Synthesis of Intermediates in the C–H Activation of Acetone with 2-Phenylazophenylgold(III) Complexes and in the C–C Coupling of Aryl Groups from Diarylgold(III) Complexes. Crystal and Molecular Structures of $[\overline{\mathrm{Au\{C_6H_3(N{=}N}}\mathrm{C_6H_4Me\text{-}4')\text{-}2\text{-}Me\text{-}5\}(acac\text{-}}C\mathrm{)Cl]}$ (acac = acetylacetonate), *cis*-$[\mathrm{Au(C_6H_4N{=}NPh\text{-}2)Cl_2(PPh_3)}]$, and $[\overline{\mathrm{Au(C_6H_4CH_2N}}\mathrm{Me_2\text{-}2)(C_6F_5)Cl}]$†

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The complex $[\overline{\mathrm{Au(C_6H_4N{=}N}}\mathrm{Ph\text{-}2)Cl_2}]$ reacts with $[\mathrm{HgR_2}]$ (R = $\mathrm{C_6H_4NO_2}$-2 or $\mathrm{C_6F_5}$) and $\mathrm{NMe_4Cl}$ (2:1:2) to give $[\overline{\mathrm{Au(C_6H_4N{=}N}}\mathrm{Ph\text{-}2)(R)Cl}]$ [R = $\mathrm{C_6H_4NO_2}$-2, (**1**); or $\mathrm{C_6F_5}$ (**2**)]. Similarly, $[\overline{\mathrm{Au(C\text{-}N}}\mathrm{)Cl_2}]$ (**3**) [C–N = $\mathrm{C_6H_3(N{=}NC_6H_4Me\text{-}4')\text{-}2\text{-}Me\text{-}5}$], prepared by the reaction of $[\mathrm{AuCl_3(tht)}]$ (tht = tetrahydrothiophene) with [Hg(C–N)Cl] and $\mathrm{NMe_4Cl}$ (1:1:1), reacts with Tl(acac) (Hacac = acetylacetone) (1:1) to give $[\overline{\mathrm{Au(C\text{-}N}}\mathrm{)(acac\text{-}}C\mathrm{)Cl}]$ (**4**). Reaction of (**2**) with $\mathrm{PPh_3}$ (1:1) leads to $[\overline{\mathrm{Au(C_6H_4N{=}N}}\mathrm{Ph\text{-}2)(C_6F_5)Cl(PPh_3)}]$ (**5**), which upon standing in dichloromethane solution decomposes to give a mixture of $[\mathrm{Au(C_6F_5)(PPh_3)}]$, $\mathrm{C_6H_4C_6F_5\text{-}1\text{-}N{=}NPh\text{-}2}$, and $[\mathrm{Au(C_6H_4N{=}NPh\text{-}2)Cl_2(PPh_3)}]$ (**6**). Crystal structures were determined for complexes (**4**), (**6**), and $[\overline{\mathrm{Au(C_6H_4CH_2N}}\mathrm{Me_2\text{-}2)(C_6F_5)Cl}]$ (**7**) [(**4**), space group $P\bar{1}$, a = 9.475(4), b = 9.923(4), c = 10.913(4) Å, α = 63.75(3), β = 84.92(3), γ = 89.41(3)°, Z = 2, R = 0.020 for 3 057 reflections at −95 °C; (**6**), space group $P2_1/n$, a = 10.361(3), b = 28.194(8), c = 10.724(4) Å, β = 116.26(2)°, Z = 4, R = 0.038 for 3 734 reflections at 20 °C; (**7**), space group $Pbca$, a = 11.996(4), b = 14.484(4), c = 18.310(7) Å, Z = 8, R = 0.045 for 1 909 reflections at 20 °C]. The three structures reveal neutral molecules with square-planar geometry around the gold atom. In complexes (**4**) and (**7**) the aryl groups act as chelating ligands, forming a five-membered ring [(**4**), Au–C 2.026(4), Au–N 2.158(3) Å; (**7**), Au–C 2.022(10), Au–N 2.128(10), Au–$\mathrm{C_6F_5}$ 2.012(11) Å] while in complex (**6**) the aryl group acts as a monodentate ligand [Au–C 2.033(5) Å]. The chloro ligand in complex (**4**) is *trans* to the carbon atom of the aryl ligand [Au–Cl 2.349(2) Å], and the acac ligand is C-bonded to the gold atom [Au–C 2.083(4) Å]. This is one of the few isolated acetylacetonatogold(III) complexes and the first structurally characterized. In complex (**6**), chloro atoms are mutually *cis* [Au–Cl (*trans* to C) 2.377(2), (*trans* to N) 2.325(2) Å]. The chloro ligand in complex (**7**) is *trans* to the aryl group of the chelating ligand [Au–Cl 2.347(3) Å]. The isolation of complexes (**1**) and (**2**) and the observed geometry of (**4**) support the pathway suggested for the C–H activation of acetone with 2-phenylazophenylgold(III) complexes.

We have recently reported[1,2] that reactions of $[\overline{\mathrm{Au(C_6H_4N{=}N}}\mathrm{Ph\text{-}2)Cl_2}]$ with different reagents such as Tl(acac) (Hacac = acetylacetone), KCN, $\mathrm{AgClO_4}$, 1,10-phenanthroline, $[\mathrm{HgR_2}]$ (R = $\mathrm{C_6F_5}$ or $\mathrm{C_6H_4N{=}NPh\text{-}2}$), and $[\mathrm{PdR_2}]$ (R = $\mathrm{C_6H_4NO_2}$-2) led to $[\overline{\mathrm{Au(C_6H_4N{=}N}}\mathrm{Ph\text{-}2)\{CH_2C(O)Me\}Cl}]$ when acetone is used as solvent, instead of the expected substitution products. We proposed a reaction pathway (see Scheme for reactions with anionic ligands) based on our experience[3] of 2-phenylazophenylgold(III) complexes and also on the isolation of intermediates such as $[\overline{\mathrm{Au(C_6H_4N{=}N}}\mathrm{Ph\text{-}2)(acac\text{-}}C\mathrm{)Cl}]$. The substitution of the chloro ligand *trans* to the nitrogen atom, as the first step to give (**A**), is essential in the proposed pathway; first, to explain the labilization of the N–Au bond, thus permitting co-ordination of the acetone molecule, and secondly to allow intramolecular transfer of the proton shown in (**D**), giving XH and complex (**E**), in which the remaining chloro ligand is *trans* to the aryl group. This type of metal/ligand co-operation in C–H activation of acetone has, as far as we are aware, been reported only once before.[4]

