Synthesis and Reactivity of Some Nitroaryl Complexes of Hg^{II} and Au^{III} – Synthesis of a Substituted Biphenyl by C–C Coupling – Crystal Structure of $[Hg(C_6H_4NO_2\text{-}3,O\mathit{n}Bu\text{-}6)_2]$

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Received June 26, 1996

Key Words: Gold / Mercury / Nitroaryl / Transmetallation / Biaryl / C–C Coupling

4-Butoxynitrobenzene reacts with $[Hg(O_2CCF_3)_2]$ and LiCl to give [Hg(R)Cl] [R = $C_6H_3NO_2$-3,O*n*Bu-6 (**1**)] which is symmetrized by Me_4NCl to give $[HgR_2]$ (**2**), the crystal structure of which has been determined. The reaction of **2** with $Me_4N[AuCl_4]$ affords $Me_4N[Au(R)Cl_3]$ (**3**) by a facile transmetallation process. Complex **3** reacts with PPh_3 (1:1) to give *cis*-$[Au(R)(PPh_3)Cl_2]$ (**4**). The diaryl complex $[\overline{Au(C_6H_4N=N}\text{-}Ph\text{-}2)(R)Cl]$ (**5**) is obtained by reaction of **3** with $[Hg(C_6H_4N=NPh\text{-}2)_2]$ through a second transmetallation reaction. Complex **5** and PPh_3 (1:1) give $[AuClPPh_3]$ and the C–C coupling biphenyl $RC_6H_4N=NPh$-2 (**6**).

Introduction

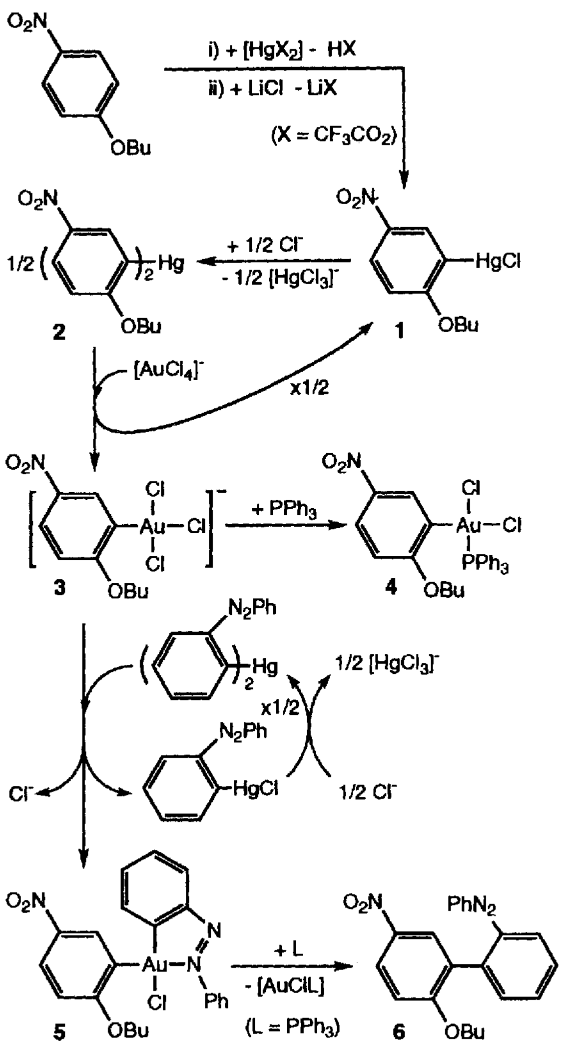
Only a limited number of nitroaryl complexes have been reported, because the usual transmetallating agents, the lithium or magnesium derivatives, are unknown or unstable[1]. However, the interest in the synthesis of this type of complexes is well documented, with reports of transmetallation using organo-lithium or -tin compounds[2], direct metallation of some nitroarenes[3], oxidative addition of nitroaryl derivatives to low-valent metal complexes[4], or reaction of a halometal complex with arylhydrazinium salts[5]. Very recently even direct nitration of aryl complexes has been reported[6]. However, we have developed the most general synthetic method to prepare nitroaryl complexes, using organomercury compounds as transmetallating agents[7]. These mercurials are very stable and easily prepared[8]. In particular, we have reported the synthesis of *o*-, *m*-, and *p*-nitrophenylgold(I) complexes[9] but only *o*-nitrophenylgold(III) species[10]. In this paper we report the mercuriation of 4-butoxynitrobenzene, the symmetrization of the resulting haloarylmercurial and the synthesis and reactivity of the arylgold(III) complexes prepared by transmetallation reactions using these mercurials.

