Synthesis of Mono-, Di-, and Tri-arylgold(III) Complexes Using Organomercury Compounds – Synthesis of the First Aurated Schiff Bases

Jose Vicente*[a], María-Dolores Bermúdez*[b], Francisco-José Carrión[b], and Peter G. Jones[c]

Grupo de Química Organometálica Departamento de Química Inorgánica Facultad de Química, Universidad de Murcia[a],
Apdo 4021, E-30071 Murcia, Spain
Telefax: (internat.) +34-68-364143
E-mail: jvs@fcu.um.es
http://www.scc.um.es/gi/gqo

Grupo de Ciencia de Materiales e Ingeniería Metalúrgica, Departamento de Ingeniería de Materiales y Fabricación, Universidad de Murcia[b],
E-30203 Cartagena, Spain
Telefax: (internat.) +34-68-505310
E-mail: mdbo@plc.um.es

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig[c],
Postfach 3329, D-38023 Braunschweig, Germany
Telefax: (internat.) +49(0)531/391-5387
E-mail: p.jones@tu-bs.de

Received June 5, 1996

Key Words: Synthesis aryl complexes of gold(III) / Mercury(II) as transmetallating agent / X-ray crystal structure / Ketonylgold(III) complex

The formylarylmercury(II) complex [Hg{C_6H(CHO)-6-(OMe)$_3$-2,3,4}$_2$] reacts with 4-butylaniline (1:2) to give [Hg{C_6H(CH=N$C_6H_4C_4H_9$-4′)-6-(OMe)$_3$-2,3,4}$_2$] (**1**) by a condensation reaction. This complex reacts with $Me_4N[AuCl_4]$ (1:1) to give [Hg{C_6H(CH=N$C_6H_4C_4H_9$-4′)-6-(OMe)$_3$-2,3,4}Cl] (**2**) and the monoarylgold(III) compound *cis*-[Au{C_6H(CH=NC_6H_4-*n*Bu-4′)-6-(OMe)$_3$-2,3,4}Cl_2] (**3**). This complex reacts with PPh_3 (1:1) to give the adduct *cis*-[Au{C_6H(CH=NC_6H_4-*n*Bu-4′)-6-(OMe)$_3$-2,3,4}Cl_2(PPh_3)] (**4**) and with $AgClO_4$ (1:1) in acetone to give the ketonyl complex *cis*-[Au{C_6H(CH=NC_6H_4-*n*Bu-4′)-6-(OMe)$_3$-2,3,4}-{CH_2C(O)Me}Cl] (**5**). *cis*-$Me_4N[Au(C_6H_4NO_2$-2)$_2Cl_2$] reacts with [Hg{C_6H_3(N=NC_6H_4OMe-4′)-2-(OMe)-5}Cl] and Me_4NCl (1:1:1) to give *cis*-[Au{C_6H_3(N=NC_6H_4OMe-4′)-2-(OMe)-5}($C_6H_4NO_2$-2)$_2$] (**6**). Similarly, *cis*-Me_4N-[Au($C_6H_4CF_3$-2)$_2Cl_2$] (**7**), obtained by treating [Hg($C_6H_4CF_3$-2)$_2$] with $Me_4N[AuCl_4]$ and Me_4NCl (1:1:1), reacts with [Hg($C_6H_4CH_2NMe_2$-2)Cl] and Me_4NCl (1:1:1) to give the triarylgold(III) complex *cis*-[Au($C_6H_4CH_2NMe_2$-2)($C_6H_4CF_3$-2)$_2$] (**8**). This complex can also be obtained by treating *cis*-[Au($C_6H_4CH_2NMe_2$-2)Cl_2] with [Hg($C_6H_4CF_3$-2)$_2$] and Me_4NCl (1:1:1). The crystal structure of **3** reveals the presence of two independent molecules, in one of which the butylphenyl group is disordered. The geometry at the gold atom is square planar; distortions may be attributed to the narrow bite angle and steric repulsion between a chloride ligand and the *ortho*-methoxy group. The greater *trans* influence of the aryl ligand causes a great difference in Au–Cl bond lengths.

In spite of the facile metallation of arenes with $[AuCl_3]_2$[1], several attempts to orthometallate azobenzenes and related arenes have proved unsuccessful[2]. The presence of a coordinating substituent in the aromatic ring is postulated to inhibit orthometallation[3]; at present, this rule has only been infringed for a few aryl- and benzyl-substituted pyridines[4a–c]. Therefore orthometallation, which is one of the classic preparative reactions for aryl complexes of Pd, Pt, Ni, Ru, Os, Ir, Mn, Re, Sn, etc.[5] has been of little use in gold chemistry. We have overcome this difficulty by using orthometallated mercury compounds to prepare 2-(phenylazo)phenyl-[6] and 2-(dimethylaminomethyl)phenyl–gold(III) complexes[7]. Other authors have since found this method useful[4c,d]. However, this route cannot be used to obtain the related gold complexes from benzylideneanilines because, contrary to previous reports[8], mercuriation occurs in the aniline ring instead of the benzylic group[9]. In this paper we report the preparation of a benzylideneaniline mercuriated at the benzylic group, and its use to prepare the first aurated Schiff bases. Using this orthometallated complex, we present a new example of C–H activation of acetone by an orthometallated gold(III) complex and new data in favour of the mechanism we have proposed[10].

