 cm^3) in place of MeCN; [Au(HL^1)Cl$_3$] was the only isolated product.

Preparation of [AuL^{1}Cl$_2$]. Method 1. A solution of [{HgL^{1}Cl}$_n$] (0.029 g, 0.074 mmol) in MeCN (20 cm^3) was added to H[AuCl$_4$] (0.025 g, 0.074 mmol) in water (15 cm^3). The pale yellow feathery solid which separated was filtered off washed well with water, and dried in vacuo to yield [AuL^{1}Cl$_2$] (0.028 g, 90%) (Found: C, 31.1. H, 1.9; N, 3.3. C$_{11}$H$_8$NAuCl$_2$ calcd.: C, 31.3; H, 1.8; N, 3.3%; ^{1}H NMR (CD$_3$SOCD$_3$): δ 9.52, 1H, d, J 6.5Hz, H^6; δ 8.4, 2H, m, H^4 + H^3; δ 7.97, 1H, dd, J 7.8, 1.6 Hz, H$^{3'(6')}$; δ 7.81, 1H, dd, J 8.0, 1.06 Hz, H$^{6'(3')}$; δ 7.70, 1H, td, J 6.5 Hz, H^5; δ 7.48, 1H, td, J 7.8, 1.06 Hz, H$^{4'(5')}$; δ 7.38, 1H, td, J 7.8, 1.6Hz, H$^{5'(4')}$).

Method 2. The above preparation was repeated on half the scale with Na[AuCl$_4$] (0.014 g, 0.037 mmol) to yield [AuL^{1}Cl$_2$] (0.014 g, 90%).

Method 3. A suspension of [Au(HL^1)Cl$_3$] (0.023 g, 0.05 mmol) was heated under reflux in aqueous MeCN (5 cm^3, 1/1) for 3 h, during which the solution became yellow and the solid changed from yellow to white. The solid was filtered off and air-dried to yield [AuL^{1}Cl$_2$] (0.017 g, 80%).

Preparation of [Au(bipy)Cl$_2$][AuCl$_4$]. A solution of bipy (0.030 g, 0.2 mmol) in MeCN (10 cm^3) was added to one of H[AuCl$_4$] (0.050 g, 0.15 mmol) in water (10 cm^3). An immediate reaction occurred, with precipitation of a bright yellow solid. This was filtered off and dried in vacuo to yield [Au(bipy)Cl$_2$][AuCl$_4$] (0.055 g, 98%) (Found: C, 15.7; H, 1.1; N, 3.7. C$_{10}$H$_8$N$_2$Au$_2$Cl$_6$ calcd.: C, 15.9; H, 1.1; N, 3.7%; ^{1}H NMR (CD$_3$SOCD$_3$): δ 9.40, 1H, d, J 5.0 Hz, H^6; δ 8.93, 1H, d, J Hz H^3; δ 8.73, 1H, t, J 7.92 Hz, H^4; δ 8.15, 1H, dd, J 7.92, 5.0 Hz, H^5).

Reaction of [Au(bipy)Cl$_2$][AuCl$_4$] with [{HgL^{1}Cl}$_n$]. [Au(bipy)Cl$_2$][AuCl$_4$] (0.025 g, 0.033 mmol) was added to a solution of [{HgL^{1}Cl}$_n$] (0.013 g, 0.033 mmol) in MeCN (15 cm^3). The yellow colour of the solution was slowly discharged as a a pale yelllow solid separated. The ^{1}H NMR spectrum of this solid revealed it to be a mixture of [Au(bipy)Cl_2]Cl and [AuL^1Cl_2].

Reaction of [Au(bipy)Cl_2][AuCl_4] with excess [{HgL^{1}Cl}$_n$]. [Au(bipy)Cl_2][AuCl_4] (0.025 g, 0.033 mmol) was added to a solution of [{HgL^{1}Cl}$_n$] (0.039 g, 0.1 mmol) in MeCN (30 cm^3). The yellow colour of the solution was slowly discharged as a pale yellow solid separated. The ^{1}H NMR spectrum of this solid revealed it to be a mixture of [Au(bipy)Cl_2]Cl and [AuL^1Cl_2].

Attempted reaction of [AuL^1Cl_2] with bipy. A mixture of [AuL^1Cl_2] (0.021 g, 0.05 mmol) and bipy (0.016 g, 0.1 mmol) in MeCN (20 cm^3) was heated under reflux for 12 h. On cooling, [AuL^1Cl_2] separated as pale-yellow needles (0.019 g). The ^{1}H NMR spectrum of the recovered solid was identical to that of an authentic sample of [AuL^1Cl_2].

Attempted reaction of [AuL^1Cl_2] with [{HgL^{1}Cl}$_n$]. A mixture of AuL^1Cl_2] (0.021 g, 0.05 mmol) and [{HgL^{1}Cl}$_n$] (0.024 g, 0.12 mmol) in MeCN (10 cm) was heated under reflux for 12 h. The pale-coloured solid that separated on cooling was shown to by ^{1}H NMR spectroscopy to be a mixture of [AuL^1Cl_2] and [{HgL^{1}Cl}$_n$].

Attempted reaction of [AuL^1Cl_2] with HCl. A suspension of [AuL^1Cl_2] (0.021 g, 0.05 mmol) in aqueous MeCN (10 cm^3, 1/1) was treated with dilute hydrochloric acid (2 drops). No apparent reaction occurred. The mixture was heated under reflux for 1 h and upon cooling [AuL^1Cl_2] reprecipitated as a yellow solid. After sequential treatment with dilute hydrochloric acid (1 cm^3) and concentrated hydrochloric acid (1 cm^3) under reflux, [AuL^1Cl_2] was recovered unchanged.

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