Results and Discussion

No reaction takes place when 4-butoxynitrobenzene is refluxed in EtOH with $[Hg(O_2CMe)_2]$. However, using the more electrophilic reagent, $[Hg(O_2CCF_3)_2]$, it is possible to prepare $[Hg(C_6H_3NO_2\text{-}3,\ O\mathit{n}Bu\text{-}6)Cl]$ (**1**) (see Scheme 1). Attempts to metallate 4-butoxynitrobenzene with $[PdCl_2(NCMe)_2]$ or $[Pd(O_2CMe)_2]$ were unsuccessful. Reaction of **1** with the symmetrizing agent NaI led to decomposition, while the addition of excess Me_4NCl gave the diarylmercurial $[Hg(C_6H_3NO_2\text{-}3,O\mathit{n}Bu\text{-}6)_2]$ (**2**).

Addition of **2** and Me_4NCl to an acetone solution of $Me_4N[AuCl_4]$ in 1:2:2 molar ratio gives the monoaryl anionic species $Me_4N[Au(C_6H_3NO_2\text{-}3,O\mathit{n}Bu\text{-}6)Cl_3]$ (**3**) (see Scheme 1) which is the only gold(III) complex isolated even when an excess of the organomercury derivative is employed. This is in contrast with the results obtained when bis(*o*-nitrophenyl)mercury was reacted with the same gold(III) complex; a *cis*-diaryl species $Me_4N[Au(R)_2Cl_2]$ was obtained even if a 1:1 molar ratio was used[11a]. Similarly, reaction of bis(*o*-trifluoromethylphenyl)mercury with Me_4NCl and $Me_4N[AuCl_4]$ in 1:1:1 molar ratio gives the corresponding $Me_4N[Au(R)_2Cl_2]$ species[11b]. The presence

Scheme 1



of Me_4NCl in the reaction mixture is required if both R groups of the mercurial are to be transmetallated, because the product of the first transmetallation, the chloroarylmercury compound **1**, requires Cl^- to be symmetrized to **2** (see Scheme 1). Alternatively, complex **3** can also be synthesized by reaction of $Me_4N[AuCl_4]$ with the chloroarylmercurial **1** in the presence of Me_4NCl, but the method with the best yield, described in the experimental section, utilizes the diarylmercury complex **2** as transmetallating reagent.

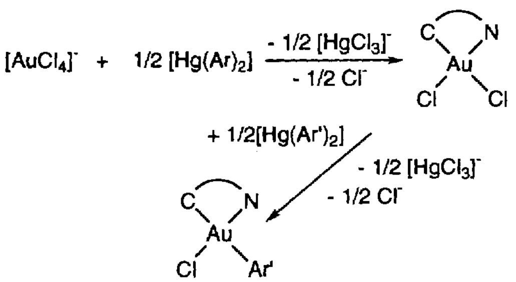
Complex **3** slowly decomposes to metallic gold when kept as a solid in air and at room temperature. It is also unstable in solution, where the decomposition process is faster. The only previously reported *m*-nitroarylgold(III) complex is the one obtained by an auration reaction of *o*-nitrophenol with $[AuCl_3]_2$ which is reported to yield $[Au(C_6H_3NO_2\text{-}3,OH\text{-}4)Cl_2(HOC_6H_4NO_2\text{-}4)]$[3a].

