Synthesis and Characterization of Mononuclear Amidogold(III) Complexes − Crystal Structure of $[Au(N_2C_{10}H_7(CMe_2C_6H_4)\text{-}6](NHC_6H_3Me_2\text{-}2,6)][PF_6]$ − Oxidation of 4-Methylaniline to Azotoluene

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Mononuclear amidogold(III) complexes $[Au(C,N,N)(NRR')][PF_6]$ [C,N,N = $N_2C_{10}H_7(CMe_2C_6H_4)$-6, where $N_2C_{10}H_8$ = 2,2′-bipy; R = H, R′ = *p*-tolyl (**5**), *o*-xylyl (**6**), isobutyl (**7**), *sec*-butyl (**8**), R = R′ = Et (**9**)], $[Au(C,N)(AcO)(NHC_6H_4NO_2\text{-}4)]$ (**10**) [C,N = $NC_5H_4(CH_2C_6H_4)$-2, where NC_5H_5 = py] and $[Au(N,N)(NHC_6H_4NO_2\text{-}4)_2][PF_6]$ (**11**) (N,N = 2,2′-bipy), have been synthesized in fairly good yields by reaction of the hydroxo, methoxo, or acetato complexes **1**–**4** {$[Au(C,N,N)(OR)][PF_6]$ [R = H (**1**), Me (**2**)], $[Au(C,N)(AcO)_2]$ (**3**), $[Au(N,N)(OH)_2][PF_6]$ (**4**)} with amines. The structure of $[Au(C,N,N)(NHC_6H_3Me_2\text{-}2,6)][PF_6]$ (**6**) has been determined by X-ray diffraction. Reaction of the hydroxo complex **4** with $NH_2C_6H_4Me$-4 gives metallic gold, the protonated ligand $[N,NH][PF_6]$ and organic products, the main one being azotoluene.

Introduction

Amido complexes of late transition metals have attracted considerable interest[1] because of their involvement as intermediates in metal-catalyzed carbon−nitrogen bond-formation processes.[2] Isolation of such intermediates is often hampered by their high reactivity. Nevertheless several stable late transition metal amides have been synthesized and their structures in the solid state as well as their reactivity investigated.[3] While gold(III) (a d^8 metal ion) complexes with ammonia,[4] bidentate,[5] and terdentate[6] amines, and related amido complexes have been widely studied, mainly from a kinetic point of view, isolated complexes with simple amide ligands[7] are still scarcely represented.[8] This shortage of data[9] and a report on the intramolecular hydroamination of alkynes catalyzed by gold(III) salts[10] prompted us to investigate the reactivity of some gold(III) complexes with various amines.

Previously, we have described the synthesis, characterization, and reactivity of gold(III) cyclometallated derivatives $[Au(C,N,N)(Y)][PF_6]$ (C,N,N = 6-benzyl-2,2′-bipyridine) with various anionic ligands Y.[11] Among these, two stable amido complexes, $[Au(C,N,N)(NHC_6H_4NO_2\text{-}4)][PF_6]$ [C,N,N = $N_2C_{10}H_7(CHMeC_6H_4)$-6 and $N_2C_{10}H_7(CMe_2C_6H_4)$-6], could be obtained by σ-ligand metathesis of the corresponding methoxo complexes with *p*-nitroaniline.

Our study on amidogold(III) complexes has been extended to different amines and to different co-ligands to verify the effectiveness of the synthetic method and the influence of the ancillary ligand on the reactivity of the amidogold(III) complex. Here we show that a number of amidogold(III) complexes can be isolated with different co-ligands. The terdentate C,N,N ligand arising from 6-(1,1-dimethylbenzyl)-2,2′-bipyridine is the most effective in stabilizing different amido complexes, whereas the bidentate C,N and N,N ligands (deprotonated 2-benzylpyridine and 2,2′-bipyridine, respectively) could stabilize only the *p*-nitroanilide derivative. The gold complex $[Au(N,N)(OH)_2][PF_6]$[12] (**4**) can promote the oxidation of amines other than *p*-nitroaniline. With *p*-toluidine the main product is azotoluene.

The selective oxidation of aromatic amines under mild conditions is of current interest, as pointed out in a recent paper relevant to oxidation processes catalysed by an iron(III) complex.[13]

Results and Discussion

During previous studies on gold(III) chemistry we had found that several complexes, $[Au(C,N,N)Y]^+$, containing both gold−carbon and gold−heteroatom bonds are accessible by treatment of acetato, hydroxo, and methoxo com-

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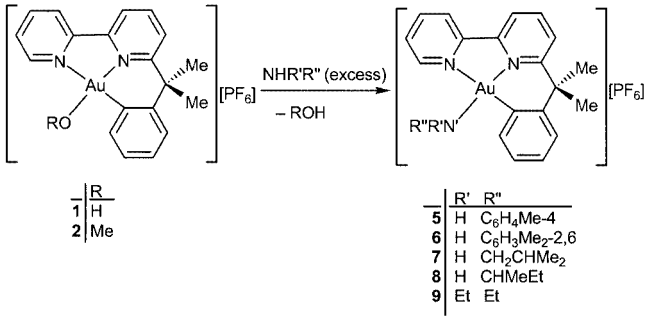
plexes with protic reagents at room temperature.[11] In particular, besides alkoxo, thiolato, and acetylide complexes, two stable gold amides have been synthesized by an exchange reaction of *p*-nitroaniline with [Au(C,N,N)(OMe)][PF_6] [C,N,N = $N_2C_{10}H_7(CHMeC_6H_4)$-6 and $N_2C_{10}H_7(CMe_2C_6H_4)$-6] in dichloromethane.[11]