We have also used organomercury compounds to prepare functionalized aryl complexes of various metals[11–17]. In the case of gold(III) derivatives, the method has allowed us to prepare mono-[6] and di-homo-[12a] and -hetero[18]-aryl complexes, some containing orthometallated ligands. We show in this paper, for the first time, that arylmercury compounds can also be used to prepare triarylgold(III) complexes. Of this family of compounds, only polyhalophenyl complexes have previously been reported[19]; the two triaryl-

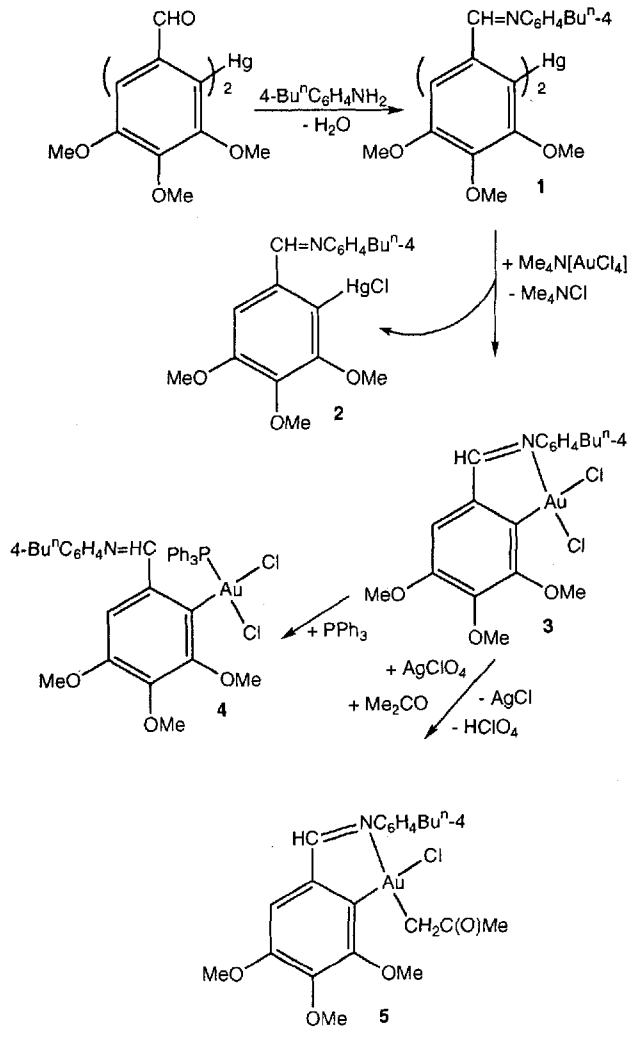
  0009–2940/96/1010–1301 $ 15.00+.25/0

gold(III) compounds reported in this paper are the first to contain other aryl groups. Some of our 2-(dimethylaminomethyl)phenyl–gold(III) complexes previously reported display a differential cytotoxicity similar to that of cisplatin[20]. We describe here a new member of this family of gold(III) complexes. Because we are interested in metal mesogens[6], we have used a *para*-butyl substituted aniline.

Results and Discussion

Condensation of *para*-butylaniline with the formylaryl complex $[Hg\{C_6H(CHO)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}_2]$[21,22] (2:1) gives the bis(benzylideneamine) complex $[Hg\{C_6H(CH{=}NC_6H_4\text{-}n\text{Bu-}4')\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}_2]$ (**1**) (see Scheme 1). We have reported a similar process using *n*-decylamine and *ortho*-phenylenediamine and the corresponding mercurial used to prepare palladium complexes[23]. This method is the only one that can be used, at present, to prepare mercurials with the mercury attached to the benzylic aryl group, because mercuration of imines $4\text{-}XC_6H_4CH{=}NC_6H_4Y\text{-}4'$ (X = H, NO_2, Y = H, Me, OMe, Cl, Br, I) occurs at the *N*-phenyl ring[9].

Scheme 1

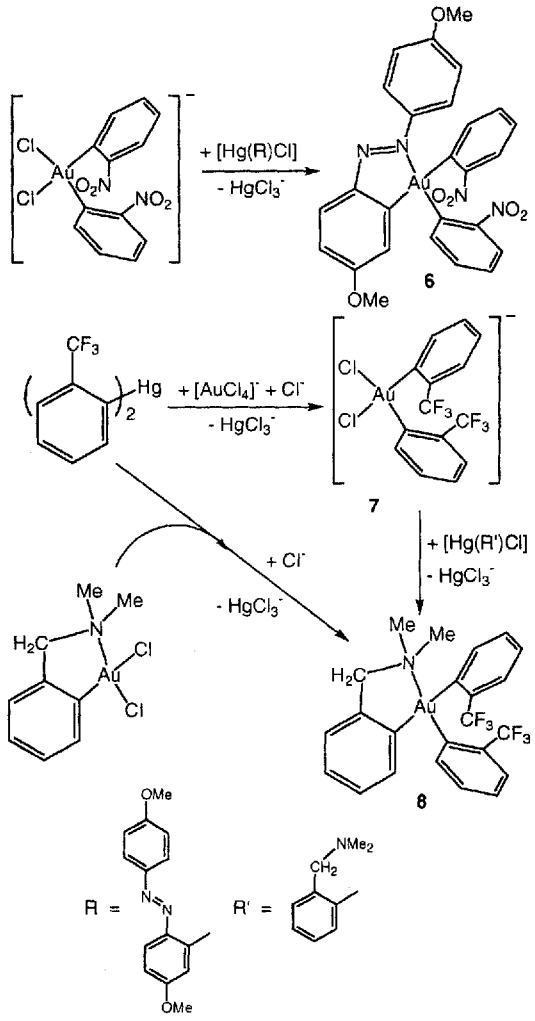


Complex **1** reacts with $Me_4N[AuCl_4]$ (1:1) to give $[Hg\{C_6H(CH{=}NC_6H_4\text{-}n\text{Bu-}4')\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}Cl]$ (**2**) and the first aurated Schiff base complex, *cis*-$[Au\{C_6H(CH{=}NC_6H_4\text{-}n\text{Bu-}4')\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}Cl_2]$ (**3**) (see Scheme 1). This reaction is similar to that using $[Hg(C_6H_4CH_2NMe_2\text{-}2)_2]$[24] but different from those starting from mercuriated azobenzenes[25] or nitrobenzene[26] because, in these cases, two aryl groups are transmetallated to give diarylgold(III) compounds even if a 1:1 molar ratio of reagents is used. Complex **3** can also be obtained by reaction between $Me_4N[AuCl_4]$ and **1** in a 2:1 molar ratio. In this case, $Me_4N[HgCl_3]$ is obtained as by-product.