When PPh_3 is added to a solution of **3** (1:1) formation of Me_4NCl and the neutral adduct *cis*-$[Au(C_6H_3NO_2\text{-}3,O\textit{n}Bu\text{-}6)Cl_2(PPh_3)]$ (**4**) takes place. After 12 h the reaction is complete and quantitative. Attempts to prepare new complexes containing oxygen donor ligands from complex **3** failed to give any stable species. Thus, **3** reacts with Tl(acac) in acetone to give a mixture of products which decompose in solution and with NaOPh metallic gold is formed even at low temperature. We have recently reported some acetylacetonato, phenoxo and hydroxo complexes containing the *o*-nitrophenyl group, which stabilizes these species because of its strong C–Au bond[12]. We have also shown that *o*-nitrophenylgold(I) complexes are much more stable than the corresponding *m*- and *p*-nitrophenyl derivatives[9].

Complex **3** reacts with $[Hg(C_6H_4N{=}NPh\text{-}2)_2]$ to give the mixed diarylcomplex $[Au(C_6H_4N{=}NPh\text{-}2)(C_6H_3NO_2\text{-}3,O\textit{n}Bu\text{-}6)Cl]$ (**5**), where the chelating arylazoaryl ligand stabilizes the complex in the solid state, although it slowly reduces **5** to metallic gold when left in solution. This fact, together with the high solubility of **5** in organic solvents, leads to a poor yield.

Complex (**5**) belongs to a class of gold(III) complexes of the general formula $[Au(\eta^2\text{-}C\ N)(\eta^1\text{-}Ar)Cl]$ previously described by us, where C N = $C_6H_4N{=}NPh\text{-}2$ and Ar = $C_6H_4N{=}NPh\text{-}2$[13a], C_6F_5[13b], $C_6H_4NO_2\text{-}2$[13a], or C N = $C_6H_4CH_2NMe_2\text{-}2$ and Ar = $C_6H_4CH_2NMe_2\text{-}2$[13c], $C_6H_4N{=}NPh\text{-}2$[13d], Ph[13e], C_6F_5[13f], $C_6H_4NO_2\text{-}2$[13g], which were all prepared following the synthetic route depicted in Scheme 2. The synthesis of **5** consitutes the first example in which the usual order of transmetallation is reversed. Addition of PPh_3 to **5** (1:1) gives, through a reductive elimination process, $[AuCl(PPh_3)]$ and the corresponding biphenyl $PhN_2C_6H_3OBu\text{-}2,NO_2\text{-}5$ (**6**) through a C–C coupling process already described by us for the synthesis of other biphenyls[14a].

Scheme 2



Spectroscopic Properties

A strong band at 335 cm^{-1} in the IR spectrum of **1** is assignable to ν(HgCl) because it is not present in the spectrum of **2** and appears where other [Hg(R)Cl] complexes usually absorb[14b]. The strong band that appears at 840 cm^{-1} in the starting material 4-butoxynitrobenzene, typical of a *p*-disubstituted phenyl ring, is not present in the spectra of **1** and **2**, thus confirming the metallation.

Trichlorogold(III) complex **3** shows bands at 355, 290, and 280 cm^{-1} assignable to ν(Cl–Au–Cl) sym. and asym., and to ν(AuCl) *trans* to carbon, respectively, and are in agreement with its anionic nature. The two bands observed at 315 and 300 cm^{-1} in complex **4** are assigned to ν(AuCl) *trans* to PPh_3 and *trans* to carbon, respectively, according to the greater *trans* influence of aryl than phosphine ligands. All these ν(AuCl) assignments are ascertained by previous data[10a,11,13d,e,f,g,15].

All complexes show bands at 1330–1340 cm^{-1} and around 1510 cm^{-1} which have been shown to correspond to $\nu_{sym}(NO_2)$ and $\nu_{asym}(NO_2)$, respectively[16].