To support our proposal we isolated the intermediate of type (**A**) with X = acac by carrying out the reaction at 0 °C or by using dichloromethane as solvent.[1,2] The proposed geometry

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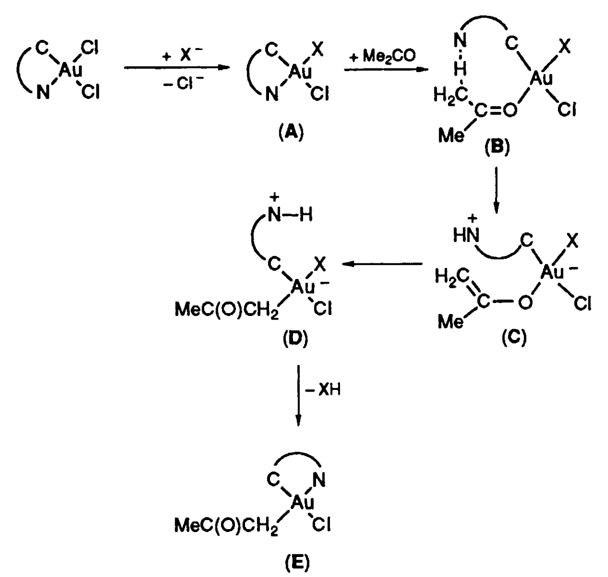
† Chloro(5-methyl-2-*p*-tolylazo-κ*N*′-phenyl-κ*C*¹)(pentane-2,4-dionato-κC³), dichloro(2-phenylazophenyl-κ*C*¹)(triphenylphosphine)-, and chloro(2-dimethylamino-κ*N*-methylphenyl-κ*C*¹)(pentafluorophenyl)-gold(III).

Supplementary data available: Further details of the structure determination (complete bond angles, H-atom co-ordinates, thermal parameters, structure factors) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD 54655.



Scheme. C–N = $C_6H_4N{=}NPh\text{-}2$; X = acac-*C*, CN, $C_6H_4N{=}NPh\text{-}2$, C_6F_5, or $C_6H_4NO_2\text{-}2$

was based on its i.r. spectrum. In this paper we report the synthesis and crystal structure of its homologue with the aryl ligand $C_6H_3(N{=}NC_6H_4Me\text{-}4')\text{-}2\text{-}Me\text{-}5$ and the isolation of two of the postulated intermediates of type (**A**) with X = $C_6H_4NO_2\text{-}2$ or C_6F_5. Our interest in the synthesis of these mixed diarylgold(III) complexes is also connected with their use as intermediates in the preparation of substituted biphenyls. Here, we describe the crystal structure of a previously reported mixed diarylgold(III) complex, the isolation of an intermediate of this coupling reaction, and the crystal structure of a product of its decomposition.

Results and Discussion

The complex $[Au(C_6H_4N{=}NPh\text{-}2)Cl_2]$, which was prepared by treating $[AuCl_3(tht)]$ (tht = tetrahydrothiophene) with $[Hg(C_6H_4N{=}NPh\text{-}2)_2]$,[5] undergoes a second transmetallation reaction when refluxed in chloroform with $[HgR_2]$ (R = $C_6H_4NO_2\text{-}2$ or C_6F_5) in the presence of NMe_4Cl (2:1:2) giving $[Au(C_6H_4N{=}NPh\text{-}2)(R)Cl]$ [R = $C_6H_4NO_2\text{-}2$, (**1**) or C_6F_5, (**2**)] [see equation (1)] in high yields. The addition of NMe_4Cl reduces the required amount of the mercurial by half because it symmetrizes [equation (ii)] the by-product $[Hg(R)Cl]$ of the transmetallation reaction [equation (i)].

$$2[Au(C_6H_4N{=}NPh\text{-}2)Cl_2] + 2[HgR_2] \longrightarrow 2[Au(C_6H_4N{=}NPh\text{-}2)(R)Cl] + 2[Hg(R)Cl] \quad \text{(i)}$$

$$2[Hg(R)Cl] + Cl^- \longrightarrow [HgR_2] + [HgCl_3]^- \quad \text{(ii)}$$

$$2[Au(C_6H_4N{=}NPh\text{-}2)Cl_2] + [HgR_2] + Cl^- \longrightarrow 2[Au(C_6H_4N{=}NPh\text{-}2)(R)Cl] + [HgCl_3]^- \quad (1)$$

These are new examples of the advantages of using organomercury derivatives as intermediates in the synthesis of organometallic compounds. We have previously used them to prepare mono- and di-(homo- or hetero-)aryl complexes of Au,[3] Pd,[6] Pt,[7] Rh,[8] Sn,[9] and Tl.[10] However, as mentioned above, our interest in the synthesis of complexes (**1**) and (**2**) is based on the fact that they could not be prepared in acetone, where only $[Au(C_6H_4N{=}NPh\text{-}2)\{CH_2C(O)Me\}Cl]$ could be isolated, and because they were assumed to be intermediates (see Scheme) in such C–H activation processes.

$$[Au(C_6H_4N{=}NPh\text{-}2)Cl_2] + [HgR_2] \longrightarrow [Au(C_6H_4N{=}NPh\text{-}2)(R)Cl] + [Hg(R)Cl]$$
$$\downarrow + \text{acetone}$$
$$[Au(C_6H_4N{=}NPh\text{-}2)\{CH_2C(O)Me\}Cl] + RH \quad (2)$$

However, they react with acetone more slowly than $[Au(C_6H_4N{=}NPh\text{-}2)Cl_2]$ does with $[HgR_2]$ in acetone to give (in both cases) $[Au(C_6H_4N{=}NPh\text{-}2)\{CH_2C(O)Me\}Cl]$. It is possible that the by-products of these reactions, $[Hg(R)Cl]$, or even the starting complex $[Au(C_6H_4N{=}NPh\text{-}2)Cl_2]$ could catalyse the direct reaction.

