

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 $[\text{Au}\{\text{C}_6\text{H}_3(\text{N}=\text{NC}_6\text{H}_4\text{Me}-4')-2\text{-Me}-5\}(\text{acac}-\text{C})\text{Cl}]$ (acac = acetylacetonate), *cis*- $[\text{Au}(\text{C}_6\text{H}_4\text{N}=\text{NPh}-2)\text{Cl}_2(\text{PPh}_3)]$, and $[\text{Au}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)(\text{C}_6\text{F}_5)\text{Cl}]$ †

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The complex $[\text{Au}(\text{C}_6\text{H}_4\text{N}=\text{NPh}-2)\text{Cl}_2]$ reacts with $[\text{HgR}_2]$ ($\text{R} = \text{C}_6\text{H}_4\text{NO}_2-2$ or C_6F_5) and NMe_4Cl (2:1:2) to give $[\text{Au}(\text{C}_6\text{H}_4\text{N}=\text{NPh}-2)(\text{R})\text{Cl}]$ [$\text{R} = \text{C}_6\text{H}_4\text{NO}_2-2$, (1); or C_6F_5 (2)]. Similarly, $[\text{Au}(\text{C}-\text{N})\text{Cl}_2]$ (3) [$\text{C}-\text{N} = \text{C}_6\text{H}_3(\text{N}=\text{NC}_6\text{H}_4\text{Me}-4')-2\text{-Me}-5$], prepared by the reaction of $[\text{AuCl}_3(\text{tht})]$ (tht = tetrahydrothiophene) with $[\text{Hg}(\text{C}-\text{N})\text{Cl}]$ and NMe_4Cl (1:1:1), reacts with $\text{Ti}(\text{acac})$ (Hacac = acetylacetonate) (1:1) to give $[\text{Au}(\text{C}-\text{N})(\text{acac}-\text{C})\text{Cl}]$ (4). Reaction of (2) with PPh_3 (1:1) leads to $[\text{Au}(\text{C}_6\text{H}_4\text{N}=\text{NPh}-2)(\text{C}_6\text{F}_5)\text{Cl}(\text{PPh}_3)]$ (5), which upon standing in dichloromethane solution decomposes to give a mixture of $[\text{Au}(\text{C}_6\text{F}_5)(\text{PPh}_3)]$, $\text{C}_6\text{H}_4\text{C}_6\text{F}_5-1\text{-N}=\text{NPh}-2$, and $[\text{Au}(\text{C}_6\text{H}_4\text{N}=\text{NPh}-2)\text{Cl}_2(\text{PPh}_3)]$ (6). Crystal structures were determined for complexes (4), (6), and $[\text{Au}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)(\text{C}_6\text{F}_5)\text{Cl}]$ (7) [(4), space group $P\bar{1}$, $a = 9.475(4)$, $b = 9.923(4)$, $c = 10.913(4)$ Å, $\alpha = 63.75(3)$, $\beta = 84.92(3)$, $\gamma = 89.41(3)^\circ$, $Z = 2$, $R = 0.020$ 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, $\beta = 116.26(2)^\circ$, $Z = 4$, $R = 0.038$ 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– 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.

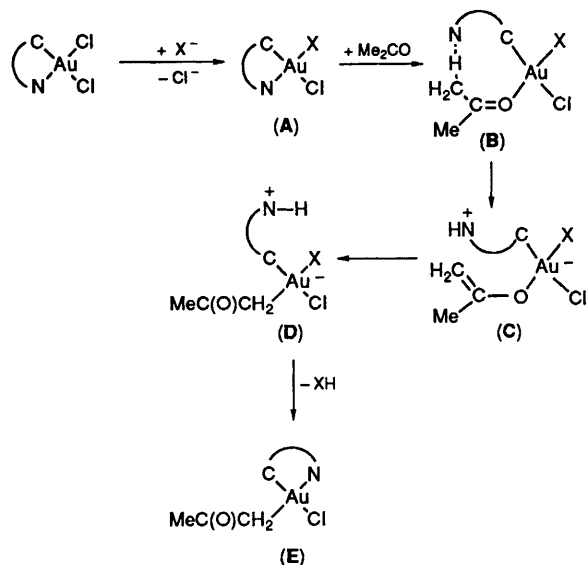
We have recently reported^{1,2} that reactions of $[\text{Au}(\text{C}_6\text{H}_4\text{N}=\text{NPh}-2)\text{Cl}_2]$ with different reagents such as $\text{Ti}(\text{acac})$ (Hacac = acetylacetonate), KCN, AgClO_4 , 1,10-phenanthroline, $[\text{HgR}_2]$ ($\text{R} = \text{C}_6\text{F}_5$ or $\text{C}_6\text{H}_4\text{N}=\text{NPh}-2$), and $[\text{PdR}_2]$ ($\text{R} = \text{C}_6\text{H}_4\text{NO}_2-2$) led to $[\text{Au}(\text{C}_6\text{H}_4\text{N}=\text{NPh}-2)\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]$ 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 experience³ of 2-phenylazophenylgold(III) complexes and also on the isolation of intermediates such as $[\text{Au}(\text{C}_6\text{H}_4\text{N}=\text{NPh}-2)(\text{acac}-\text{C})\text{Cl}]$. 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