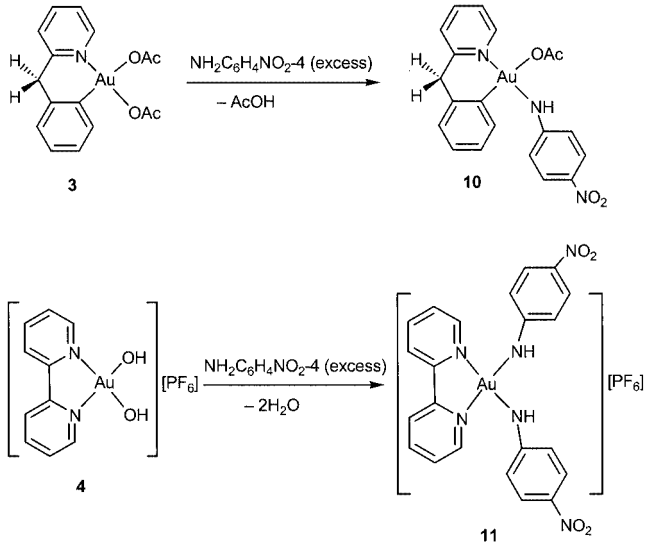
New amidogold(III) complexes with three different ancillary ligands, all containing nitrogen donor atoms, have been obtained by the addition of different amines to hydroxo, methoxo, or acetato complexes under mild conditions that required excess amine to drive the equilibrium reaction to completion. The nature of the ancillary ligand dramatically affects the outcome of the reaction: with the terdentate cyclometallated ligand $N_2C_{10}H_7(CMe_2C_6H_4)$-6 both alkyl- and arylamides are obtained in fairly good yields (Scheme 1), whereas with the bidentate C,N ligand $NC_5H_4(CH_2C_6H_4)$-2 and the N,N ligand 2,2′-bipyridine only *p*-nitroanilide complexes have been isolated (Scheme 2). Addition of even large amounts of *p*-nitroaniline to complex **3** gives only substitution of one AcO group. Isolation of stable bis(amido) complexes other than the *p*-nitroaniline derivative, at least for complex **4**, is probably hampered by their high reactivity.



	R
1	H
2	Me

	R'	R"
5	H	C_6H_4Me-4
6	H	$C_6H_3Me_2$-2,6
7	H	CH_2CHMe_2
8	H	CHMeEt
9	Et	Et

Scheme 1



Scheme 2

Alkylamido complexes **7**–**9** were obtained simply in a one-pot reaction in high yields, whereas arylamido complexes **5** and **6** required either the use of molecular sieves to trap water or further treatment of the crude mixture with excess amine (see Exp. Sect.). With complex **2** the trend observed suggests that the exchange reaction proceeds, at least in this case, by nucleophilic attack of the amine at the gold centre followed by proton transfer to the coordinated methoxide ligand and elimination of methanol. Reaction of the more basic amine $NHEt_2$ goes to completion within a few hours. For complexes **3** and **4** other mechanisms could be operative: thus, for the neutral complex **3** dissociation of the acetato group *trans* to the carbon atom can be envisaged. Coordination of the amine and successive deprotonation should follow to give the amido species.

Complexes **5**–**11** are air-stable compounds with relatively high melting points and good stability in solution: no decomposition was observed even for amides having β-hydrogen atoms (**7**–**9**). In the FAB mass spectra (positive ions) of compounds **5**, **6**, **8**, **9**, and **11** the molecular ions [M^+] ([M − H], for **8**) have been observed. In the spectrum of the isobutylamido derivative **7** the major peak (100% intensity) corresponds to the species [Au(C,N,N)(NBA − H)], which is probably formed by an exchange reaction of the nitrobenzyl alcohol (NBA) with the amido complex. Peaks corresponding to this species are also found in the mass spectra of the alkylamido complexes **8** and **9**. The neutral complex [Au(C,N)(OAc)($NHC_6H_4NO_2$-4)] (**10**) gives a medium-intensity peak, corresponding to [M − AcO], as is also observed for the starting bis(acetato) complex. Of the two possible geometrical isomers, *trans*-N(am)–Au–N(py) or *trans*-N(am)–Au–C (am = amide; py = pyridine), the IR and NMR spectra, taken together, support a *trans*-N–Au–N arrangement. Indeed the acetato group stretching vibrations are observed at values consistent with an acetato group *trans* to a carbon atom (see Exp. Sect.) and the chemical shift of the H^6 proton at a value similar to that found for the bis(acetato) complex. The high *trans* influence of the deprotonated amine,[6e] with respect to that of the pyridine nitrogen atom, is probably responsible for making thermodynamically stable the isomer with high *trans*-influencing ligands in mutually *cis* positions. Analogous results were found for the reaction of the dichloro complexes [Au(C,N)Cl_2] with excess PPh_3, where only one chloride ion was replaced to give [Au(C,N)(PPh_3)Cl]$^+$, having a *trans*-P–Au–N arrangement [C,N = $C_6H_4CH_2NMe_2$-2,[14a] $NC_5H_4(CRR'C_6H_4)$-2[14b]].