Because we have not been able to grow crystals of complexes (**1**) or (**2**), or of $[Au(C_6H_4N{=}NPh\text{-}2)(acac)Cl]$ the other previously isolated intermediate in the activation of acetone,[2] we decided to prepare a homologue of this complex containing the *para*-disubstituted group $C_6H_3(N{=}NC_6H_4Me\text{-}4')\text{-}2\text{-}Me\text{-}5$ instead of $C_6H_4N{=}NPh\text{-}2$. The starting complex $[Au(C\text{–}N)Cl_2]$ (**3**) [C–N = $C_6H_3N{=}NC_6H_4Me\text{-}4')\text{-}2\text{-}Me\text{-}5$], can be prepared by treating $[AuCl_3(tht)]$ with $[Hg(C\text{–}N)Cl]$ and NMe_4Cl (1:1:1). The reaction of complex (**3**) with Tl(acac) (1:1) gives the desired complex $[Au(C\text{–}N)(acac\text{-}C)Cl]$ (**4**), for which the crystal structure was determined (see below).

Reported acac complexes of gold(III) are limited to $[AuMe_2(acac\text{-}O)]$[11] and $[AuMe_2(acac\text{-}C)L]$,[12] of which only the complex with L = $PPhMe_2$ has been isolated. A C-bonded coordination of the acac ligand is assumed in this complex on the basis of its ^1H n.m.r. and i.r. spectra.

We are also interested in the synthesis of mixed diarylgold(III) complexes because they are easily reduced to gold(I) complexes, giving biphenyl compounds [equation (3)].[3] These reactions,

$$[AuR(R')Cl] + PPh_3 \longrightarrow [AuCl(PPh_3)] + R\text{–}R' \quad (3)$$

when R = $C_6H_4N{=}NPh\text{-}2$, are generally rapid at room temperature, which makes it difficult to isolate any intermediate. However, the great stability of the C_6F_5 gold derivatives makes complex (**2**) suitable for the synthesis of such intermediates. Addition of PPh_3 (1:1) to a solution of complex (**2**) gives $[Au(C_6H_4N{=}NPh\text{-}2)(C_6F_5)Cl(PPh_3)]$ (**5**). Attempts to prepare single crystals for an *X*-ray diffraction study, by slow diffusion of n-hexane into a dichloromethane solution of complex (**5**), led after 24 h to three separate crops of crystals, two orange corresponding to complexes (**5**) and $[Au(C_6H_4N{=}NPh\text{-}2)Cl_2(PPh_3)]$ (**6**), and a third colourless $[Au(C_6F_5)(PPh_3)]$. The only suitable crystals for *X*-ray diffraction study were those of complex (**6**), which we had already synthesized by the reaction of $[Au(C_6H_4N{=}NPh\text{-}2)Cl_2]$ with PPh_3 (1:1).[5] The mother-liquor from the crystallization process contained the biphenyl compound $C_6F_5C_6H_4N{=}NPh\text{-}2$. It is possible that the sequence of reactions (4) occurs. Therefore, complex (**2**)

$$2[Au(C_6H_4N{=}NPh\text{-}2)(C_6F_5)Cl(PPh_3)] \longrightarrow [Au(C_6H_4N{=}NPh\text{-}2)Cl_2(PPh_3)]\ (\mathbf{6}) + [Au(C_6H_4N{=}NPh\text{-}2)(C_6F_5)_2(PPh_3)]$$
$$\downarrow$$
$$[Au(C_6F_5)(PPh_3)] + C_6F_5C_6H_4N{=}NPh\text{-}2 \quad (4)$$

reacts differently with PPh_3 from other mixed diarylgold(III) complexes, which give $[AuCl(PPh_3)]$ as the reduction product.

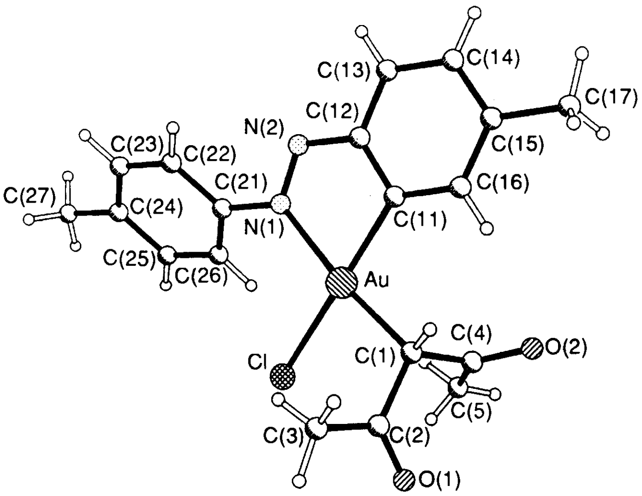


Figure 1. The molecule of complex (**4**) in the crystal. Radii are arbitrary

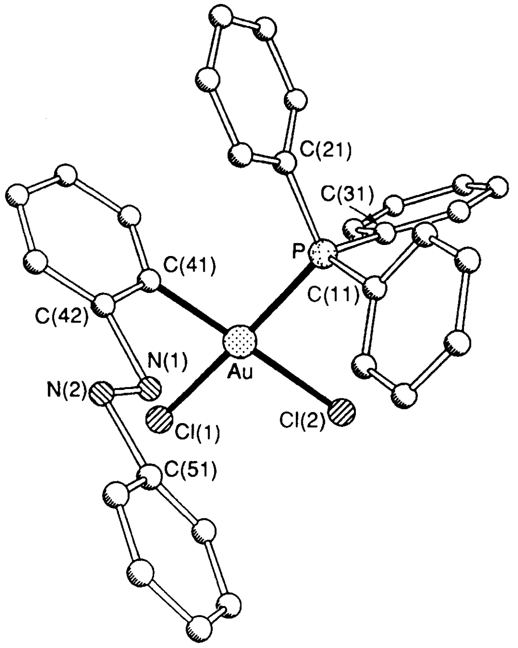


Figure 2. The molecule of complex (**6**) in the crystal. Radii are arbitrary; H-atoms omitted for clarity

In connection with this reductive-elimination process, we have also observed that complexes containing the ligand $C_6H_4CH_2NMe_2$-2 are more resistant to C–C coupling of the two aryl groups. We have only observed this coupling with $[Au(C_6H_4CH_2NMe_2\text{-}2)(Ph)Cl]$; it does not occur with $[Au(C_6H_4CH_2NMe_2\text{-}2)(C_6F_5)Cl]$ (**7**), a complex whose synthesis we have previously described. A comparison of crystal data for both complexes might provide some information about their different behaviours. We have described the crystal structure of the former;[13] that of complex (**7**) is presented below.