† Chloro(5-methyl-2-*p*-tolylazo- κ N'-phenyl- κ C¹)(pentane-2,4-dionato- κ C³), dichloro(2-phenylazophenyl- κ C¹)(triphenylphosphine)-, and chloro(2-dimethylamino- κ N-methylphenyl- κ C¹)(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.

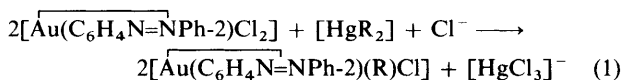
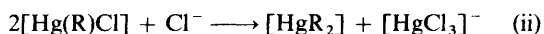
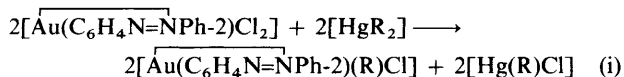


Scheme. C-N = C₆H₄N=NPh-2; X = acac-C, CN, C₆H₄N=NPh-2, C₆F₅, or C₆H₄NO₂-2

was based on its i.r. spectrum. In this paper we report the synthesis and crystal structure of its homologue with the aryl ligand C₆H₃(N=NC₆H₄Me-4')-2-Me-5 and the isolation of two of the postulated intermediates of type (A) with X = C₆H₄NO₂-2 or C₆F₅. 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.

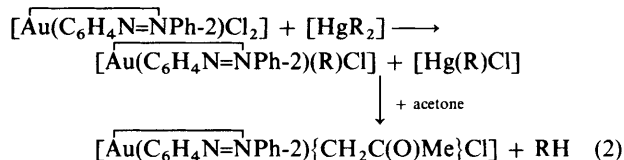
Results and Discussion

The complex [Au(C₆H₄N=NPh-2)Cl₂], which was prepared by treating [AuCl₃(tht)] (tht = tetrahydrothiophene) with [Hg(C₆H₄N=NPh-2)₂],⁵ undergoes a second transmetalation reaction when refluxed in chloroform with [HgR₂] (R = C₆H₄NO₂-2 or C₆F₅) in the presence of NMe₄Cl (2:1:2) giving [Au(C₆H₄N=NPh-2)(R)Cl] [R = C₆H₄NO₂-2, (1) or C₆F₅, (2)] [see equation (1)] in high yields. The addition of NMe₄Cl reduces the required amount of the mercurial by half because it symmetrizes [equation (ii)] the by-product [Hg(R)Cl] of the transmetalation reaction [equation (i)].



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(C₆H₄N=NPh-2){CH₂C(O)Me}Cl] could be isolated, and because they were assumed to be intermediates (see Scheme) in such C-H activation processes.

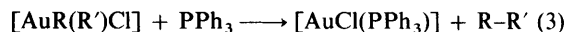


However, they react with acetone more slowly than [Au(C₆H₄N=NPh-2)Cl₂] does with [HgR₂] in acetone to give (in both cases) [Au(C₆H₄N=NPh-2){CH₂C(O)Me}Cl]. It is possible that the by-products of these reactions, [Hg(R)Cl], or even the starting complex [Au(C₆H₄N=NPh-2)Cl₂] could catalyse the direct reaction.