Complexes **4** and **5** show strong absorptions at 690 cm^{-1} assignable to monosubstituted aryl rings, arising from the phosphane ligand in **4** and the free phenyl ring of the arylazoaryl group in **5**.

The ^{1}H-NMR spectra of all compounds exhibit the expected sets of resonances. ^{1}H-NMR spectra of **4** and **5** at room temperature show non-equivalent O-CH_2 protons, implying hindered rotation of the butoxy group. Variable temperature ^{1}H-NMR spectra were recorded for complex **5**, but the non-equivalence was observed at all temperatures (between 50°C and −50°C). To assign the signals of the ^{13}C-NMR spectrum of **1** and **2** we used the values for $[Hg(C_6H_4NO_2\text{-}2)Cl]$ and $[Hg(C_6H_4NO_2\text{-}2)_2]$ and the concept of additivity of substituent effects. The instability of **3** and **5** precludes the observation of signals of some quaternary carbons.

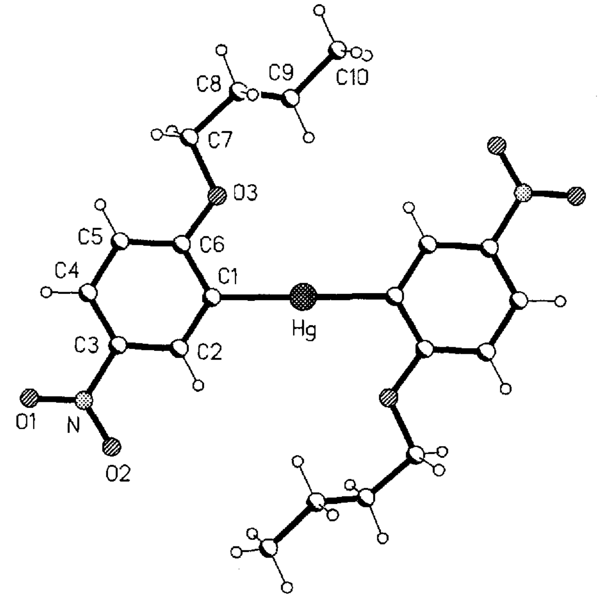
Structure of Complex 2

The complex displays inversion symmetry; as a consequence, the coordination at mercury is exactly linear and the aryl groups are coplanar. The C–Hg bond distances [2.068(3) Å] are similar to those in other aryl mercury(II) compounds whose crystal structures have been solved with similar accuracy[14b,17a–b]. The presence of one or two *ortho* substituents sometimes leads to a rotation of the two aryl planes relative to one antoher[17b–d]. The intramolecular Hg···O(3) contact is 3.015(2) Å which is much longer than that observed in $[\overline{HgCl\{C_6HC(O)}O\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}]$ [2.573(4) Å] where a weak Hg···O bond is postulated[14b].

No significant differences in C–C bond distances in the aryl groups are observed [1.396(5)–1.379(5) Å] in spite of the presence of two mutually *trans* groups, each with different mesomeric effects and essentially co-planar with the aromatic ring [interplanar angles 5° to the nitro and 2° to the $-OCH_2-$ group]; thus some degree of $\pi(\text{aryl})\rightarrow p\pi(N)$ bonding might be expected, and the bonds C(1)–C(2) and C(4)–C(5) should be shorter than the other four. Moreover, the endocyclic angles at C(3) [122.4(3)°] and C(6) [122.1(3)°] bonded to the nitro and O*n*Bu groups, respectively, are significantly larger than the others [118.3(3)–119.2(3)°]. These data are consistent with our observations in other nitroaryl metal complexes[18]. We conclude again that, from a structural point of view, a nitro group attached to an arene does not exert a −M mesomeric but rather a −I inductive effect. We have rationalized this[18] using the isovalent hybridization concept[19]. This problem has also been discussed from other theoretical points of view[20].