Spectroscopic Properties and Structures of Complexes (**1**)—(**7**).—Complexes (**1**)—(**6**) show one or two bands in the region 400—300 cm^{-1}, depending on the number of chloro ligands in the molecule. The band corresponding to the monochloro-complexes appears at 300—310 cm^{-1}, which is assignable to ν(AuCl) *trans* to an aryl group. This means that the geometry of complexes (**1**) and (**2**) is that assumed in the Scheme. Because it is easy to cleave the N–Au bond,[5] it is reasonable to assume that the observed band for complex (**5**) corresponds to ν(AuCl) *trans* to C_6H_4N=NPh-2. The second band for complexes $[Au(C\text{–}N)Cl_2]$ (**3**) and $[Au(C_6H_4N{=}NPh\text{-}2)Cl_2(PPh_3)]$ (**6**) appears at 345 and 320 cm^{-1}, respectively, being assignable to ν(AuCl) *trans* to N and P, respectively. For complex (**7**) the presence of ν(AuCl) at 318 cm^{-1} was used to assign the chloro ligand as *trans* to the phenyl group. These assignments[5,14] are now corroborated by the crystal structures (see below).

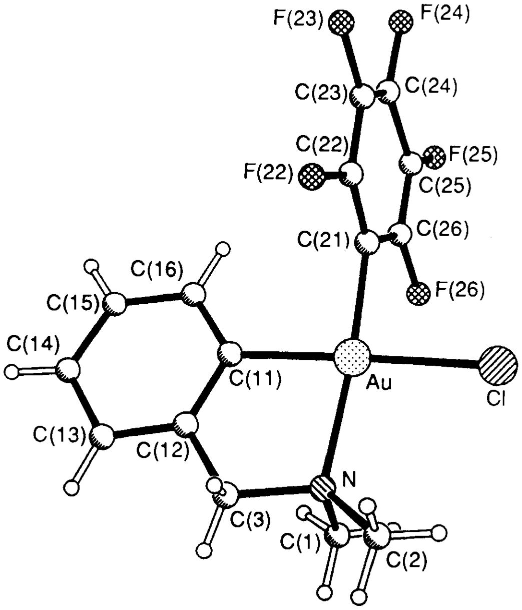


Figure 3. The molecule of complex (**7**) in the crystal. Radii are arbitrary; H-atoms omitted for clarity

All complexes show bands corresponding to the type of substitution of the aryl groups. Thus, those containing the C_6H_4N=NPh-2 group exhibit two strong absorptions at 760 (orthometallated ring) and 690 cm^{-1} (Ph) while the other type of complexes show bands at 840m (orthometallated ring) and 820 cm^{-1} (C_6H_4Me-4).

A strong absorption at 1 230 cm^{-1} for complexes (**1**) and (**2**) is not observed for (**5**). In our experience, this seems to be connected with the cleavage of the N–Au bond; $[Au(C_6H_4N{=}NPh\text{-}2)Cl_2]$ shows this band, whereas $[Au(C_6H_4N{=}NPh\text{-}2)Cl_2(PPh_3)]$ (with no Au–N bond) does not. Characteristic bands of the substituents of the aryl groups ($C_6H_4NO_2$-2, 1 510s, 1 330s, and 850m; C_6F_5, 1 500m, 1 050s, and 800 cm^{-1}) and of the other ligands [ν(CO) in (**4**) at 1 685 cm^{-1}] are also observed.

Selected ^1H, ^{13}C, and ^{19}F n.m.r. data for some complexes are shown in the Experimental section.

The crystal structures of complexes (**4**), (**6**), and (**7**) (see Figure 1, 2, and 3, respectively) reveal neutral molecules with square-planar geometry around the gold atom. In complexes (**4**) and (**7**) the aryl groups act as chelating ligands, forming five-membered rings [(**4**), Au–C(11) 2.026(4), Au–N(1) 2.158(3); (**7**), Au–C(11) 2.022(10); Au–N 2.128(10), Au–C(21) 2.012(11) Å]. The chloride in complex (**4**) is *trans* to the carbon atom of the aryl group [Au–Cl 2.349(2) Å] and the acac ligand *C*-bonded to the gold atom [Au–C(1) 2.083(4) Å], as was assumed for its homologue $[Au(C_6H_4N{=}NPh\text{-}2)(acac\text{-}C)Cl]$ based on i.r. and n.m.r. data.[2] This is one of the few isolated acetylacetonatogold(III) complexes[11,12] and, to the best of our knowledge, the first to be structurally characterized. The chloro ligands in complex (**6**) are mutually *cis* [Au–Cl(2) 2.377(2), Au–Cl(1) 2.325(2) Å] and, in complex (**7**), *trans* to the phenyl group.