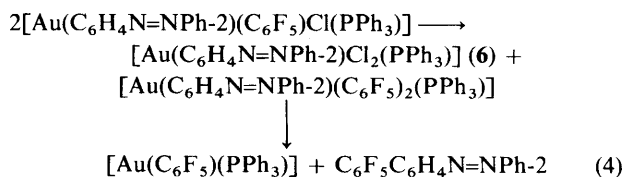
Because we have not been able to grow crystals of complexes (1) or (2), or of [Au(C₆H₄N=NPh-2)(acac)Cl] the other previously isolated intermediate in the activation of acetone,² we decided to prepare a homologue of this complex containing the *para*-disubstituted group C₆H₃(N=NC₆H₄Me-4')-2-Me-5 instead of C₆H₄N=NPh-2. The starting complex [Au(C-N)Cl₂] (3) [C-N = C₆H₃(N=NC₆H₄Me-4')-2-Me-5], can be prepared by treating [AuCl₃(tht)] with [Hg(C-N)Cl] and NMe₄Cl (1:1:1). The reaction of complex (3) with Tl(acac) (1:1) gives the desired complex [Au(C-N)(acac)Cl] (4), for which the crystal structure was determined (see below).

Reported acac complexes of gold(III) are limited to [AuMe₂(acac-O)]¹¹ and [AuMe₂(acac-C)L],¹² of which only the complex with L = PPhMe₂ 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,



when R = C₆H₄N=NPh-2, are generally rapid at room temperature, which makes it difficult to isolate any intermediate. However, the great stability of the C₆F₅ gold derivatives makes complex (2) suitable for the synthesis of such intermediates. Addition of PPh₃ (1:1) to a solution of complex (2) gives [Au(C₆H₄N=NPh-2)(C₆F₅)Cl(PPh₃)] (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(C₆H₄N=NPh-2)Cl₂(PPh₃)] (6), and a third colourless [Au(C₆F₅)(PPh₃)]. The only suitable crystals for X-ray diffraction study were those of complex (6), which we had already synthesized by the reaction of [Au(C₆H₄N=NPh-2)Cl₂] with PPh₃ (1:1).⁵ The mother-liquor from the crystallization process contained the biphenyl compound C₆F₅C₆H₄N=NPh-2. It is possible that the sequence of reactions (4) occurs. Therefore, complex (2)



reacts differently with PPh₃ from other mixed diarylgold(III) complexes, which give [AuCl(PPh₃)] as the reduction product.

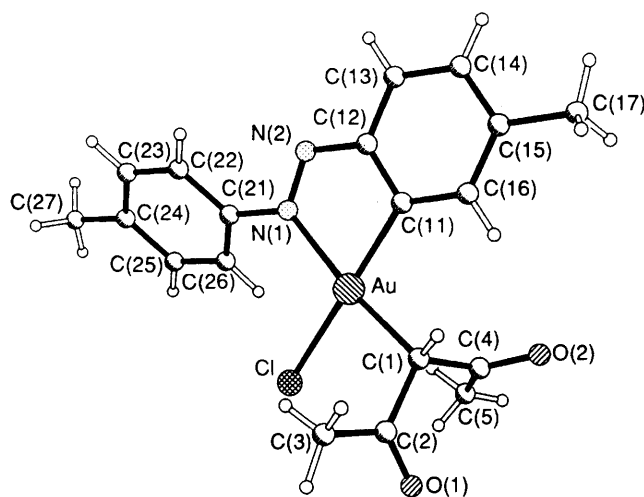


Figure 1. The molecule of complex (4) in the crystal. Radii are arbitrary

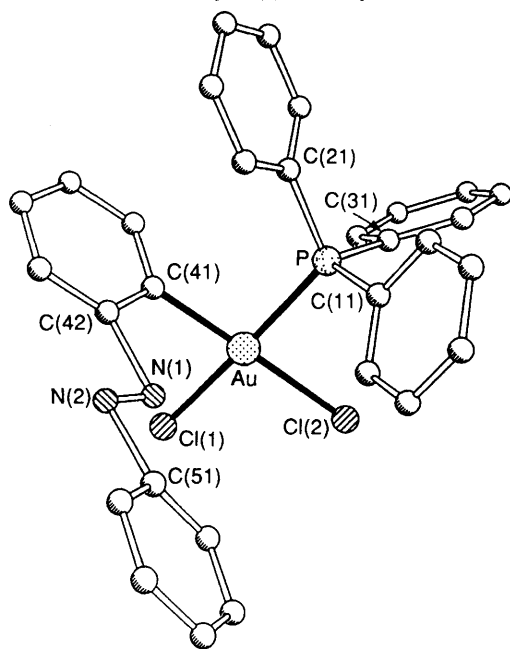


Figure 2. The molecule of complex (6) in the crystal. Radii are arbitrary; H-atoms omitted for clarity