Gold(III) complexes containing 2-arylazoaryl groups have shown their ability to deprotonate the methyl group of methylketones to give *C*-ketonylgold(III) complexes[10]. According to the mechanism we have proposed, this activation process only occurs when the N–Au bond is weak. Thus, all attempts to produce this kind of C–H activation with 2-(dimethylaminomethyl)phenyl have failed[27] as a consequence of its strong N–Au bond. Differentiated reactivity is also seen in the reaction of PPh_3 with $[Au(C_6H_4CH_2NMe_2\text{-}2)Cl_2]$ to give $[Au(C_6H_4CH_2NMe_2\text{-}2)Cl(PPh_3)]Cl$[24] whereas it reacts with $[Au(C_6H_4N{=}NPh\text{-}2)Cl_2]$ to give $[Au(C_6H_4N{=}NPh\text{-}2)Cl_2(PPh_3)]$[28]. To test the latter reaction as a criterion of the ability of an orthometallated gold(III) complex to deprotonate acetone [when reacted with $AgClO_4$, to give an acetonylgold(III) complex], we reacted **3** with PPh_3 and found that the N–Au bond is weak enough to be cleaved, giving the adduct *cis*-$[Au\{C_6H(CH{=}NC_6H_4\text{-}n\text{Bu-}4')\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}Cl_2(PPh_3)]$ (**4**) (see Scheme 1). Accordingly, **3** reacts with $AgClO_4$ (1:1) in acetone to give the acetonyl complex *cis*-$[Au\{C_6H(CH{=}NC_6H_4\text{-}n\text{Bu-}4')\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}\{CH_2C(O)Me\}Cl]$ (**5**). This underlines the relevance of the N–Au bond cleavage in the C–H activation process of methylketones.

We have demonstrated the utility of organomercury derivatives as transmetallating reagents to prepare functionalized mono- and di-homo- and -hetero-arylgold(III) complexes[6,11a,18]. To see whether the method can be used to prepare triaryl derivatives, we planned to prepare them by reacting diarylgold(III) complexes with arylmercurials. Thus, *cis*-$Me_4N[Au(C_6H_4NO_2\text{-}2)_2Cl_2]$ reacts with $[Hg\{C_6H_3(N{=}NC_6H_4OMe\text{-}4')\text{-}2\text{-}(OMe)\text{-}5\}Cl]$ and Me_4NCl (1:1:1) to give *cis*-$[Au\{C_6H_3(N{=}NC_6H_4OMe\text{-}4')\text{-}2\text{-}(OMe)\text{-}5\}(C_6H_4NO_2\text{-}2)_2]$ (**6**). To widen the scope of the method we prepared a new diarylgold(III) complex *cis*-$Me_4[Me_4N][Au(C_6H_4CF_3\text{-}2)_2Cl_2]$ (**7**) (see Scheme 2), by reacting $[Hg(C_6H_4CF_3\text{-}2)_2]$ with $Me_4N[AuCl_4]$ and Me_4NCl (1:1:1), and reacted it with $[Hg(C_6H_4CH_2NMe_2\text{-}2)Cl]$ and Me_4NCl (1:1:1) to give the triarylgold(III) complex *cis*-$[Au(C_6H_4CH_2NMe_2\text{-}2)(C_6H_4CF_3\text{-}2)_2]$ (**8**) (see Scheme 2). This complex can also be obtained by reacting *cis*-$[Au(C_6H_4CH_2NMe_2\text{-}2)(Cl_2)]$ with $[Hg(C_6H_4CF_3\text{-}2)_2]$ and Me_4NCl (1:1:1). Complexes **7** and **8** are the first *ortho*-trifluoromethylphenylgold(III) complexes and **6** and **8** the first triarylgold(III) complexes not to contain polyhalophenyl groups.

Scheme 2



Structure of Complexes

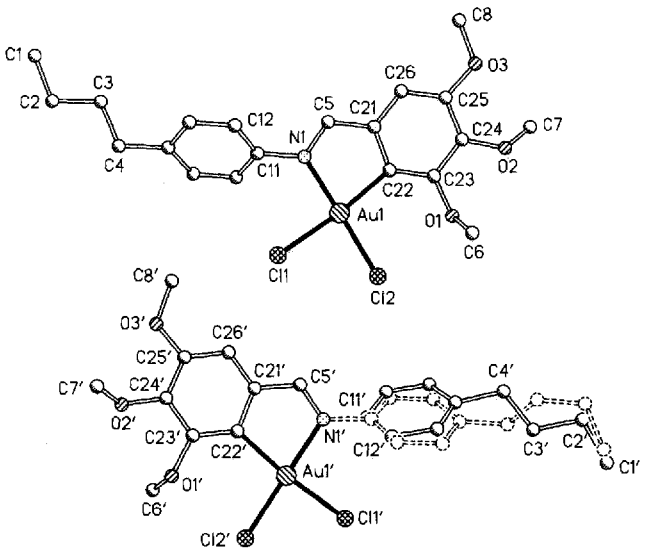
The organomercury complexes **1** and **2** and the aurated Schiff base **4** show bands at 1620–1615 (m) cm^{-1}, assignable to ν(C=N), whereas this absorption appears at slightly lower frequency (1610 cm^{-1}) in complexes **3** and **5**, probably due to the coordination of the imine nitrogen to the metallic center. One strong absorption at 1700 cm^{-1} in the ketonyl complex **5** and at 326 cm^{-1} in **2** are assignable to ν(C=O) and ν(Hg–Cl), respectively. Accordingly, the latter is not observed in **1**.