Table 1. Crystal data

Compound	(4)	(6)	(7)
Formula	$C_{19}H_{20}AuClN_2O_2$	$C_{30}H_{24}AuCl_2N_2P$	$C_{15}H_{12}AuClF_5N$
M	540.8	711.4	533.7
Space group	$P\bar{1}$	$P2_1/n$	*Pbca*
Temperature (°C)	−95	20	20
a/Å	9.475(4)	10.361(3)	11.996(4)
b/Å	9.923(4)	28.194(8)	14.484(4)
c/Å	10.913(4)	10.724(4)	18.310(7)
α/°	63.75(3)		
β/°	84.92(3)	116.26(2)	
γ/°	89.41(3)		
U/Å^3	916.1	2 809.6	3 181.3
Z	2	4	8
D_c/Mg m^{-3}	1.96	1.68	2.23
F(000)	520	1 384	2 000
μ/mm^{-1}	8.2	5.5	9.5
$2\theta_{max}$(°)	50	50	50
No. of reflections:			
measured	6 422	7 205	2 797
independent	3 214	4 936	2 794
R_{int}	0.013	0.022	
observed [$>4\sigma(F)$]	3 057	3 734	1 909
Absorption correction	DIFABS *	ψ scans	ψ scans
Transmission factor range	0.83—1.27	0.56—0.88	0.22—1.00
R	0.020	0.038	0.045
R'	0.026	0.044	0.058
g	0.0003	0.000 15	0.0035
No. of parameters	232	115	208
S	1.2	1.8	0.9
Maximum Δ/σ	0.006	0.003	0.001
Maximum Δρ/e Å^{-3}	1.0	1.9	2.5

* DIFABS, N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158

Table 2. Atomic co-ordinates ($\times 10^4$) for compound (**4**)

Atom	*x*	*y*	*z*
Au	6 820.1(1)	6 134.2(1)	2 151.3(1)
Cl	7 910(1)	7 894(1)	2 691(1)
N(1)	4 673(3)	6 251(3)	2 934(3)
N(2)	3 775(3)	5 417(3)	2 786(3)
C(1)	8 756(4)	5 836(4)	1 252(4)
C(2)	9 728(4)	7 232(4)	610(3)
C(3)	9 249(4)	8 616(4)	−561(4)
C(4)	9 462(4)	4 504(4)	2 292(4)
C(5)	9 784(5)	4 503(5)	3 608(4)
O(1)	10 919(3)	7 165(3)	960(3)
O(2)	9 768(3)	3 456(3)	2 038(3)
C(11)	5 814(4)	4 566(4)	1 798(3)
C(12)	4 353(4)	4 481(4)	2 226(3)
C(13)	3 439(4)	3 430(4)	2 163(4)
C(14)	3 996(4)	2 428(4)	1 692(3)
C(15)	5 431(4)	2 489(4)	1 253(3)
C(16)	6 329(4)	3 569(4)	1 309(3)
C(17)	5 994(5)	1 376(5)	758(4)
C(21)	4 065(4)	7 225(4)	3 486(3)
C(22)	2 732(4)	7 825(4)	3 130(3)
C(23)	2 125(4)	8 679(4)	3 733(4)
C(24)	2 806(4)	8 955(4)	4 689(4)
C(25)	4 140(4)	8 365(4)	5 004(3)
C(26)	4 770(4)	7 508(4)	4 404(3)
C(27)	2 124(5)	9 861(5)	5 363(4)

Complex (7) has essentially the same geometry as its homologue $[Au(C_6H_4CH_2NMe_2\text{-}2)(Ph)Cl]$. All distances to the gold atom are in the range observed for the two modifications, both with three independent molecules, of the phenyl complex, except for the N–Au bond distance which is slightly shorter in complex (7) [2.128(10) *vs.* 2.169 (av) Å]. This difference could be connected with the different tendencies of these two complexes to give with PPh_3 a biphenyl as the reductive-elimination product. It is reasonable to assume that one important step in this reaction is cleavage of the N–Au bond to give the PPh_3 adduct. Because this cleavage is much more facile with $C_6H_4N{=}NPh\text{-}2$ than with $C_6H_4CH_2NMe_2\text{-}2$, complexes $[Au(C_6H_4N{=}NPh\text{-}2)(R)Cl]$ generally react with PPh_3 to give biphenyls, for example with R = $C_6H_4(N{=}NPh)\text{-}2$, Ph, C_6F_5, or $C_6H_4NO_2\text{-}2$, whereas for the complexes $[Au(C_6H_4CH_2NMe_2\text{-}2)(R)Cl]$ only R = Ph reacts in this way.

It is interesting that all the substitution reactions here and previously described[3] occur on the ligand *trans* to N rather than *trans* to C as would be expected on the basis of their different *trans* effects. This is also observed in some other related palladium complexes.[15]

Experimental

Recording of the i.r. spectra, the C, H, and N analyses, conductance measurements, and melting-point determinations were performed as described elsewhere.[8] Proton and ^{13}C n.m.r. spectra (in $CDCl_3$) were recorded on a Brucker 200AC spectrometer and ^{19}F n.m.r. spectra (in $CDCl_3$) on a Varian FT80 spectrometer. Chemical shifts in p.p.m. are referred to $SiMe_4$ or $CFCl_3$, respectively. Carbon atoms are numbered according to the atom numbering used in the formulae and the hydrogen atoms according to the numbers given to their parent atoms. Reactions were carried out with magnetic stirring without special precautions to exclude light or moisture. All complexes are non-conducting in acetone solution. Complex (6) is better prepared as described previously.[5] Complex (7)[14] and organomercury compounds[2] were obtained as reported.

Table 3. Bond lengths (Å) and angles (°) for compound (**4**)