In the IR spectra, weak to medium $\tilde{\nu}$(N–H) absorptions are observed in the range 3200–3336 cm^{-1}. In the ^1H NMR spectra the N*H* resonance could be assigned due to exchange with D_2O. In complexes **5**–**8** the NH resonance is shifted downfield with respect to the free ligand with $\Delta\delta$ = 1.5, 1.5, 2, and 1.6 ppm, respectively. In complexes **7** and **8** H–N–C–H spin–spin coupling, not present in the free amines, is observed. H–N–C–H spin–spin coupling has been reported in amine solutions when either the nitrogen atom is weakly basic or the nitrogen lone pair is coordinated with a Lewis acid.[15] Thus, it appears that substi-

tution of a hydrogen ion with an [Au(C,N,N)] group lowers the basicity of the nitrogen atom of the amine.

Because the NHCHMeEt ligand in complex **8** has a stereogenic carbon atom β to the metal atom, the methylene protons are diastereotopic, giving rise to two sets of multiplets. Also, in complex **9** the two hydrogen atoms on each methylene group of the NEt_2 ligand are diastereotopic: the two signals are very broad at ambient temperature but a well-resolved ABX_3 pattern is observed at −20 °C. As reported previously for other N,N,C aurated derivatives,[11] the six-membered C,N ring is fluxional on the NMR time scale. Thus, one resonance alone is observed for the methyl protons on the benzylic carbon atom of complexes **5**−**9**: no significant variation is observed on lowering the temperature from 20 to −80 °C.

A diffraction study of suitable crystals of complex **6** revealed a structure that consists of $[Au(C,N,N)(NHC_6H_3Me_2\text{-}2,6)]^+$ cations and PF_6^- anions packed in a molar ratio 1:1 with normal van der Waals contacts. An ORTEP view of the cation with the atom labelling scheme is shown in Figure 1. Selected bond lengths and angles are reported in Table 1.

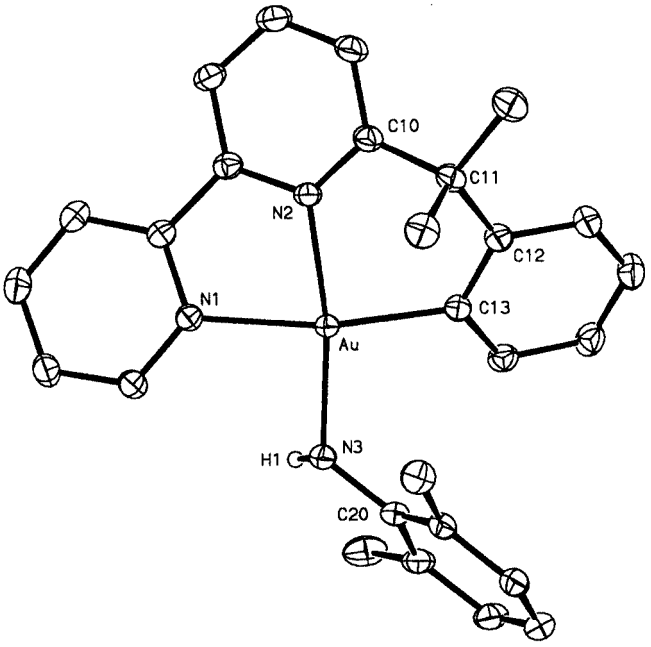


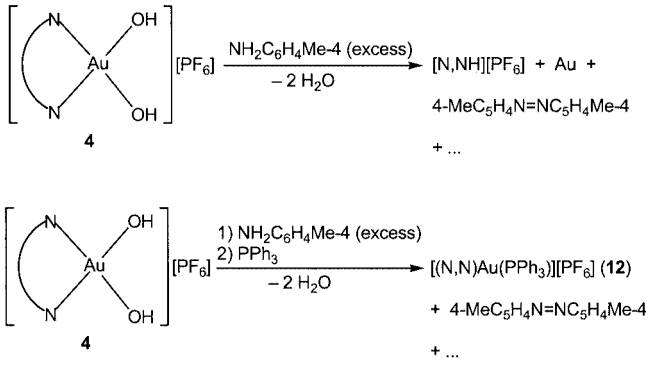
Figure 1. ORTEP view of the cation in compound **6**; ellipsoids are drawn at the 30% probability level

Table 1. Selected bond lengths [Å] and angles [°] with e.s.d.s in parentheses for the complex cation in compound **6**

Au−N(1)	2.128(2)	Au−N(2)	2.056(2)
Au−N(3)	2.015(2)	Au−C(13)	2.018(2)
N(3)−C(20)	1.401(3)	N(3)−H(1)	0.84(3)
N(1)−Au−N(2)	79.1(1)	N(1)−Au−N(3)	90.9(1)
N(1)−Au−C(13)	164.1(1)	N(2)−Au−N(3)	169.4(1)
N(2)−Au−C(13)	91.4(1)	N(3)−Au−C(13)	99.1(1)
Au−N(3)−C(20)	126.1(2)	Au−N(3)−H(1)	99(2)
C(20)−N(3)−H(1)	112(2)		