It is well established that bands in the 400–200 cm^{-1} region assignable to ν(Au–Cl) in square-planar gold(III) complexes are of value for structural diagnostics. Thus, in neutral complexes, ν(Au–Cl) *trans* to carbon tends to appear in the region 320–290 cm^{-1}, but as low as 280 cm^{-1} for anionic complexes[6,7,10,24–26,28,29]. The sequences of *trans* influence aryl > phosphane > N donor ligand determines that ν(Au–Cl) *trans* to P or N donor ligands lies at higher frequency than ν(Au–Cl) *trans* to carbon (by 13–25 cm^{-1}[7,28,30] and 45–65 cm^{-1}[6,7,24,28], respectively). Therefore, the bands observed in the region 280–312 cm^{-1} (310 in **3**, 305 in **4**, 312 in **5**, and 280 and 300 in **7**), at 315 in **4**, and at 360 cm^{-1} (in **3**) are assignable, respectively, to ν(Au–Cl) *trans* to the aryl, PPh_3, and the imine nitrogen. These assignments are consistent with the crystal structures of some related complexes. Thus, the crystal structure of [Au{C_6H(N=NPh-2)Cl_2(PPh_3)}] also shows the same *cis* geometry as **4**[7]. We have described crystal structures of three arylketonylgold(III) complexes[10,29e]. In all of them both carbon donor ligands are *cis*, as in **5**. The structures proposed for all complexes are shown in Schemes 1 and 2.

Complexes **4**, **6**–**8** slowly decompose in solution, thus precluding the recording of their $^{13}C\{^1H\}$-NMR spectra. The other NMR spectra [^1H (**1**–**6**, **8**), ^{13}C (**1**–**3**, **5**), ^{31}P (**4**), and ^{19}F (**7**, **8**)] show the expected set of resonances for the proposed structures (see Scheme 1).

Complex **7** behaves as a 1:1 electrolyte in acetone solution (Λ_M = 117 Ω^{-1} cm^2 mol^{-1}).

Figure 1. The two independent molecules of complex **3** in the crystal. H atoms are omitted for clarity. Both disorder components of the second (lower) molecule are shown[a]



[a] Bond lengths [Å] and angles [°] at Au (values for both molecules): Au(1)–N(1) 2.040(3), 2.057(3), Au(1)–C(22) 2.043(4), 2.042(4), Au(1)–Cl(2) 2.2739(11), 2.2669(11), Au(1)–Cl(1) 2.3457(11), 2.3586(11); N(1)–Au(1)–C(22) 81.41(14), 81.2(2), N(1)–Au(1)–Cl(2) 175.08(11), 176.42(11), C(22)–Au(1)–Cl(2) 98.93(12), 98.29(12), N(1)–Au(1)–Cl(1) 93.03(10), 93.04(10), C(22)–Au(1)–Cl(1) 169.03(12), 168.73(12), Cl(2)–Au(1)–Cl(1) 87.42(4), 88.04(4).

Crystal Structure of Complex 3

Complex **3** was studied by X-ray diffraction methods (Figure 1). There are two independent molecules in the asymmetric unit, of which one is disordered in the butylphenyl moiety; here we present values only for the ordered molecule (although those of the second molecule are not greatly different). Its geometry at the gold atom is square planar, distorted somewhat by the narrow N(1)–Au(1)–C(22) and Cl(2)–Au(1)–Cl(1) [81.41(14) and 87.42(4)°] and the wide N(1)–Au(1)–Cl(1) and C(22)–Au(1)–Cl(2) angles [93.03(10) and 98.93(12)°]. This distortion is different from that found in the related complex *cis*-[Au{C_6H_3(N=NC$_6H_4$Me-4')-2-(Me)-5}Cl_2][10].

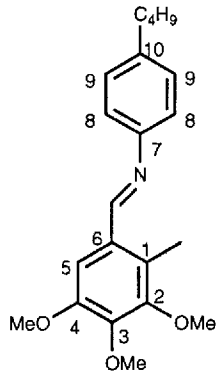
Here, the narrowing of the chelate "bite" angle [80.1(2)°] is accompanied by the widening of the N–Au–Cl bond angle [98.5(1)°] while the other two angles are near 90°. Repulsion between Cl(2) and the *ortho*-methoxy group in complex **3** (Cl1···O1 2.99 Å) could explain these differences. The greater *trans* influence of the aryl ligand compared to the imine ligand gives rise to a striking difference in Au–Cl bond lengths [Au(1)–Cl(1): 2.3457(11) Å, Au(1)–Cl(2): 2.2739(11) Å]. These distances are almost identical to those found in *cis*-[Au{C_6H_3(N=NC_6H_4Me-4′)-2-(Me)-5}Cl_2][10]. However, the Au–C [2.043(4) Å] and Au–N [2.040(3) Å] bond distances in **3** are, respectively, longer and shorter than those in the above-mentioned azophenyl complex [2.021(5), 2.069(4) Å][10].

We thank *Dirección General de Investigación Científica y Técnica* (PB-92-0982-C), *Fundación Cultural CAM* and the *Fonds der Chemischen Industrie* for financial support. F. J. C. is grateful to *Ministerio de Educación y Ciencia* (Spain) for a Grant.

Experimental

The NMR spectra, elemental analyses, conductance measurements in acetone and melting-point determinations were carried out as described elsewhere[13a]. IR spectra were recorded in Nujol mulls on a Nicolet Magna FT-550. Chemical shifts are referred to TMS [^{1}H, ^{13}C{^{1}H}], H_3PO_4 [^{31}P{^{1}H}] or $CFCl_3$ (^{19}F). Reactions were carried out at room temperature without special precautions against moisture unless otherwise stated. [Hg{C_6H(CHO)-6-(OMe)$_3$-2,3,4}$_2$][21], *cis*-Me_4N[Au($C_6H_4NO_2$-2)$_2Cl_2$][26], [Hg{C_6H_3-(N=NC_6H_4OMe-4′)-2-(OMe)-5}Cl][31], [Hg($C_6H_4CF_3$-2)$_2$][32] and [Hg($C_6H_4CH_2NMe_2$-2)Cl][33] were prepared as described. Scheme 3 shows the atom numbering used for NMR assignments.