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

Figure 1. The molecule of compound **2** in the crystal. Radii are arbitrary. Only the asymmetric unit is numbered[a]

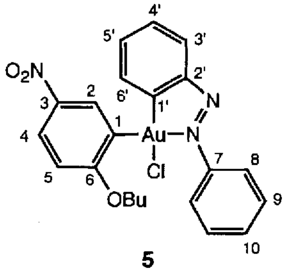


[a] Selected bond lengths [Å] and angles [°]: Hg–C(1) 2.068(3), C(1)–C(2) 1.391(5), C(1)–C(6) 1.393(5), C(2)–C(3) 1.389(5), C(3)–C(4) 1.379(5), C(3)–N 1.466(5), C(4)–C(5) 1.383(5), C(5)–C(6) 1.396(5), C(6)–O(3) 1.367(4), C(7)–O(3) 1.447(4), N–O(2) 1.224(5), N–O(1) 1.226(5); C(1)#1–Hg–C(1) 180.0, C(2)–C(1)–C(6) 118.3(3), C(2)–C(1)–Hg 122.8(3), C(6)–C(1)–Hg 118.8(3), C(3)–C(2)–C(1) 119.2(3), C(4)–C(3)–C(2) 122.4(3), C(4)–C(3)–N 119.1(3), C(2)–C(3)–N 118.5(4), C(3)–C(4)–C(5) 119.0(3), C(4)–C(5)–C(6) 119.0(3), O(3)–C(6)–C(1) 114.6(3), O(3)–C(6)–C(5) 123.3(3), C(1)–C(6)–C(5) 122.1(3), O(2)–N–O(1) 123.2(4), O(2)–N–C(3) 118.2(3), O(1)–N–C(3) 118.6(4), C(6)–O(3)–C(7) 118.7(3); symmetry transformation used to generate equivalent atoms: #1 $-x + 1$, $-y + 1$, $-z + 1$.

Experimental

Recording of the NMR spectra (using TMS as a reference) and elemental analyses were performed as described elsewhere[21], ^{13}C NMR of **6** was recorded in a Bruker AC-300 spectrometer. IR spectra were recorded in Nujol mulls on a Nicolet Magna FT-550. 4-Butoxynitrobenzene was prepared as described[22]. Reactions were carried out at room temp. Scheme 3 shows the atom numbering used for complex **5**.

Scheme 3



5

$[Hg(C_6H_3NO_2\text{-}3,OnBu\text{-}6)Cl]$ (**1**): To a solution of 4-butoxynitrobenzene (4.05 g, 20.75 mmol) in MeOH (50 ml), solid $[Hg(O_2CCF_3)_2]$ (8.86 g, 20.77 mmol) was added and the mixture stirred under reflux for 50 h. After cooling to room temperature, a saturated MeOH solution of LiCl (0.92 g, 21.70 mmol) was added and the white precipitate that immediately deposited was filtered off and washed, first with water (4 × 50 ml) and then with *n*-hexane

(3 × 15 ml). The residue was extracted in a Soxhlet with Et_2O. Evaporation of the solvent gave white needles. Yield 4.52 g (51%). M.p. 136°C. – $C_{10}H_{12}ClHgNO_3$ (430.2): calcd. C 27.9, H 2.8, N 3.3; found C 27.1, H 3.0, N 3.7. ^1H NMR ([D_6]DMSO): δ = 1.00 [t, ^3J(HH) = 7 Hz, 3H, Me], 1.52 (m, 2H, CH_2Me), 1.78 (m, 2H, CH_2Et), 4.16 [t, ^3J(HH) = 6 Hz, 2H, CH_2O], 7.21 [d, ^3J(HH) = 8 Hz, 1H, 5-H], 8.18 [dd, ^3J(HH) = 8 Hz, ^4J(HH) = 3 Hz, 1H, 4-H], 8.43 [d, ^4J(HH) = 3 Hz, 1H, 2-H]. – ^{13}C NMR ([D_6]DMSO): δ = 13.67 (Me), 18.64 (CH_2Me), 30.50 (CH_2Et), 68.41 (CH_2O), 110.99 (C-5), 125.90 (C-2), 132.6 (C-4), 141.20, 142.40 (C-1, C-3), 165.60 (C-6).