The gold atom in the cation displays a distorted square-planar coordination, with atoms Au(1), N(2), N(3), and C(13) essentially coplanar [maximum distances from their best plane being +0.005(2) Å for N(3) and −0.011(1) Å for Au], whereas atom N(1) is displaced by 0.484(2) Å out of the best plane. The distortion from the ideal square-planar geometry is probably due to the limited flexibility of the tridentate substituted bipyridine ligand. A similar distortion has been found in $[Au(C,N,N)Cl]^+$, which differs from the present one only in the substitution of the amido ligand with a chloride.[16] Bond lengths and angles in the present cation can be compared with those found in $[Au(C,N,N)Cl]^+$. Thus, the Au−N(1) and Au−C(13) bond lengths [2.128(2) and 2.018(2) Å, respectively] reported here are very similar to those in $[Au(C,N,N)Cl]^+$ [2.121(5) and 2.009(6) Å, respectively]. The slight elongation of the present Au−N(2) distance [2.056(2) Å] with respect to that of $[Au(C,N,N)Cl]^+$ [2.009(4) Å] indicates that the *trans* influence of the amide ligand is stronger than that of the chloride ligand. In the absence of suitable structural data[17] the Au(1)−N(3) bond length [2.015(2) Å] can be compared to the Pt−N distance found in *trans*-$[PtCl(NHC_6H_4I\text{-}4)(PEt_3)_2]$ [2.006(4) Å] and in a number of other (amido)Pt complexes (ref.[3l] and refs. therein). The six-membered metallacycle is in a boat conformation, with atoms N(2), C(10), C(12), and C(13) essentially coplanar, maximum deviations from their best plane being +0.025(2) and −0.025(2) Å for C(12) and C(10), respectively, whereas Au and C(11) lie 0.543(1) and 0.641(2) Å, respectively, above their best plane.

Reaction of complex **3** with amines other than *p*-nitroaniline led to mixtures of unidentified products and a small amount of gold. In contrast, complex **4** was quickly decomposed by the addition of amines and, with *p*-toluidine, it was possible to identify the main reaction products (Scheme 3). In addition to gold, which separated as a dark powder, 2,2′-bipyridine was recovered almost quantitatively (80%) as the salt $[N,NH][PF_6]$. Chromatography on silica gel of the organic fraction allowed us to isolate azotoluene (*trans* isomer) in 43% yield, based on the gold complex.



Scheme 3

The formation of azobenzene, as the main by-product, was observed in the oxidative carbonylation of amines cata-

lyzed by gold complexes, in particular when $HAuCl_4$ was employed in the reaction with aniline.[18] Azobenzene derivatives are also by-products in the $FeCl_2py_4^+$-catalyzed transformation of aromatic amines by H_2O_2,[13] as well as the main products of the ferrate oxidation of anilines, both in homogeneous[19] and in heterogeneous phases.[20] Different reaction mechanisms for the formation of azo compounds in the homogeneous phase have been claimed.[13,19]

In our case a bis(amido) intermediate can be envisaged for the formation of azotoluene. *N*,*N*′-Di-*p*-tolylhydrazine could form by N−N coupling of the bis(amido) complex $[Au(N,N)(NHC_6H_4Me_2\text{-}4)_2][PF_6]$, analogous to **11**, and then be oxidized to azotoluene.[21] This implies an unstable gold(I) intermediate $[Au(N,N)(solv)][PF_6]$ (solv = H_2O, MeCN). In an attempt to trap it, the reaction was carried out in the presence of PPh_3 (Scheme 3). Indeed, a gold(I) intermediate (**12**) was isolated, although not quantitatively, and identified as the known complex $[(N,N)Au(PPh_3)][PF_6]$.[22] The isolobal analogy between the cations $[(N,N)H]^+$ and $[(N,N)Au(PPh_3)]^+$ is notable.

Experimental Section

General: The gold complexes $[Au(C,N,N)Cl][PF_6]$ and $[Au(C,N)Cl_2]$ were obtained according to ref.[11] and ref.[14b], respectively. All the amines were used as received from commercial sources; the solvents were purified and dried according to standard methods. Celite (filter agent) and molecular sieves (4 Å) were purchased from Aldrich, and silica gel (70−230 mesh ASTM) from Merck. Elemental analyses were performed with a Perkin−Elmer Elemental Analyzer 240B by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari). Conductivities were measured with a Philips PW 9505 conductimeter. Infrared spectra were recorded with a Perkin−Elmer 983 spectrophotometer; the values are given in cm^{-1}. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 299.9 and 121.4 MHz, respectively. Chemical shifts are given in ppm relative to internal TMS (^1H) or external H_3PO_4 (^{31}P). Mass spectra were obtained with a VG 7070 instrument operating under FAB conditions, with 3-nitrobenzyl alcohol (NBA) as supporting matrix or EI conditions. GC/MS analyses were conducted with a Hewlett-Packard G1800B Gas Chromatograph Electron Ionization Detector (GCD System).

[Au(C,N,N)(OH)][PF$_6$] (1): An aqueous solution of KOH (0.033 g, 0.59 mmol) was added to an aqueous suspension of $[Au(C,N,N)Cl][PF_6]$ (0.179 g, 0.27 mmol). The mixture was heated under reflux for 1 h whilst stirring and then filtered. The volume of the colourless filtrate was reduced in a rotary evaporator until crystallization was observed. The resultant white product was collected by filtration and dried in vacuo. Yield: 0.128 g (75%), m.p. 170 °C. $C_{19}H_{18}AuF_6N_2OP$ (632.32): calcd. C 36.09, H 2.87, N 4.43; found C 35.91, H 2.71, N 4.33. Λ_M ($5\cdot10^{-4}$ mol·dm^{-3}, Me_2CO) = 106 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (Nujol): $\tilde{\nu}$ = 3360 m (broad) (OH), 1599 s, 1561 m, 1082 m, 1025 s, 846 vs (broad) cm^{-1}. ^1H NMR ([D$_6$]acetone): δ = 9.21 (dd, ^3J = 5.4, ^4J = 1.9 Hz, 1 H, H$^{6'}$), 8.92−7.18 (m, 10 H, other aromatics), 4.58 (s, 1 H, OH), 2.11 (s, 6 H, CH_3) ppm. MS (FAB$^+$): *m*/*z* (%) = 487 (100) [M$^+$], 470 (30) [Au(C,N,N)], 393 (10) [M − OH − C_6H_5], 273 (50) [C,N,N].