Scheme 3



[Hg{C_6H(CH=N$C_6H_4C_4H_9$-4′)-6-(OMe)$_3$-2,3,4}$_2$] (**1**): To a solution of [Hg{C_6H(CHO)-6-(OMe)$_3$-2,3,4}$_2$] (410 mg, 0.70 mmol) in toluene (50 ml), 4-butylaniline was added (200 mg, 1.40 mmol) and the mixture stirred over molecular sieves for 24 h. Removal of the solvent to dryness and addition of CH_2Cl_2 (4 × 10 ml) gave a brown suspension that was filtered through $MgSO_4$ (anh.). Evaporation to ca. 5 ml and addition of Et_2O (25 ml) gave unreacted [Hg{C_6H(CHO)-6-(OMe)$_3$-2,3,4}$_2$] and **1** as a pale yellow oil (299 mg, 0.70 mmol). Yield (50%). – $C_{40}H_{48}HgN_2O_6$ (853.4): calcd. C 56.3, H 5.7, N 3.3; found C 55.8, H 5.2, N 3.1. – IR (Nujol): ν(C=N) = 1620 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, $^3J_{HH}$ = 8 Hz, 3H, Me), 1.32 (m, 2H, CH_2Me), 1.53 (m, 2H, $CH_2C_6H_4$), 2.52 (m, 2H, CH_2Et), 3.91 (s, 3H, OMe), 3.92 (s, 3H, OMe), 3.97 (s, 3H, OMe), 6.93, 6.98 (AB, $^3J_{HH}$ = 8 Hz, 4H, C_6H_4), 7.11 (s, 1H, 5-H), 8.64 (s, 1H, CH=N). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 13.8 (Me), 22.2 (CH_2), 33.8 (CH_2), 35.1 (CH_2), 56.1 (OMe), 60.8 (OMe)$_2$, 112.8 (C-5), 121.1, 128.8 (C-8, C-9), 138.8 (C-1), 140.5 (C-6), 145.0 (C-10), 148.0, 150.9, 152.7, 158.6 (C-2, C-3, C-4, C-7), 161.5 (CH=N).

[Hg{C_6H(CH=N$C_6H_4C_4H_9$-4′)-6-(OMe)$_3$-2,3,4}Cl] (**2**) *and cis*-[Au{C_6H(CH=NC_6H_4-*n*Bu-4′)-6-(OMe)$_3$-2,3,4}Cl_2] (**3**): To a solution of **1** (370 mg, 0.43 mmol) in CH_2Cl_2 (50 ml) solid Me_4N[$AuCl_4$] (180 mg, 0.43 mmol) was added and the mixture stirred for 24 h. The precipitate was separated by filtration through $MgSO_4$ (anh.) and the solution concentrated to 2 ml. Addition of Et_2O (10 ml) gave **3** as a yellow-orange precipitate (193 mg, 0.32 mmol). Evaporation of the filtrate to dryness and addition of *n*-hexane (10 ml) gave **2** as a cream coloured solid (143 mg, 0.26 mmol). – **2**: M.p. 125°C, yield 60%. – IR (Nujol): ν(C=N) = 1615; ν(Hg–Cl) = 326 cm^{-1}. – $C_{20}H_{24}ClHgNO_3$ (562.5): calcd. C 42.7, H 4.3, N 2.5; found C 42.5, H 4.4, N 2.5. – ^{1}H NMR ($CDCl_3$): δ = 0.94 (t, $^3J_{HH}$ = 8 Hz, 3H, Me), 1.36 (sext, $^3J_{HH}$ = 8 Hz, 2H, CH_2Me), 1.61 (quint, $^3J_{HH}$ = 8 Hz, 2H, CH_2Et), 2.63 (t, $^3J_{HH}$ = 8 Hz, 2H, $CH_2C_6H_4$), 3.93 (s, 3H, OMe), 3.95 (s, 3H, OMe), 3.96 (s, 3H, OMe), 6.99 (s, 1H, H-5), 7.23, 7.36 (AB, $^3J_{HH}$ = 8 Hz, 4H, C_6H_4), 8.70 (s, 1H, CH=N). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 14.0 (Me), 22.4, 33.7, 35.3 (CH_2), 56.4, 61.0, 61.2 (OMe), 113.0 (C-5), 121.5, 129.5 (C-8, C-9), 135.2 (C-1), 142.4, 143.6 (C-6, C-10), 145.9, 153.3, 154.5, 156.7 (C-2, C-3, C-4, C-7), 157.9 (CH=N). – **3**: M.p. 195°C (dec.), yield 75%. – IR (Nujol): ν(C=N) = 1610; ν(Au–Cl) = 360, 310 cm^{-1}. – $C_{20}H_{24}AuCl_2NO_3$ (594.3): calcd. C 40.4, H 4.1, Au 33.1, N 2.4; found C 40.7, H 3.9, Au 33.3, N 2.6. – ^{1}H NMR ($CDCl_3$): δ = 0.93 (t, $^3J_{HH}$ = 8 Hz, 3H, Me), 1.36 (sext, $^3J_{1111}$ = 8 Hz, 2H, CH_2Me), 1.60 (quint, $^3J_{HH}$ = 8 Hz, 2H, CH_2Et), 2.64 (t, $^3J_{HH}$ = 8 Hz, 2H, $CH_2C_6H_4$), 3.88 (s, 3H, OMe), 3.89 (s, 3H, OMe), 4.00 (s, 3H, OMe), 7.04 (s, 1H, C_6H), 7.26 (m, 4H, C_6H_4), 8.32 (s, 1H, CH=N). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 14.0 (Me), 22.5 (CH_2Me), 33.4 (CH_2Et), 35.4 ($CH_2C_6H_4$), 56.6, 61.7, 62.7 (OMe), 111.4 (C-5), 123.6 (C-8), 124.4 (C-9), 137.9, 139.7, 143.4 (C-1, C-6, C-10), 143.9, 145.0, 147.4, 151.8 (C-2, C-3, C-4, C-7), 153.7 (CH=N). – Single crystals of **3** were grown from CH_2Cl_2/*n*-hexane by the liquid diffusion method.