[Hg($C_6H_3NO_2$-3, OnBu-6)$_2$] (**2**): To a solution of **1** (208 mg, 0.48 mmol) in acetone (40 ml) solid Me_4NCl (431 mg, 3.93 mmol) was added and the mixture stirred for 36 h. The solvent was removed to dryness and the residue extracted with CH_2Cl_2 (3 × 5 ml) and filtere through $MgSO_4$ (anh.). Evaporation to ca. 1 ml and addition of Et_2O/*n*-hexane (1:1, 30 ml) gave white crystals of **2**. Yield 110 mg, 80%. M.p. 189°C. – $C_{20}H_{24}HgN_2O_6$ (589.0): calcd. C 40.8, H 4.1, N 4.8; found C 40.1, H 3.9, N 5.0. ^1H NMR ($CDCl_3$): δ = 1.00 [t, ^3J(HH) = 7 Hz, 6H, Me], 1.55 (m, 4H, CH_2Me), 1.84 (m, 4H, CH_2Et), 4.10 [t, ^3J(HH) = 6 Hz, 4H, CH_2O], 7.02 [d, 2H, 5-H, ^3J(HH) = 8 Hz], 8.16 [dd, 2H, 4-H, ^3J(HH) = 8 Hz, ^4J(HH) = 3 Hz], 8.33 [d, 2H, 2-H, ^4J(HH) = 3 Hz]. – ^{13}C NMR ($CDCl_3$): δ = 13.91 (Me), 19.41 (CH_2Me), 31.21 (CH_2Et), 68.74 (CH_2O), 110.43 (C-5), 128.37 (C-2), 133.22 (C-4), 142.53 (C-3), 157.40 (C-1), 168.48 (C-6). – Single crystals of **2** were obtained from dichloromethane/*n*-hexane.

X-Ray Structure Determination of Compound **2**: $C_{20}H_{24}HgN_2O_6$, space group $P2_1/c$, a = 4.0610(8), b = 20.993(5), c = 12.066(3) Å, β = 90.85(2)°, V = 1028.5 Å^3, Z = 2, λ(Mo-K_α) = 0.71073 Å, μ = 7.5 mm^{-1}, F(000) = 572, D_x = 1.902 Mg m^{-3}, T = −100°C. A colourless needle ca. 0.55 × 0.15 × 0.08 mm was mounted in inert oil. 2630 intensities were measured on a Siemens P4 diffractometer to $2\Theta_{max}$ 55°, of which 2359 were unique (R_{int} 0.015). The structure was solved assuming an Hg atom on an inversion centre and refined anisotropically on F^2 (program SHELXL-93, G. M. Sheldrick, University of Göttingen). H atoms were included using a riding model or rigid methyl groups. Because of instrumental difficulties ψ-scans could not be measured, and a "ΔF" absorption correction was therefore performed, with transmission factors 0.225–0.582 (program SHELXA, G. M. Sheldrick, unpublished). The final $wR(F^2)$ was 0.039, with conventional $R(F)$ 0.019, for 134 parameters and 115 restraints (to light atom displacement parameters); S 0.90, max. $\Delta\rho$ 0.42 e Å^{-3}.

Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, and can be obtained on quoting the reference number CSD-405072 and a full literature citation.