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 $[Au(C_6H_4CH_2NMe_2-2)(Ph)Cl]$; it does not occur with $[Au(C_6H_4CH_2NMe_2-2)(C_6F_5)Cl]$ (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 $400-300\text{ cm}^{-1}$, depending on the number of chloro ligands in the molecule. The band corresponding to the monochloro-complexes appears at $300-310\text{ cm}^{-1}$, which is assignable to $\nu(AuCl)$ *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

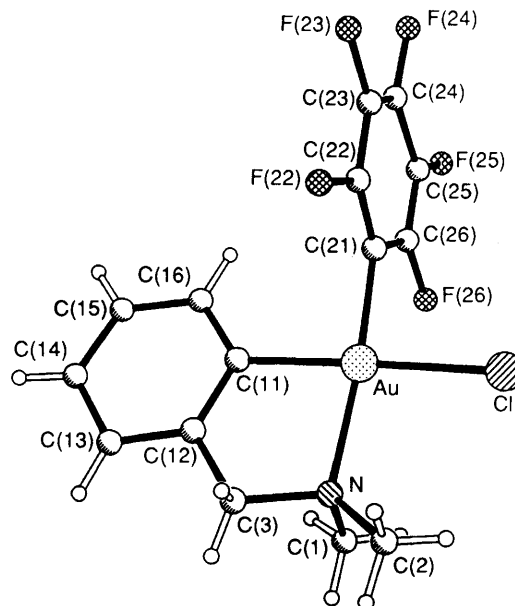


Figure 3. The molecule of complex (7) in the crystal. Radii are arbitrary; H-atoms omitted for clarity

the observed band for complex (5) corresponds to $\nu(AuCl)$ *trans* to $C_6H_4N=NPh-2$. The second band for complexes $[Au(C-N)Cl_2]$ (3) and $[Au(C_6H_4N=NPh-2)Cl_2(PPh_3)]$ (6) appears at 345 and 320 cm^{-1} , respectively, being assignable to $\nu(AuCl)$ *trans* to N and P, respectively. For complex (7) the presence of $\nu(AuCl)$ 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).

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 1230 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; $[Au(C_6H_4N=NPh-2)Cl_2]$ shows this band, whereas $[Au(C_6H_4N=NPh-2)Cl_2(PPh_3)]$ (with no Au-N bond) does not. Characteristic bands of the substituents of the aryl groups ($C_6H_4NO_2-2$, $1510s$, $1330s$, and $850m$; C_6F_5 , $1500m$, $1050s$, and 800 cm^{-1}) and of the other ligands [$\nu(CO)$ in (4) at 1685 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 $[Au(C_6H_4N=NPh-2)(acac-C)Cl]$ 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 ₁₅ H ₂₀ AuClN ₂ O ₂	C ₃₀ H ₂₄ AuCl ₂ N ₂ P	C ₁₅ H ₁₂ AuClF ₅ N
<i>M</i>	540.8	711.4	533.7
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>
Temperature (°C)	-95	20	20
<i>a</i> /Å	9.475(4)	10.361(3)	11.996(4)
<i>b</i> /Å	9.923(4)	28.194(8)	14.484(4)
<i>c</i> /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)		
<i>U</i> /Å ³	916.1	2 809.6	3 181.3
<i>Z</i>	2	4	8
<i>D</i> _c /Mg m ⁻³	1.96	1.68	2.23
<i>F</i> (000)	520	1 384	2 000
μ /mm ⁻¹	8.2	5.5	9.5
2 θ _{max} (°)	50	50	50
No. of reflections:			
measured	6 422	7 205	2 797
independent	3 214	4 936	2 794
<i>R</i> _{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
<i>R</i>	0.020	0.038	0.045
<i>R</i> '	0.026	0.044	0.058
<i>g</i>	0.0003	0.000 15	0.0035
No. of parameters	232	115	208
<i>S</i>	1.2	1.8	0.9
Maximum Δ/σ	0.006	0.003	0.001
Maximum $\Delta\rho/e$ 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	<i>x</i>	<i>y</i>	<i>z</i>
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(C₆H₄CH₂NMe₂-2)(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 PPh₃ 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 PPh₃ adduct. Because this cleavage is much more facile with C₆H₄N=NPh-2 than with C₆H₄CH₂NMe₂-2, complexes [Au(C₆H₄N=NPh-2)(R)Cl] generally react with PPh₃ to give biphenyls, for example with R = C₆H₄(N=NPh)-2, Ph, C₆F₅, or C₆H₄NO₂-2, whereas for the complexes [Au(C₆H₄CH₂NMe₂-2)(R)Cl] only R = Ph reacts in this way.