cis-[Au{C_6H(CH=NC_6H_4-*n*Bu-4′)-6-(OMe)$_3$-2,3,4}Cl_2(PPh_3)] (**4**): To a solution of **3** (200 mg, 0.33 mmol) in CH_2Cl_2 (50 ml) solid PPh_3 (89 mg, 0.34 mmol) was added and the mixture stirred for 12 h. Removal of the solvent to dryness and addition of Et_2O (10 ml) gave **4** as an orange solid (181 mg, 0.21 mmol). M.p. 85°C (dec.), yield 64%. – IR (Nujol): ν(C=N) = 1620; ν(Au–Cl) = 315, 305 cm^{-1}. – $C_{38}H_{39}AuCl_2NO_3P$ (856.6): calcd. C 53.3, H 4.6, Au 23.0, N 1.6; found C 53.2, H 4.8, Au 23.5, N 1.7. – ^{1}H NMR ($CDCl_3$): δ = 0.95 (t, $^3J_{HH}$ = 7 Hz, 3H, Me), 1.40 (m, 2H, CH_2Me), 1.64 (m, 2H, CH_2Et), 2.64 (t, $^3J_{HH}$ = 7 Hz, 2H, $CH_2C_6H_4$), 3.95 (s, 3H, OMe), 3.96 (s, 3H, OMe), 3.98 (s, 3H, OMe), 7.00 (s, 1H, H-5), 7.49 (m, 19H, C_6H_4 + PPh_3), 8.71 (s, 1H, CH=N). – ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 27.1 (s).

cis-[Au{C_6H(CH=NC_6H_4-*n*Bu-4′)-6-(OMe)$_3$-2,3,4}{CH_2C(O)Me}Cl] (**5**): To a solution of **3** (100 mg, 0.16 mmol) in acetone (30 ml) solid $AgClO_4$ (33 mg, 0.16 mmol) was added and the mixture stirred for 2 h. Removal of the solvent to dryness and addition of CH_2Cl_2 (20 ml) gave a suspension that was filtered through $MgSO_4$ (anh.). The yellow solution was evaporated to dryness and Et_2O/*n*-hexane (1:2, 15 ml) added to give **5** as a yellow solid (60 mg, 0.1 mmol). M.p. 130°C (dec.), yield 60%. – IR (Nujol): ν(C=O) = 1700; ν(C=N) = 1615; ν(Au–Cl) = 312 cm^{-1}. – $C_{23}H_{29}AuClNO_4$ (615.9): calcd. C 44.8, H 4.7, Au 32.0, N 2.3; found C 44.5, H 4.6, Au 32.5, N 2.0. – ^{1}H NMR ($CDCl_3$): δ =

0.93 (t, $^3J_{HH}$ = 8 Hz, 3H, Me), 1.38 (sext, $^3J_{HH}$ = 8 Hz, 2H, CH_2Me), 1.60 (m, 2H, CH_2Et), 2.32 (s, 3H, MeCO), 2.65 (t, $^3J_{HH}$ = 8 Hz, 2H, $CH_2C_6H_4$), 3.84 (s, 3H, OMe), 3.89 (s, 3H, OMe), 3.96 (s, 3H, OMe), 4.14 (s, 2H, CH_2CO), 7.02 (s, 1H, H-5), 7.18, 7.23 (AB, $^3J_{HH}$ = 7.5 Hz, 4H, C_6H_4), 8.40 (s, 1H, CH=N). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 14.0 (Me), 22.5 (CH_2Me), 29.5 (*Me*CO), 31.6 (CH_2CO), 33.5 (CH_2Et), 35.3 ($CH_2C_6H_4$), 56.5, 61.2, 61.6 (OMe), 111.6 (C-5), 123.5 (C-8), 128.6 (C-9), 136.0 (C-1), 139.5 (C-6), 143.5 (C-10), 143.9 (C-2), 148.2 (C-3), 153.1 (C-4), 156.6 (C-7), 175.5 (C=N), 209.0 (C=O).

cis-[Au{C_6H_3(N=NC_6H_4OMe-4′)-2-(OMe)-5}($C_6H_4NO_2$-2)$_2$] (**6**): To a solution of *cis*-Me_4N[Au($C_6H_4NO_2$-2)$_2Cl_2$] (200 mg, 0.35 mmol) in EtOH (50 ml), solid [Hg{C_6H_3(N=NC_6H_4OMe-4′)-2-(OMe)-5}Cl] (167 mg, 0.35 mmol) and Me_4NCl (38.4 mg, 0.35 mmol) were added and the mixture refluxed for 15 h. Evaporation of the solvent and extraction of the residue with CH_2Cl_2 (3 × 5 ml) gave a yellow solution and a white precipitate that was filtered through $MgSO_4$ (anh.). The solution was concentrated to 1 ml and Et_2O/*n*-hexane (1:5, 20 ml) added. Upon cooling to 0°C, **6** was obtained as an orange-yellow solid (125.6 mg, 0.18 mmol). M.p. 123°C (dec.), yield 52%. – $C_{26}H_{21}AuN_4O_6$ (682.4): calcd. C 45.8, H 3.1, N 8.2, Au 28.9; found C 45.8, H 3.5, N 8.1, Au 28.9. – ^1H NMR ($CDCl_3$): δ = 4.04 (s, 3H, OMe), 4.16 (s, 3H, OMe), 7.36–7.98 (m, 15H, aromatic protons).