Me_4N[Au($C_6H_3NO_2$-3,OnBu-6)Cl_3] (**3**): To a solution of $Me_4N[AuCl_4]$ (97.60 mg, 0.25 mmnol) in acetone (50 ml), solid [Hg($C_6H_3NO_2$-3,O*n*Bu-6)$_2$] (69.30 mg, 0.12 mmol) and Me_4NCl (27.30 mg, 0.25 mmol) were added and the suspension stirred for 48 h. Removal of the solvent to dryness and addition of CH_2Cl_2 (15 ml) gave a yellow solution and a white solid that was filtered off and identified by IR as $Me_4N[HgCl_3]$. The yellow solution was evaporated to dryness and Et_2O added to afford **3** as a pale yellow solid. Yield 116 mg (81%). M.p. 153°C, Λ_M = 136.9 Ω^{-1} cm^2 M^{-1} (5.0 · 10^{-4} M in acetone]. – $C_{14}H_{24}AuCl_3N_2O_3$ (571.7): calcd. C 29.4, H 4.2, N 4.9, Au 34.5; found C 28.8, H 4.4, N 4.9, Au 34.2. – ^1H NMR ($CDCl_3$): δ = 0.98 [t, ^3J(HH) = 7 Hz, 3H, Me], 1.66 (m, 2H, CH_2Me), 1.82 (m, 2H, CH_2Et), 3.46 (s, 12H, Me_4N^+), 4.15 [t, ^3J(HH) = 6 Hz, 2H, CH_2O), 6.91 [d, 1H, 5-H, ^3J(HH) = 9 Hz], 7.90 [d, 1H, 2-H, ^3J(HH) = 3 Hz], 7.98 [dd, 1H, 4-H, ^3J(HH) = 9 Hz, ^4J(HH) = 3 Hz]. – ^{13}C NMR ([D_6]acetone): δ = 14.06 (Me), 19.75 (CH_2Me), 31.67 (CH_2Et), 69.55 (Me_4N^+), 72.00 (CH_2O), 112.32 (C-5), 123.82 (C-2), 128.76 (C-4), 163.71 (C-6). – The quaternary C-1 and C-3 signals were not observed, probably because of the instability of this complex.

[Au($C_6H_3NO_2$-3,OnBu-6)Cl_2(PPh_3)] (**4**): To a solution of Me_4N[Au($C_6H_3NO_2$-3, O*n*Bu-6)Cl_3] (**3**) (50 mg, 0.09 mmol) in CH_2Cl_2 (15 ml) solid PPh_3 (23.4 mg, 0.09 mmol) was added and the mixture stirred at 0°C for 12 h. The precipitate was separated by filtration and the solution evaporated to dryness. Addition of Et_2O/*n*-hexane (5 ml, 1:1) gave a pale yellow precipitate that was recrystallized from CH_2Cl_2/*n*-hexane. Yield 59 mg (90%). M.p. 175°C. – $C_{28}H_{27}AuCl_2NO_3P$ (724.4): calcd. C 46.4, H 3.8, N 1.9, Au 27.2; found C 46.2, H 4.5, N 1.7, Au 27.5. – ^1H NMR ($CDCl_3$): δ = 1.01 [t, ^3J(HH) = 7 Hz, 3H, Me), 1.47–1.65 [m, 4H, $(CH_2)_2$], 3.52 (m, 1H, CH_2O), 3.79 (m, 1H, CH_2O), 6.24 [d, 1H, 5-H, ^3J(HH) = 9 Hz], 7.34–7.63 (m, 15H, PPh_3), 7.76–7.94 (m, 2H, 2-H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 14.0 (Me), 19.2 (CH_2Me), 31.5 (CH_2Et), 69.1 (CH_2O), 111.2 (C-5), 123.4 (C-4), 129.9 (C-2), 136.2 (C-1), 141.9 (C-3), 160.6 (C-6).