[Au(C,N,N)(OMe)][PF$_6$] (2): This was prepared according to ref.[11]

[Au(C,N)(AcO)$_2$] (3): Solid AcOAg (0.339 g, 2.03 mmol) was added to a suspension of $[Au(C,N)Cl_2]$ (0.401 g, 0.92 mmol) in acetone (20 mL). The resulting suspension was stirred at room temperature for 8 h and then filtered through Celite. Addition of diethyl ether to the concentrated solution afforded a creamy solid product. Recrystallization from chloroform/diethyl ether gave an analytical sample. Yield: 0.300 g (67%), m.p. 152 °C (dec.). $C_{16}H_{16}AuNO_4$ (483.30): calcd. C 39.76, H 3.34, N 2.90; found C 39.23, H 3.14, N 2.92. IR (Nujol): $\tilde{\nu}$ = 1668 vs and 1627 vs (C=O), 1568 m, 1307 vs and 1278 vs (C−O), 1042 m, 1031 m, 1007 m, 762 s, 704 m, 679 s cm^{-1}. ^1H NMR ($CDCl_3$): δ = 9.02 (d, ^3J = 5.1 Hz, 1 H, H^6), 8.03−7.01 (m, 7 H, other aromatic H), 4.38 (s, 2 H, CH_2), 2.11 (s, 3 H, Me), 2.04 (s, 3 H, Me) ppm. MS (FAB$^+$): *m*/*z* (%) = 533 (20) $[Au(C,N)_2]$, 424 (100) [M − CH_3CO_2].

[Au(N,N)(OH)$_2$][PF$_6$] (4): This was prepared according to ref.[12]

[Au(C,N,N)(NH-*p*-tol)][PF$_6$] (5). Method (a): Solid *p*-toluidine (0.064 g, 0.6 mmol) was added to a solution of **1** (0.126 g, 0.2 mmol) in dichloromethane (20 mL). The resulting red−orange solution was stirred at room temperature for 15 h in the presence of activated molecular sieves. The filtered solution was then concentrated to a small volume and diethyl ether added to give a red−orange solid product. Yield: 0.118 g (82%). **Method (b):** Solid *p*-toluidine (0.042 g, 0.39 mmol) was added to a solution of **2** (0.082 g, 0.13 mmol) in dichloromethane (15 mL). The resulting red−orange solution was stirred for 23 h at room temperature and then concentrated to a small volume. Addition of diethyl ether gave a red−orange precipitate of the equilibrium mixture (^1H NMR criterion) which was treated with excess *p*-toluidine in dichloromethane solution for 24 h to give complete conversion of **2**. Yield: 0.072 g (76%), m.p. 193−194 °C. $C_{26}H_{25}AuF_6N_3P$ (721.46): calcd. C 43.28, H 3.49, N 5.83; found C 42.80, H 3.35, N 5.61. Λ_M ($5\cdot10^{-4}$ mol·dm^{-3}, Me_2CO) = 120 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (Nujol): $\tilde{\nu}$ = 3300 w (NH), 1600 s, 1560 m, 1500 s, 1250 s, 1160 m, 1100 m, 1070 m, 1040 m, 1025 vs, 846 vs (broad), 780 s, 640 w cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 9.24 (dd, ^3J = 5.4, ^4J = 1.0 Hz, 1 H, H$^{6'}$), 8.66−7.06 (m, 10 H, other aromatic H), 6.97 (d, ^3J = 8.4 Hz, 2 H, H^{ortho}), 6.89 (d, ^3J = 8.4 Hz, 2 H, H^{meta}), 5.07 (s, 1 H, NH), 2.23 (s, 3 H, Me), 2.12 (s, 6 H, Me) ppm. MS (FAB$^+$): *m*/*z* (%) = 576 (100) [M$^+$], 470 (45) [Au(C,N,N)], 273 (40) [C,N,N].

[Au(C,N,N)(NH-*o*-xylyl)][PF$_6$] (6): Liquid *o*-xylidine (0.073 g, 0.6 mmol) was added to a solution of **1** (0.126 g, 0.2 mmol) in dichloromethane (20 mL). The resulting dark red solution was stirred at room temperature for 15 h in the presence of activated molecular sieves. The solution was then filtered and concentrated to a small volume and diethyl ether added to give a dark red solid product. Yield: 0.115 g (78%), m.p. 192 °C. $C_{27}H_{27}AuF_6N_3P$ (735.45): calcd. C 44.09, H 3.70, N 5.71%; found C 44.00, H 4.04, N 5.61. Λ_M ($5\cdot10^{-4}$ mol·dm^{-3}, Me_2CO) = 125 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (Nujol): $\tilde{\nu}$ = 3300 w (NH), 1590 s, 1220 s, 1080 m, 1038 s, 1020s, 840 vs (broad), 770 vs, 640 m cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 9.12 (d, ^3J = 5.4 Hz, 1 H, H$^{6'}$), 8.61−6.84 (m, 10 H, other aromatic H), 7.03. (d, ^3J = 7.3 Hz, 2 H, H^{meta}), 6.92 (t, ^3J = 7.3 Hz, 1 H, H^{para}), 5.04 (s, 1 H, NH), 2.31 [s, 6 H, 2 Me (xylydine)], 2.12 [s, 6 H, 2 Me (bipy)] ppm. MS (FAB$^+$): *m*/*z* (%) = 590 (100) [M$^+$], 470 (65) [Au(C,N,N)], 273 (30) [C,N,N]. Crystals suitable for a diffraction study were obtained by slow diffusion of diethyl ether into a dichloromethane solution of **6**.