Au–Cl	2.349(2)	Au–N(1)	2.158(3)
Au–C(1)	2.083(4)	Au–C(11)	2.026(4)
N(1)–N(2)	1.261(5)	N(1)–C(21)	1.439(6)
N(2)–C(12)	1.404(6)	C(1)–C(2)	1.521(5)
C(1)–C(4)	1.507(5)	C(2)–C(3)	1.504(5)
C(2)–O(1)	1.215(5)	C(4)–C(5)	1.494(7)
C(4)–O(2)	1.215(6)	C(11)–C(12)	1.412(5)
C(11)–C(16)	1.382(6)	C(12)–C(13)	1.391(6)
C(13)–C(14)	1.387(7)	C(14)–C(15)	1.394(5)
C(15)–C(16)	1.401(6)	C(15)–C(17)	1.504(7)
C(21)–C(22)	1.403(5)	C(21)–C(26)	1.378(6)
C(22)–C(23)	1.378(7)	C(23)–C(24)	1.398(7)
C(24)–C(25)	1.393(5)	C(24)–C(27)	1.502(7)
C(25)–C(26)	1.387(6)		
Cl–Au–N(1)	98.7(1)	Cl–Au–C(1)	90.0(1)
N(1)–Au–C(1)	171.1(2)	Cl–Au–C(11)	176.6(1)
N(1)–Au–C(11)	78.8(1)	C(1)–Au–C(11)	92.6(2)
Au–N(1)–N(2)	115.2(3)	Au–N(1)–C(21)	130.6(3)
N(2)–N(1)–C(21)	113.9(3)	N(1)–N(2)–C(12)	114.4(3)
Au–C(1)–C(2)	114.0(3)	Au–C(1)–C(4)	109.1(2)
C(2)–C(1)–C(4)	112.0(3)	C(1)–C(2)–C(3)	118.8(3)
C(1)–C(2)–O(1)	119.5(3)	C(3)–C(2)–O(1)	121.3(3)
C(1)–C(4)–C(5)	119.4(4)	C(1)–C(4)–O(2)	119.3(4)
C(5)–C(4)–O(2)	121.3(3)	Au–C(11)–C(12)	110.4(3)
Au–C(11)–C(16)	131.2(3)	C(12)–C(11)–C(16)	118.3(4)
N(2)–C(12)–C(11)	121.1(4)	N(2)–C(12)–C(13)	117.2(3)
C(11)–C(12)–C(13)	121.6(4)	C(12)–C(13)–C(14)	118.5(3)
C(13)–C(14)–C(15)	121.2(4)	C(14)–C(15)–C(16)	119.2(4)
C(14)–C(15)–C(17)	119.5(4)	C(16)–C(15)–C(17)	121.2(3)
C(11)–C(16)–C(15)	121.0(3)	N(1)–C(21)–C(22)	119.7(4)
N(1)–C(21)–C(26)	119.7(3)	C(22)–C(21)–C(26)	120.6(4)
C(21)–C(22)–C(23)	118.9(4)	C(22)–C(23)–C(24)	121.5(4)
C(23)–C(24)–C(25)	118.3(4)	C(23)–C(24)–C(27)	121.2(4)
C(25)–C(24)–C(27)	120.6(4)	C(24)–C(25)–C(26)	121.1(4)
C(21)–C(26)–C(25)	119.6(3)		

[Au(C$_6$H$_4$N=NPh-2)(C$_6$H$_4$NO$_2$-2)Cl] (**1**).—Solid [Hg(C$_6$H$_4$NO$_2$-2)$_2$] (60 mg, 0.14 mmol) and NMe$_4$Cl (30 mg, 0.28 mmol) were added to a chloroform (50 cm^3) suspension of [Au(C$_6$H$_4$N=NPh-2)Cl$_2$] (120 mg, 0.28 mmol). After refluxing for 1 h, the suspension was filtered through anhydrous MgSO$_4$, giving an orange solution which was evaporated to *ca.* 1 cm^3. Diethyl ether (15 cm^3) was then added to precipitate complex (**1**) as a yellow solid. Yield 70%, m.p. 170 °C (decomp) (Found: C, 40.8; H, 2.1; Au, 35.9; N, 6.9. C$_{18}$H$_{13}$AuClN$_3$O$_2$ requires C, 40.4; H, 2.4; Au, 36.8; N, 7.8%).

[Au(C$_6$H$_4$N=NPh-2)(C$_6$F$_5$)Cl] (**2**).—Solid [Hg(C$_6$F$_5$)$_2$] (250 mg, 0.48 mmol) was added to a chloroform (60 cm^3) suspension of [Au(C$_6$H$_4$N=NPh-2)Cl$_2$] (430 mg, 0.96 mmol). After refluxing the mixture for 5 h the suspension was filtered through anhydrous MgSO$_4$ and the resulting orange solution evaporated to *ca.* 1 cm^3. Addition of diethyl ether–n-hexane (1:5, 30 cm^3) gave a yellow solid, which was recrystallized from dichloromethane–n-hexane (1:8). Yield 75%, m.p. 152 °C (Found: C, 37.4; H, 2.0; Au, 33.3; N, 5.1. C$_{18}$H$_9$AuClF$_5$N$_2$ requires C, 37.2; H, 1.6; Au, 33.9; N, 4.8%). ^{19}F n.m.r.: δ −156.7 (m, *m*-F), −150.2 (t, *p*-F, J_{FF} = 20 Hz), and −113.9 p.p.m. (m, *o*-F).

Table 4. Atomic co-ordinates (× 10^4) for compound (**6**)

Atom	*x*	*y*	*z*
Au	5 437.1(3)	5 911.2(1)	5 444.5(3)
P	4 683(2)	6 227.4(6)	3 260(2)
Cl(1)	6 193(2)	5 535.5(7)	7 583(2)
Cl(2)	7 832(2)	6 128.7(8)	5 941(2)
C(12)	4 210(5)	7 128(2)	2 097(4)
C(13)	4 236	7 622	2 148
C(14)	4 870	7 855	3 427
C(15)	5 477	7 593	4 657
C(16)	5 451	7 098	4 606
C(11)	4 818	6 866	3 326
C(22)	2 513(5)	5 796(2)	943(6)
C(23)	1 079	5 717	7
C(24)	−16	5 956	169
C(25)	323	6 274	1 266
C(26)	1 758	6 353	2 202
C(21)	2 853	6 114	2 040
C(32)	6 069(5)	5 485(2)	2 738(5)
C(33)	6 710	5 248	2 016
C(34)	7 027	5 491	1 053
C(35)	6 704	5 973	813
C(36)	6 063	6 211	1 536
C(31)	5 746	5 967	2 498
C(43)	1 294(5)	5 909(2)	5 429(6)
C(44)	579	5 525	4 582
C(45)	1 269	5 250	3 976
C(46)	2 673	5 359	4 216
C(41)	3 388	5 742	5 062
C(42)	2 698	6 017	5 669
N(1)	3 890(14)	6 470(3)	6 588(9)
N(2)	3 106(11)	6 584(6)	6 883(14)
C(51)	4 253(9)	7 023(2)	7 720(8)
C(52)	3 420	7 372	7 940
C(53)	4 076	7 776	8 708
C(54)	5 564	7 832	9 257
C(55)	6 397	7 483	9 037
C(56)	5 741	7 079	8 268