It is interesting that all the substitution reactions here and previously described³ 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 ¹³C n.m.r. spectra (in CDCl₃) were recorded on a Bruker 200AC spectrometer and ¹⁹F n.m.r. spectra (in CDCl₃) on a Varian FT80 spectrometer. Chemical shifts in p.p.m. are referred to SiMe₄ or CFCl₃, 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 compounds² 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(C₆H₄N=NPh-2)(C₆H₄NO₂-2)Cl] (1).—Solid [Hg(C₆H₄NO₂-2)₂] (60 mg, 0.14 mmol) and NMe₄Cl (30 mg, 0.28 mmol) were added to a chloroform (50 cm³) suspension of [Au(C₆H₄N=NPh-2)Cl₂] (120 mg, 0.28 mmol). After refluxing for 1 h, the suspension was filtered through anhydrous MgSO₄, giving an orange solution which was evaporated to ca. 1 cm³. Diethyl ether (15 cm³) 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. C₁₈H₁₃AuClN₃O₂ requires C, 40.4; H, 2.4; Au, 36.8; N, 7.8%).

[Au(C₆H₄N=NPh-2)(C₆F₅)Cl] (2).—Solid [Hg(C₆F₅)₂] (250 mg, 0.48 mmol) was added to a chloroform (60 cm³) suspension of [Au(C₆H₄N=NPh-2)Cl₂] (430 mg, 0.96 mmol). After refluxing the mixture for 5 h the suspension was filtered through anhydrous MgSO₄ and the resulting orange solution evaporated to ca. 1 cm³. Addition of diethyl ether-n-hexane (1:5, 30 cm³) 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. C₁₈H₉AuClF₅N₂ requires C, 37.2; H, 1.6; Au, 33.9; N, 4.8%). ¹⁹F 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).

[Au{C₆H₃(N=NC₆H₄Me-4')-2-Me-5}Cl₂] (3).—Solid [Hg{C₆H₃(N=NC₆H₄Me-4')-2-Me-5}Cl] (100 mg, 0.22 mmol) and NMe₄Cl (25 mg, 0.22 mmol) were added to an acetone (50 cm³) suspension of [AuCl₃(tht)] (88 mg, 0.22 mmol), and the

Table 4. Atomic co-ordinates (× 10⁴) 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)

mixture stirred for 12 h. The solution was evaporated to dryness, the residue extracted with dichloromethane (3 × 10 cm³), and the suspension filtered through anhydrous MgSO₄. The red solution was concentrated to ca. 1 cm³ and diethyl ether (20 cm³) 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. C₁₄H₁₂AuCl₂N₂ requires C, 35.3;

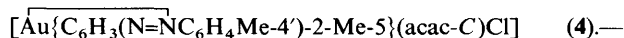
Table 6. Atomic co-ordinates ($\times 10^4$) for compound (7)

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 ($^\circ$) 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%. ^1H 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), $^4J(\text{H-H}) = 2$ Hz].



Solid $\text{Ti}(\text{acac})$ (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%. $\text{C}_{19}\text{H}_{20}\text{AuClN}_2\text{O}_2$ requires C, 42.2; H, 3.7; Au, 36.4; N, 5.2%) ^1H 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'), $^3J(\text{H-H}) = 8$], 7.59 [m, 1 H, H(6)], 8.03 [d, 1 H, H(3), $^3J(\text{H-H}) = 8$ Hz], and 8.07 [d, 1 H, H(4)], ^{13}C , δ 21.54, 22.73 ($\text{C}_6\text{H}_4\text{Me}$), 31.59 (MeCO), 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).

$[\text{Au}(\text{C}_6\text{H}_4\text{N}=\text{NPh-2})(\text{C}_6\text{F}_5\text{Cl})(\text{PPh}_3)]$ (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. $\text{C}_{18}\text{H}_{13}\text{AuClN}_3\text{O}_2$ 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 $20\text{--}23^\circ$. 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.

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