[Au(C,N,N)(NH-*i*Bu)][PF$_6$] (7): Liquid isobutylamine (0.102 g, 1.4 mmol) was added to a solution of **2** (0.092 g, 0.14 mmol) in dichloromethane (15 mL). The resulting greenish solution was stirred at room temperature for 6 h and then concentrated to a

small volume. Addition of diethyl ether gave a greenish-yellow precipitate of the analytical sample. Yield: 0.095 g (97%), m.p. 153 °C. $C_{23}H_{27}AuF_6N_3P$ (687.45): calcd. C 40.18, H 3.96, N 6.11; found C 40.26, H 3.81, N 5.79. Λ_M ($5\cdot10^{-4}$ mol·dm^{-3}, Me_2CO) = 128 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (Nujol): $\tilde{\nu}$ = 3300 w (NH), 1596 s, 1562 m, 1064 m, 1042 s, 850 vs (broad) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 9.25 (dd, ^3J = 5.4, ^4J = 1.0 Hz, 1 H, H$^{6'}$), 8.62−7.32 (m, 10 H, other aromatic H), 3.30 (t, $^3J_{HN-CH}$ = 9.0 Hz, 1 H, NH), 2.98 (dd, $^3J_{H,C-CH}$ = 6.6, $^3J_{H,C-NH}$ = 9.0 Hz, 2 H, CH_2), 2.09 (s, 6 H, Me), 1.96 (m, 1 H, CH), 1.10 (d, ^3J = 6.8, 6 H, Me) ppm. FAB$^+$: *m*/*z* (%) = 622 (100) [Au(C,N,N)(NBA − H)], 470 (35) [Au(C,N,N)], 273 (40) [C,N,N].

[Au(C,N,N)(NH-*s*Bu)][PF$_6$] (8): Liquid *sec*-butylamine (0.102 g, 1.4 mmol) was added to a solution of **2** (0.092 g, 0.14 mmol) in dichloromethane (15 mL). The resulting orange solution was stirred at room temperature for 23 h and then concentrated to a small volume. Addition of diethyl ether gave an orange precipitate of the analytical sample. Yield: 0.086 g (89%), m.p. 150 °C (dec.). $C_{23}H_{27}AuF_6N_3P$ (687.45): calcd. C 40.18, H 3.96, N 6.11; found C 40.06, H 3.72, N 5.83. Λ_M ($5\cdot10^{-4}$ mol·dm^{-3}, Me_2CO) = 126 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (Nujol): $\tilde{\nu}$ = 3280 w (NH), 1590 s, 1520 m, 1080 s, 1040 s, 846 vs (broad) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 9.50 (dd, ^3J = 5.4, ^4J = 1.0 Hz, 1 H, H$^{6'}$), 8.58−7.27 (m, 10 H, other aromatics), 3.35 (d, $^3J_{HN-CH}$ = 4.0 Hz, 1 H, NH), 3.15 (m, 1 H, CH), 2.12 (s, 6 H, Me), 1.79 (m, 1 H, CH_AH$_B$), 1.64 (m, 1 H, CH$_A$$H_B$), 1.35 (d, ^3J = 6.3 Hz, 3 H, CH_3CH), 1.03 (t, ^3J = 7.3, 7.6 Hz, 3 H, CH_3CH$_2$) ppm. MS (FAB$^+$): *m*/*z* (%) = 622 (100) [Au(C,N,N)(NBA − H)], 541 (10) [M − H], 470 (40) [Au(C,N,N)], 273 (75) [C,N,N].

[Au(C,N,N)(NEt$_2$)][PF$_6$] (9): Liquid diethylamine (0.095 g, 1.3 mmol) was added to a solution of **2** (0.083 g, 0.13 mmol) in dichloromethane (15 mL). The resulting red solution was stirred at room temperature for 2 h then concentrated to a small volume. Addition of diethyl ether gave a dark orange precipitate of the analytical sample. Yield 0.086 g (96%), m.p. 160 °C. $C_{23}H_{27}AuF_6N_3P$ (687.45): calcd. C 40.18, H 3.96, N 6.11; found C 39.87, H 3.81, N 5.86. Λ_M ($5\cdot10^{-4}$ mol·dm^{-3}, Me_2CO) = 120 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (Nujol): $\tilde{\nu}$ = 1595 s, 1576 m, 1082 s, 1021 s, 846 vs (broad) cm^{-1}. ^{1}H NMR (CD_2Cl_2, −20 °C): δ = 9.37 (d, ^3J = 4.8 Hz, 1 H, H$^{6'}$), 8.57−7.29 (m, 10 H, other aromatics), 3.04 (m, ^2J = 14.3 Hz, ^3J = 7.0 Hz, 2 H, CH_AH$_B$), 2.62 (m, ^2J = 14.3 Hz, ^3J = 7.0 Hz, 2 H, CH$_A$$H_B$), 2.12 (s, 6 H, Me), 1.24 (t, ^3J = 7.0 Hz, 6 H, CH_3−CH$_2$) ppm. MS (FAB): *m*/*z* (%) = 622 (37) [Au(C,N,N)(NBA − H)], 542 (82) [M$^+$], 470 (90) [Au(C,N,N)], 273 (64) [C,N,N].