Table 5. Bond lengths (Å) and angles (°) for compound (**6**)

Au–P	2.296(2)	Au–Cl(1)	2.325(2)
Au–Cl(2)	2.377(2)	Au–C(41)	2.033(5)
P–C(11)	1.804(5)	P–C(21)	1.793(5)
P–C(31)	1.793(6)	C(42)–N(1)	1.747(11)
N(1)–N(2)	1.043(21)	N(2)–C(51)	1.675(16)
P–Au–Cl(1)	175.7(1)	P–Au–Cl(2)	88.8(1)
Cl(1)–Au–Cl(2)	91.9(1)	P–Au–C(41)	91.8(2)
Cl(1)–Au–C(41)	87.6(2)	Cl(2)–Au–C(41)	178.1(2)
Au–P–C(11)	111.2(2)	Au–P–C(21)	116.6(2)
C(11)–P–C(21)	104.2(2)	Au–P–C(31)	107.8(2)
C(11)–P–C(31)	112.0(3)	C(21)–P–C(31)	105.0(3)
P–C(11)–C(12)	119.8(1)	P–C(11)–C(16)	120.1(1)
P–C(21)–C(22)	121.4(2)	P–C(21)–C(26)	118.6(2)
P–C(31)–C(32)	117.4(2)	P–C(31)–C(36)	121.9(2)
Au–C(41)–C(46)	121.3(2)	Au–C(41)–C(42)	118.7(2)
C(43)–C(42)–N(1)	133.1(5)	C(41)–C(42)–N(1)	106.8(5)
C(42)–N(1)–N(2)	86.9(12)	N(1)–N(2)–C(51)	85.9(10)

[Au{C$_6$H$_3$(N=NC$_6$H$_4$Me-4′)-2-Me-5}Cl$_2$] (**3**).—Solid [Hg{C$_6$H$_3$(N=NC$_6$H$_4$Me-4′)-2-Me-5}Cl] (100 mg, 0.22 mmol) and NMe$_4$Cl (25 mg, 0.22 mmol) were added to an acetone (50 cm^3) suspension of [AuCl$_3$(tht)] (88 mg, 0.22 mmol), and the mixture stirred for 12 h. The solution was evaporated to dryness, the residue extracted with dichloromethane (3 × 10 cm^3), and the suspension filtered through anhydrous MgSO$_4$. The red solution was concentrated to *ca.* 1 cm^3 and diethyl ether (20 cm^3) was added, giving a brick-red microcrystalline solid, which was filtered off, washed with diethyl ether, and dried under vacuum. Yield 78%, m.p. 225 °C (decomp.) (Found: C, 35.6; H, 2.9; Au, 40.9; N, 6.0. C$_{14}$H$_{12}$AuCl$_2$N$_2$ requires C, 35.3;

Table 6. Atomic co-ordinates (× 10^4) for compound (**7**)

Atom	*x*	*y*	*z*
Au	2 372.8(3)	5 443.0(3)	5 297.4(2)
Cl	1 066(2)	6 320(2)	4 642(2)
N	2 599(7)	4 429(6)	4 470(6)
C(1)	1 776(10)	3 691(8)	4 614(9)
C(2)	2 461(9)	4 770(10)	3 693(8)
C(3)	3 769(8)	4 069(8)	4 545(6)
C(11)	3 537(7)	4 676(6)	5 817(6)
C(12)	4 057(7)	4 055(6)	5 344(7)
C(13)	4 876(9)	3 447(7)	5 642(7)
C(14)	5 188(9)	3 506(8)	6 347(7)
C(15)	4 669(9)	4 126(8)	6 806(7)
C(16)	3 826(9)	4 701(8)	6 551(7)
C(21)	2 177(8)	6 267(7)	6 173(6)
C(22)	2 901(9)	6 991(7)	6 334(7)
C(23)	2 774(11)	7 540(9)	6 932(8)
C(24)	1 920(14)	7 405(10)	7 399(8)
C(25)	1 144(11)	6 701(11)	7 236(8)
C(26)	1 296(10)	6 140(9)	6 644(7)
F(22)	3 791(6)	7 127(5)	5 900(5)
F(23)	3 479(7)	8 235(6)	7 070(6)
F(24)	1 768(10)	7 924(7)	7 990(5)
F(25)	282(7)	6 547(8)	7 702(5)
F(26)	550(6)	5 480(5)	6 534(5)

Table 7. Bond lengths (Å) and angles (°) for compound (**7**)