Me_4N[*cis*-Au($C_6H_4CF_3$-2)$_2Cl_2$] (**7**): To a solution of Me_4N[$AuCl_4$] (180 mg, 0.44 mmol) in acetone (20 ml), solid [Hg($C_6H_4CF_3$-2)$_2$] (200 mg, 0.44 mmol) and Me_4NCl (46.4 mg, 0.44 mmol) were added and the mixture refluxed until completely colourless (5 h). Removal of the solvent and extraction with CH_2Cl_2 (3 × 5 ml) gave a colourless solution and a white precipitate that was filtered through $MgSO_4$ (anh). Evaporation of the solvent to ca. 1 ml and addition of Et_2O (20 ml) gave **7** as a white solid (167 mg, 0.26 mmol). M.p. 115°C (dec.), yield 60%. Λ_M = 117 Ω^{-1} cm^2 mol^{-1} (5.0×10^{-4} M in acetone). – ^{19}F NMR ($CDCl_3$): δ = –61.5. – $C_{18}H_{20}AuCl_2F_6N$ (632.2): calcd. C 34.2, H 3.2, Au 31.1, N 2.2; found C 33.9, H 3.5, Au 31.7, N 2.0.

cis-[Au($C_6H_4CH_2NMe_2$-2)($C_6H_4CF_3$-2)$_2$] (**8**). – *Method a:* To a solution of **7** (100 mg, 0.16 mmol) in acetone (50 ml), solid [Hg($C_6H_4CH_2NMe_2$-2)Cl] (59 mg, 0.16 mmol) and Me_4NCl (17 mg, 0.16 mmol) were added and the suspension refluxed for 6 h. The solvent was evaporated to dryness, the residue extracted with CH_2Cl_2 (3 × 5 ml) and the suspension filtered through $MgSO_4$ (anh.). Concentration to ca. 1 ml, cooling at 0°C and slow addition of *n*-hexane gave **8** as a white precipitate (41 mg, 0.06 mmol). M.p. 112°C, yield 40%. – ^1H NMR ($CDCl_3$): δ = 3.1 (s, 6H, Me), 4.2 (s, 2H, CH_2), 6.7–7.8 (m, 12H, C_6H_4). – ^{19}F NMR ($CDCl_3$): δ = –64.1, –65.2. – $C_{23}H_{20}AuF_6N$ (621.4): calcd. C 44.5, H 3.2, Au 31.7, N 2.2; found C 44.1, H 3.5, Au 32.1, N 2.0.

Method b: To a solution of *cis*-[Au($C_6H_4CH_2NMe_2$-2)Cl_2] (60 mg, 0.15 mmol) in EtOH (25 ml) solid [Hg($C_6H_4CF_3$-2)$_2$] (76 mg, 0.15 mmol) and Me_4NCl (16 mg, 0.15 mmol) were added and the mixture refluxed for 24 h. Evaporation of the solvent, extraction of the residue with Et_2O (3 × 5 ml) and filtration through $MgSO_4$ anh. gave a colourless solution. Concentration to 2 ml and slow addition of n-hexane (15 ml) gave **8** as a white solid (29 mg, 0.05 mmol). Yield: 31%.

X-ray Structure Determination of Compound **3**. – $C_{20}H_{24}AuCl_2NO_3$, space group $P\bar{1}$, a = 11.8494(14), b = 12.192(2), c = 16.014(2) Å, α = 77.672(10), β = 73.906(10), γ = 68.763(8)°, V = 2055.3 Å^3, Z = 4, λ(Mo-K_α) = 0.71073 Å, μ = 7.4 mm^{-1}, F(000) = 1152, D_x = 1.921 Mg m^{-3}, T = –100°C. An orange prism ca. 0.7 × 0.25 × 0.15 mm was mounted in inert oil. 9700 intensities were measured on a Siemens P4 diffractometer to $2\Theta_{max}$ = 55°, of which 9371 were unique (R_{int} = 0.023). An absorption correction based on ψ-scans was performed, with transmission factors 0.533–0.971. The structure was solved by the heavy-atom method and refined anistropically on F^2 (program SHELXL-93, G. M. Sheldrick, University of Göttingen). H atoms were included using a riding model or rigid methyl groups. In one of the two independent molecules the butylphenyl group is disordered over two positions (Figure 1) and the dimensions of the disorder components should be interpreted with caution. The final $wR(F^2)$ was 0.050, with conventional $R(F)$ = 0.026, for 460 parameters and 490 restraints (to light atom displacement parameters and disorder components); S = 0.87, max. Δρ = 0.92 e Å^{-3}. – Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, and can be obtained on quoting the reference number CSD-405324 and a full literature citation.

[1] [1a] M. S. Karash, H. S. Isbell, *J. Am. Chem. Soc.* **1931**, *53*, 3053. – [1b] M. S. Karash, T. M. Beck, *J. Am. Chem. Soc.* **1934**, *56*, 2057.

[2] [2a] R. Hüttel, A. Konietzny, *Chem. Ber.* **1973**, *106*, 2098. – [2b] F. Calderazzo, D. Belli Dell'Amico, *J. Organomet. Chem.* **1974**, *C59*, 76. – [2c] P. K. Monaghan, R. J. Puddephatt, *Inorg. Chim. Acta* **1975**, *15*, 231.

[3] P. W. J. de Graaf, J. Boersma, G. J. M. van der Kerk, *J. Organomet. Chem.* **1976**, *105*, 399.

[4] [4a] M. A. Cinellu, A. Zucca, S. Stoccoro, G. Minghetti, M. Manassero, M. Sansoni, *J. Chem. Soc., Dalton Trans.* **1995**, 2865. – [4b] C.-W. Chan, W.-T. Wong, C.-M. Che, *Inorg. Chem.* **1994**, *33*, 1266. – [4c] E. C. Constable, T. A. Leese, *J. Organomet. Chem.* **1989**, 363. – [4d] E. C. Constable, R. P. G. Henney, T. A. Lecse, D. A. Tocher, *J. Chem. Soc., Dalton Trans.* **1990**, 443.

[5] I. Omae, *Organometallic Intramolecular-coordination Compounds*, Elsevier, **1986**.

[6] J. Vicente, M. D. Bermúdez, F. J. Carrión, G. Martínez-Nicolás, *J. Organomet. Chem.* **1994**, *480*, 103 and references therein.

[7] J. Vicente, M. D. Bermúdez, J. Escribano, M. P. Carrillo, P. G. Jones, *J. Chem. Soc., Dalton Trans.* **1990**, 3083 and references therein.

[8] H. B. Sing, W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.* **1985**, 821.

[9] K. Ding, Y. Wu, H. Hu, L. Shen, X. Wang, *Organometallics* **1992**, *11*, 3849.

[10] J. Vicente, M. D. Bermúdez, M. P. Carrillo, P. G. Jones, *J. Chem. Soc., Dalton Trans.* **1992**, 1975, and references therein.