[Au(C,N)(OAc)(NHC$_6$H$_4$NO$_2$-4)] (10): Solid *p*-nitroaniline (0.138 g, 1 mmol) was added to a solution of complex **3** (0.120 g, 0.25 mmol) in dichloromethane (20 mL); the resulting yellow solution was then stirred for 24 h at room temperature. During this period the solution turned red−orange. Addition of diethyl ether to the concentrated solution caused precipitation of the equilibrium mixture (^{1}H NMR criterion). The mixture was then subjected to the procedure described above until complete conversion of **3** occurred. Yield: 0.085 g (60%), m.p. 157 °C (dec.). $C_{20}H_{18}AuN_3O_4$ (561.37): calcd. C 42.79, H 3.23, N 7.49; found C 42.68, H 3.15, N 7.27. IR (Nujol): $\tilde{\nu}$ = 3330 m (N−H), 1624 s (C=O), 1583 vs (NO_2), 1299 vs (broad) (C−O) + (NO_2), 1182 s, 1111 vs, 834 m, 753 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.94 (d, ^3J = 5.6 Hz,1 H, H^6), 8.02−7.01 (m, 7 H, other aromatic H), 7.89 (d, ^3J = 9.3 Hz, 2 H, H^{meta}), 6.65 (d, ^3J = 9.3 Hz, 2 H, H^{ortho}), 4.75 (s, 1 H, NH), 4.38 (s, 2 H, CH_2), 2.00 (s, 3 H, Me) ppm. MS (FAB$^+$): *m*/*z* (%) = 533 (100) [Au(C,N)$_2$], 502 (68) [M − $MeCO_2$], 366 (40) [Au(C,N)].

[Au(N,N)(NHC$_6$H$_4$NO$_2$-4)$_2$][PF$_6$] (11): Solid *p*-nitroaniline (0.341 g, 2.44 mmol) was added to a solution of **4** (0.130 g, 0.24 mmol) in acetone (20 mL); the resulting yellow solution was stirred at room temperature for 53 h. During this period the solution turned deep red. Addition of diethyl ether to the concentrated solution gave a red product, which was washed with methanol to give an analytical sample. Yield: 0.037 g (20%), m.p. 163 °C. $C_{22}H_{18}AuF_6N_6O_4P$ (772.39): calcd. C 34.20, H 2.35, N 10.88; found C 33.98, H 2.22, N 10.45. Λ_M ($5\cdot10^{-4}$ mol·dm^{-3}, Me_2CO) = 120 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (Nujol): $\tilde{\nu}$ = 3336 m (N−H), 1602 s, 1585 vs (NO_2), 1342 vs (broad) (NO_2), 1251 s, 1113 vs, 846 vs (broad) cm^{-1}. ^{1}H NMR ([D$_6$]acetone): δ = 9.35 (d, ^3J = 5.6 Hz, 2 H, H^6), 9.06 (d, ^3J = 7.6 Hz, 2 H, H^3), 8.79 (td, ^3J = 7.8, ^4J = 1.5 Hz, 2 H, H^4), 8.29 (t, ^3J = 7.1 Hz, 2 H, H^5), 7.78 (d, ^3J = 9.0 Hz, 4 H, H^{meta}), 7.10 (d, ^3J = 9.0 Hz, 4 H, H^{ortho}), 6.03 (s, 2 H, NH) ppm. MS (FAB$^+$): *m*/*z* (%) = 627 (20) [M$^+$], 490 (82) [M − NHC$_6$H$_4$NO$_2$-4], 353 [Au(N,N)].

Reaction of [Au(N,N)(OH)$_2$][PF$_6$] (4) with NH$_2$C$_6$H$_4$Me-4: Solid *p*-toluidine (0.098 g, 0.92 mmol) was added to a stirred solution of **4** (0.122 g, 0.23 mmol) in MeCN (20 mL); the resulting solution was stirred for 24 h at room temperature. During this period the solution turned dark red, and separation of a dark powder was observed. After filtration through Celite, the solution was concentrated to a small volume; subsequent addition of diethyl ether afforded a dirty white precipitate that was filtered off and identified as [N,NH][PF$_6$][23] (0.056 g, 80%). The mother liquor was concentrated to dryness to give a dark red solid, which was taken up with benzene and eluted through a column (15 × 1 cm) of silica gel. Removal of the solvent from the first eluate gave an orange crystalline product that was identified as *trans*-azotoluene. Yield: 0.021 g (43.4% with respect to complex **4**), m.p. 140 °C. MS (EI$^+$): *m*/*z* = 211 [MH$^+$], 119 [M − $C_6H_5CH_2$], 92 [C_6H_5Me]. ^{1}H NMR ($CDCl_3$): δ = 7.81 (d, ^3J = 8.1 Hz, 2 H), 7.30 (d, ^3J = 8.1 Hz, 2 H), 2.42 (s, 3 H, Me) ppm.