Au–Cl	2.347(3)	Au–N	2.128(10)
Au–C(11)	2.022(10)	Au–C(21)	2.012(11)
N–C(1)	1.478(15)	N–C(2)	1.515(18)
N–C(3)	1.504(13)	C(3)–C(12)	1.503(17)
C(11)–C(12)	1.396(14)	C(11)–C(16)	1.389(17)
C(12)–C(13)	1.429(14)	C(13)–C(14)	1.347(18)
C(14)–C(15)	1.378(17)	C(15)–C(16)	1.391(16)
C(21)–C(22)	1.393(15)	C(21)–C(26)	1.377(16)
C(22)–C(23)	1.362(18)	C(22)–F(22)	1.346(14)
C(23)–C(24)	1.348(21)	C(23)–F(23)	1.339(16)
C(24)–C(25)	1.412(21)	C(24)–F(24)	1.330(17)
C(25)–C(26)	1.366(20)	C(25)–F(25)	1.360(17)
C(26)–F(26)	1.324(14)		
Cl–Au–N	95.4(3)	Cl–Au–C(11)	177.3(3)
N–Au–C(11)	82.4(4)	Cl–Au–C(21)	90.5(3)
N–Au–C(21)	172.6(4)	C(11)–Au–C(21)	91.8(4)
Au–N–C(1)	106.6(8)	Au–N–C(2)	115.5(7)
C(1)–N–C(2)	109.3(10)	Au–N–C(3)	107.0(7)
C(1)–N–C(3)	110.9(9)	C(2)–N–C(3)	107.5(9)
N–C(3)–C(12)	108.0(9)	Au–C(11)–C(12)	111.7(8)
Au–C(11)–C(16)	127.9(8)	C(12)–C(11)–C(16)	120.4(9)
C(3)–C(12)–C(11)	119.5(9)	C(3)–C(12)–C(13)	122.5(10)
C(11)–C(12)–C(13)	117.9(11)	C(12)–C(13)–C(14)	121.2(11)
C(13)–C(14)–C(15)	120.0(11)	C(14)–C(15)–C(16)	121.0(12)
C(11)–C(16)–C(15)	119.4(11)	Au–C(21)–C(22)	122.9(8)
Au–C(21)–C(26)	120.7(8)	C(22)–C(21)–C(26)	116.4(11)
C(21)–C(22)–C(23)	122.8(11)	C(21)–C(22)–F(22)	118.6(10)
C(23)–C(22)–F(22)	118.5(10)	C(22)–C(23)–C(24)	120.6(12)
C(22)–C(23)–F(23)	121.3(12)	C(24)–C(23)–F(23)	118.1(13)
C(23)–C(24)–C(25)	118.1(13)	C(23)–C(24)–F(24)	122.5(14)
C(25)–C(24)–F(24)	119.3(14)	C(24)–C(25)–C(26)	120.6(13)
C(24)–C(25)–F(25)	119.1(13)	C(26)–C(25)–F(25)	120.1(13)
C(21)–C(26)–C(25)	121.3(12)	C(21)–C(26)–F(26)	121.3(11)
C(25)–C(26)–F(26)	117.4(11)		

H, 2.5; Au, 41.4; N, 5.9%. ^{1}H n.m.r.: δ 2.46 (s, 3 H, Me), 2.53 (s, 3 H, Me), 7.30—7.76 [m, 6 H, all aryl protons except H(6)], and 7.96 [d, 1 H, H(6), ^4J(H–H) = 2 Hz].

$[\overline{\mathrm{Au}\{\mathrm{C_6H_3(N{=}N}}\mathrm{C_6H_4Me\text{-}4')\text{-}2\text{-}Me\text{-}5\}(acac\text{-}}C\mathrm{)Cl}]$ (**4**).—Solid Tl(acac) (80.5 mg, 0.26 mmol) was added to a dichloromethane (25 cm^3) solution of complex (**3**) (127 mg, 0.26 mmol). After 15 min the white precipitate was filtered off and the solution concentrated to *ca.* 1 cm^3. The addition of diethyl ether–n-hexane (1:5, 20 cm^3) then gave a yellow solid, which was filtered off, washed with n-hexane, and dried under vacuum. Yield 86%, m.p. 193 °C (decomp.) (Found: C, 42.5; H, 3.9; Au, 37.1; N, 5.1%. $C_{19}H_{20}AuClN_2O_2$ requires C, 42.2; H, 3.7; Au, 36.4; N, 5.2%) ^{1}H n.m.r.: δ 2.39 [s, 6 H, (MeCO)], 2.48 (s, 3 H, Me of aryl), 2.55 (s, 3 H, Me of aryl), 4.73 [s, 1 H, CHC(O)], 7.34, 7.81 [AB system, 4 H, H(2′,6′), H(3′,4′), ^3J(H–H) = 8], 7.59 [m, 1 H, H(6)], 8.03 [d, 1 H, H(3), ^3J(H–H) = 8 Hz], and 8.07 [d, 1 H, H(4)], ^{13}C, δ 21.54, 22.73 (C_6H_4*Me*), 31.59 (*Me*CO), 61.11 (CH), 124.57, 129.16 [C(2′), C(3′)], 129.87, 132.34, 132.38 [C(6), C(4), C(3)], 143.19, 147.66 [C(5), C(4′)], 148.27, 150.09 [C(2), C(1)], 160.38 [C(1)], and 203.81 (CO).

$[\mathrm{Au(C_6H_4N{=}NPh\text{-}2)(C_6F_5)Cl(PPh_3)}]$ (**5**).—Solid PPh_3 (15 mg, 0.06 mmol) was added to a dichloromethane (20 cm^3) solution of complex (**2**) (30 mg, 0.06 mmol). The yellow solution changed immediately to orange-red. After 5 min the solvent was reduced in volume to *ca.* 1 cm^3 and n-hexane (10 cm^3) added to give an orange solid. Yield 73%, m.p. 145 °C (Found: C, 51.5; H, 3.6; Au, 23.4; N, 3.4. $C_{18}H_{13}AuClN_3O_2$ requires C, 51.3; H, 2.9; Au, 23.4; N, 3.3%).

X-*Ray Structure Determinations.*—Intensity data were collected on a Siemens four-circle diffractometer using monochromated Mo-K_α radiation. Cell constants were refined from setting angles of *ca.* 50 reflections in the range 2θ 20—23°. Structures were solved by the heavy-atom method and subjected to anisotropic full-matrix least-squares refinement. Hydrogen atoms were included using a riding model. Weighting schemes of the form $w^{-1} = \sigma^2(F) + gF^2$ were employed. Exception: for compound (**6**) the non-co-ordinated part of the phenylazophenyl ligand was poorly defined, presumably because of disorder. All phenyl rings were constrained to idealized geometry, with isotropic carbon. Clearly, the dimensions of the disordered moiety are unreliable, but no sensible disorder model could be refined. Details of data collection and structure refinement are presented in Table 1, final atomic co-ordinates in Tables 2, 4, and 6, and bond lengths and angles in Tables 3, 5, and 7.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

We thank Dirección Generale de Investigación Científica y Técnica (Spain) (PB89-0430) and the Fonds der Chemischen Industrie for financial support. M. D. B. is grateful for a grant from Ministerio de Educacion y Ciencia (Spain).

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Received 6th *April* 1990; *Paper* 0/01559H