[11] Gold(III) complexes, see for example: [11a] J. Vicente, M. D. Bermúdez, F. J. Carrión, P. G. Jones, *J. Organomet. Chem.* **1996**, *508*, 53. – [11b] J. Vicente, M. D. Bermúdez, M. J. Sánchez-Santano, J. Payá, *Inorg. Chim. Acta* **1990**, *174*, 53, and references therein.

[12] Gold(I) complexes, see for example: J. Vicente, A. Arcas, P. G. Jones, J. Lautner, *J. Chem. Soc., Dalton Trans.* **1990**, 451, and references therein.

[13] Palladium(II) complexes, see for example: [13a] J. Vicente, J. A. Abad, R. Fernández-de-Bobadilla, P. G. Jones, M. C. Ramírez de Arellano, *Organometallics* **1996**, *15*, 24. – [13b] J. Vicente, A. Arcas, M. V. Borrachero, E. Molíns, C. Miravitlles, *J. Organomet. Chem.* **1989**, *359*, 127, and references therein.

[14] Platinum(II) complexes, see for example: [14a] J. Vicente, J. A. Abad, F. Teruel, J. Garcia, *J. Organomet. Chem.* **1988**, *345*, 233. – [14b] J. Vicente, M. T. Chicote, J. Martin, P. G. Jones, C. Fittschen, G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.* **1986**, 2215.

[15] Rhodium(III) complexes, see for example: [15a] J. Vicente, J. A. Abad, F. J. Lahoz, F. J. Plou, *J. Chem. Soc., Dalton Trans.* **1990**, 1459. – [15b] J. Vicente, J. Martín, X. Soláns, M. Font-Altaba, *Organometallics* **1989**, *8*, 357, and references therein.

[16] Thallium(III) complexes, see for example: J. Vicente, J. A. Abad, J. F. Gutierrez-Jugo, P. G. Jones, *J. Chem. Soc., Dalton Trans.* **1989**, 2241.

[17] Tin(IV) complexes, see for example: J. Vicente, M. T. Chicote, M. C. Ramirez-de-Arellano, P. G. Jones, *J. Chem. Soc., Dalton Trans.* **1992**, 1839, and references therein.
[18] J. Vicente, M. D. Bermúdez, J. Escribano, *Organometallics* **1991**, *10*, 3380, and references therein.
[19] See for example: [19a] R. Usón, A. Laguna, M. D. Villacampa, *Inorg. Chim. Acta* **1986**, *122*, 81. – [19b] A. Laguna, M. Laguna, J. Jimenez, A. J. Fumanal, *J. Organomet. Chem.* **1990**, *396*, 121. – [19c] R. Usón, A. Laguna, M. Laguna, J. Jimenez, M. E. Durana, *Inorg. Chim. Acta* **1990**, *168*, 89. – [19d] R. Usón, A. Laguna, *Coord. Chem. Rev.* **1986**, *70*, 1. – [19e] H. Schmidbaur, *Gmelin Handbook der Anorganischen Chemie, Organogold Compounds*, Springer, Berlin, **1980**.
[20] R. V. Parish, B. P. Howe, J. P. Wright, J. Mack, R. G. Pritchard, R. G. Buckley, A. M. Elsome, S. P. Fricker, *Inorg. Chem.* **1996**, *35*, 1659.
[21] J. Vicente, J. A. Abad, A. Sandoval, P. G. Jones, *J. Organomet. Chem.* **1992**, *434*, 1.
[22] T. M. Sharp, *J. Chem. Soc.* **1937**, 852.
[23] J. Vicente, J. A. Abad, J. Gil-Rubio, P. G. Jones, E. Bembenek, *Organometallics* **1993**, *12*, 4151.
[24] J. Vicente, M. T. Chicote, M. D. Bermúdez, *J. Organomet. Chem.* **1984**, *268*, 191.
[25] J. Vicente, M. T. Chicote, M. D. Bermúdez, X. Soláns, M. Font Altaba, *J. Chem. Soc., Dalton Trans.* **1984**, 557.
[26] J. Vicente, M. T. Chicote, A. Arcas, M. Artigao, *Inorg. Chim. Acta* **1982**, *65*, L251.
[27] J. Vicente, M. D. Bermúdez, M. T. Chicote, M. J. Sánchez-Santano, *J. Chem. Soc., Dalton Trans.* **1990**, 1945.
[28] J. Vicente, M. T. Chicote, M. D. Bermúdez, *Inorg. Chim. Acta* **1982**, *63*, 35.
[29] [29a] J. Vicente, M. T. Chicote, M. D. Bermudez, M. J. Sánchez-Santano, P. G. Jones, C. Fittschen, G. M. Sheldrick, *J. Organomet. Chem.* **1986**, *310*, 401. – [29b] J. Vicente, M. T. Chicote, M. D. Bermúdez, M. J. Sánchez-Santano, P. G. Jones, *J. Organomet. Chem.* **1988**, *354*, 381. – [29c] J. Vicente, M. D. Bermúdez, M. T. Chicote, M. J. Sánchez-Santano, *J. Organomet. Chem.* **1989**, *371*, 129. – [29d] J. Vicente, M. D. Bermúdez, M. T. Chicote, M. J. Sánchez-Santano, *J. Organomet. Chem.* **1990**, *381*, 285. – [29e] J. Vicente, M. D. Bermúdez, M. P. Carrillo, P. G. Jones, *J. Organomet. Chem.* **1993**, *456*, 305.
[30] J. Vicente, A. Arcas, M. Mora, X. Solans, M. Font-Altaba, *J. Organomet. Chem.* **1986**, *309*, 369.
[31] P. V. Roling, D. D. Kirt, J. L. Dill, S. Hall, *J. Organomet. Chem.* **1976**, *116*, 39.
[32] A. N. Nesmeyanov, *Selected Works in Organic Chemistry*, Pergamon Press, London, **1963**.
[33] A. F. M. J. van der Ploeg, C. E. M. van der Kolk, G. van Koten, *J. Organomet. Chem.* **1981**, *21*, 283.

[96118]