Reaction of [Au(N,N)(OH)$_2$][PF$_6$] (4) with NH$_2$C$_6$H$_4$Me-4 and PPh$_3$: A solution of PPh_3 (0.131 g, 0.5 mmol) in MeCN was added to a stirred solution of complex **4** (0.266 g, 0.5 mmol) and *p*-toluidine (0.214 g, 2 mmol) in MeCN (20 mL). The reaction mixture was stirred for 24 h at room temperature, filtered through Celite and concentrated to a small volume. Addition of diethyl ether afforded a dirty white product that was recrystallized from dichloromethane/diethyl ether to give an analytical sample, which was identified as [(N,N)Au(PPh_3)][PF$_6$] (**12**) (0.195 g, 51%), m.p. 195 °C (dec.). $C_{28}H_{23}AuF_6N_2P_2$ (760.39): calcd. C 44.22, H 3.05, N 3.68; found C 44.38, H 3.22, N 3.62. ^{1}H NMR (CD_2Cl_2): δ = 8.63 (d, ^3J = 4.1 Hz, 2 H, H^6), 8.33 (d, ^3J = 8.0 Hz, 2 H, H^3), 8.19 (t, ^3J = 7.3 Hz, 2 H, H^4), 7.72 (t, ^3J = 7.6 Hz, 2 H, H^5), 7.67−7.52 [m, 15 H, P(C$_6$$H_5$)$_3$] ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 31.3 (s, *P*Ph$_3$), −144.06 (sept, J_{P-F} = 711.1 Hz, *P*F$_6$) ppm. The mother liquor, containing organic products, was concentrated to dryness. The residue was then taken up with benzene and eluted through a column (20 × 1 cm) of silica gel. Removal of the solvent from the first eluate gave an orange crystalline product, which was identified as *trans*-azotoluene, yield 0.027 g (25.7%).

X-ray Data Collection and Structure Determination: Crystal data and other experimental details are summarized in Table 2. The diffraction experiment was carried out with a Bruker SMART CCD area-detector diffractometer at 223 K using Mo-K_α radiation (λ = 0.71073 Å) with a graphite crystal monochromator in the incident beam. Cell parameters and orientation matrix were obtained from the least-squares refinement of 141 reflections measured in three different sets of 15 frames each, in the range 3° < θ < 23°. At the

end of data collection the first 50 frames, containing 325 reflections, were recollected to monitor crystal decay, which was not observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT,[24a] and an absorption correction was applied (SADABS)[24b] to the 19993 collected reflections, 7461 of which are unique, with R_{int} = 0.0307 ($R_{int} = \Sigma|F_o^2 - F_{mean}^2|/\Sigma F_o^2$). Calculations were performed with a Pentium III PC using the Personal Structure Determination Package,[25] and the physical constants tabulated therein. Scattering factors and anomalous dispersion corrections were taken from ref.[26] The structure was solved by direct methods (SHELXS 86)[27] and refined by full-matrix least squares using all reflections and minimizing the function $\Sigma w(F_o^2 - k|F_c|^2)^2$ (refinement on F^2). Anisotropic thermal factors were refined for all non-hydrogen atoms. The seven hydrogen atoms bonded to N(3) and to the two methyl groups of the 2,6-xylidine ligand were detected in the final Fourier maps and refined with fixed thermal parameters. The other hydrogen atoms were placed in their ideal positions (C−H = 0.97 Å, *B* 1.10 times that of the carbon atom to which they are attached) and not refined. In the final difference Fourier map the maximum residual was 0.96(13) e/Å^3 at 0.70 Å from Au. CCDC-189011 contains the atomic coordinates of the structure model, the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystallographic data

Compound	**6**
Empirical formula	$C_{27}H_{27}AuF_6N_3P$
Formula mass	735.47
Colour	orange
Crystal system	triclinic
Space group	$P\bar{1}$ (no.2)
a [Å]	9.772(1)
b [Å]	11.234(1)
c [Å]	12.429(1)
α [°]	107.44(1)
β [°]	95.64(1)
γ [°]	92.74(1)
V [Å^3]	1291.1(2)
Z	2
F(000)	716
D_c [g·cm^{-3}]	1.892
T [K]	223
Crystal dimensions [mm]	0.096 × 0.225 × 0.366
μ(Mo-K_α) [cm^{-1}]	58.11
Min./max. transmiss. factors	0.41/1.00
Scan mode	ω
Frame width [°]	0.30
Time per frame [s]	20
No. of frames	2650
Detector−sample distance [cm]	4.00
θ range[°]	3−26
Reciprocal space explored	full sphere
No. of reflections: total/independent	19993/7461
R_{int}	0.031
Final R_2/R_{2w} indices[a] (F^2, all reflections)	0.035/0.049
Conventional R_1 index [$I > 2\sigma(I)$]	0.019
Reflections with $I > 2\sigma(I)$	6839
No. of variables	364
Goodness of fit[b]	0.94

[a] $R_2 = [\Sigma(|F_o^2 - kF_c^2|)/\Sigma F_o^2]$, $R_2w = [\Sigma w(F_o^2 - kF_o^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [b] $[\Sigma w(F_o^2 - kF_c^2)^2/(N_o - N_v)]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (0.02F_o^2)^2]^{1/2}$, N_o is the number of observations and N_v the number of variables.

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