[Au(η^2-C_6H_4N=NPh-2)($C_6H_3NO_2$-3,OnBu-6)Cl] (**5**): To a solution of **3** (209 mg, 0.37 mmol) in CH_2Cl_2 (45 ml), solid [Hg(C_6H_4N=NPh-2)$_2$] (104 mg, 0.18 mmol) was added and the mixture stirred for 48 h, during which decomposition to metallic gold was observed. Filtration through $MgSO_4$ (anh.), evaporation to dryness and addition of *n*-hexane/Et_2O (1:1, 10 ml) gave a brick-red precipitate. Yield 67.5 mg (30%). M.p. 95°C (dec.). – $C_{22}H_{21}AuClN_3O_3$ (607.8): calcd. C 43.5, H 3.5, N 6.9, Au 32.4; found C 43.2, H 3.1, N 6.5, Au 31.9. – ^1H NMR ($CDCl_3$): δ = 0.79 [t, ^3J(HH) = 7 Hz, 3H, Me], 1.26 (m, 2H, CH_2Me), 1.65 (m, 2H, CH_2Et), 4.06 (m, 2H, CH_2O), 6.64, 6.68 (dd, 1H, 4-H, ^4J(HH) = 2 Hz, ^3J(HH) = 8 Hz), 6.88 [d, 1H, 5-H, ^3J(HH) = 8 Hz], 7.27 [dd, 1H, 4-H′, ^3J(HH) = 1.4 Hz], 7.45–7.61 (m, 5H, Ph), 8.07–8.22 (m, 3H, C_6H_4), 8.27 [d, 1H, 2-H, ^4J(HH) = 3 Hz]. – ^{13}C NMR ($CDCl_3$): δ = 13.5 (Me), 18.9 (CH_2Me), 30.8 (CH_2Et), 68.9 (CH_2O), 111.8 (C-5), 114.6, 123.4, 126.8, 127.5, 129.3, 129.9, 130.6, 130.9, 132.0 (arylic carbons), 141.9 (C-1′, C-3), 147.5, 150.0 (C-2′, C-7), 161.8 (C-6). The instability of **5** in solution probably precludes the observation of all quaternary carbons.

Preparation of the Biphenyl **6**: To solution of **5** (52 mg, 0.08 mmol) in CH_2Cl_2 (20 ml), solid PPh_3 (23.4 mg, 0.04 mmol) was added and the mixture stirred at room temp. for 8 h. Filtration through $MgSO_4$ (anh.), evaporation to dryness and addition of *n*-hexane/Et_2O (3:1, 5 ml) gave a white solid [$AuClPPh_3$] (31.0 mg, 0.06 mmol) and a red solution that was concentrated in vacuo and gave an orange solid. Yield 22.5 mg (75%). M.p. 65°C. – MS (70 eV); *m/z* (%): 375 (2.3) [M^+], 302 (70.3), [M^+ − BuO], 257 (28.6) [M^+ − BuO − NO_2], 168 (17.6) [$C_{12}H_{10}N$], 139 (31.8) [$C_6H_5NO_3$], 119 (4.5) [C_8H_7O], 105 (12.7) [$C_6H_5N_2$], 91 (2.4) [C_6H_3O], 77 (100) [Ph], 51 (26.3) [C_4H_3]. – ^1H-NMR ($CDCl_3$): δ = 0.71 [t, ^3J(HH) = 7 Hz, 3H, Me], 1.16 (m, 2H, CH_2Me), 1.43 (m, 2H, CH_2Et), 3.88 [t, ^3J(HH) = 6 Hz, 2H, CH_2O], 6.90 (m, 1H, C_6H_3), 7.26–7.80 (m, 10H, C_6H_4 + C_6H_3 + Ph), 8.30 (m, 1H, C_6H_3). – ^{13}C NMR ($CDCl_3$): δ = 13.5 (Me), 18.8 (CH_2Et), 30.7 (CH_2Me), 68.8 (CH_2O), 110.5, 115.6, 122.9 (2 C), 125.3, 127.19, 128.7, 128.9, 129.2 (2 C), 131.0 (2 C) and 131.8 (C-aryl), 138.6 (C-1, C-1′), 141.2 (C-3), 150.1, 152.5 (C-2′, C-7), 160.3 (C-6). – $C_{22}H_{21}N_3O_3$ (375.4): calcd. C 70.4, H 5.6, N 11.2; found C 70.1, H 5.4, N 10.9.

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