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FULL PAPER

Synthesis and reactivity of arylgold(III) complexes from aromatic hydrocarbons *via* C–H bond activation

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Received 19th March 2001, Accepted 8th June 2001
First published as an Advance Article on the web 30th July 2001

The reactions of anhydrous gold(III) chloride $[AuCl_3]_2$ with aromatic hydrocarbons (ArH) such as benzene, toluene, xylenes, mesitylene, cumene, methoxybenzene and chlorobenzene, and the following treatment with 2,6-lutidine (lut) gave stable arylgold(III) complexes $[AuArCl_2(lut)]$. These auration reactions proceeded heterogeneously in hexane and homogeneously in diethyl ether. The ^1H NMR spectra of the arylgold(III) complexes revealed that aurations towards aromatic compounds take place regiospecifically at the position with higher electron density and with less steric hindrances. The *trans* configuration of the arylgold(III) complexes was established by means of their far-IR spectra and confirmed for $[Au(2,5\text{-}Me_2C_6H_3)Cl_2(lut)]$ by its single-crystal X-ray structure. The reactions of $[AuArCl_2(lut)]$ (Ar = phenyl, 2,5-xylyl) with a terminal alkyne, phenyacetylene (HC≡CPh), afforded arylated phenylacetylenes ArC≡CPh.

Introduction

The activation of aromatic C–H bonds by transition metals is a subject of current interest in organometallic chemistry.[1] Generally, the cleavage of the C–H bond proceeds *via* an oxidative addition or an electrophilic substitution mechanism by metal complexes having low or high oxidation states, respectively. C–H/olefin coupling with an Ru(0) complex[2] and the Fujiwara reaction using a Pd(II) compound[3] are the typical catalytic systems used for the above types of activation.

Concerning the C–H bond activation by gold compounds, Kharasch and Isbell[4] demonstrated in 1931 that reaction of anhydrous gold(III) chloride with neat benzene or toluene, or with other aromatic compounds such as biphenyl and methyl salicylate in petroleum ether readily produces the arylgold(III) complex $[(AuArCl_2)_2]$. Liddle and Parkin[5] and de Graaf *et al.*[6] re-investigated this study during the 1970s. The former group emphasized the instability of the dimeric arylgold(III) complexes $[(AuArCl_2)_2]$ and isolated the products as ligand-stabilized arylgold(III) species $[AuArCl_2(L)]$ ($L = PPh_3$, pyridine, SPr_2). In contrast, the latter workers succeeded in isolating the ligand-free dimeric complexes $[(AuArCl_2)_2]$ using carbon tetrachloride as the solvent. However, carbon tetrachloride is now very expensive owing to its restricted supply for fear of damaging further the ozone layer. To investigate and further develop the chemistry of C–H bond activation by gold(III) compounds, it has become necessary to improve the synthetic methods of arylgold(III) species by C–H bond activation. Establishment of the general method for preparing arylgold(III) complexes, structural analysis of the 2,5-xylylgold(III) complex $[Au(2,5\text{-}Me_2C_6H_3)Cl_2(lut)]$ prepared in this study and investigation of the reactivity of the arylgold(III) complexes with unsaturated compounds forms the basis of this report.

Results and discussion

Synthesis and properties of the arylgold(III) complexes

First, the reaction between anhydrous gold(III) chloride $[AuCl_3]_2$ and benzene was investigated in THF, hexane and diethyl ether. In THF colloidal gold precipitated gradually over the course of the reaction and phenylgold(III) species could not be obtained at all. On the other hand, in hexane the above reaction proceeded heterogeneously at 20 °C and the dimeric phenylgold(III) complex $[(AuPhCl_2)_2]$ was obtained. This complex is quite unstable both in the solid state and in solution. On standing in air the yellow colour of the complex changed to a brownish yellow within 10 min, and colloidal gold precipitated from a fresh solution of THF, diethyl ether, dichloromethane or chloroform.

Accordingly, in order to facilitate judgment of the formation and characterization of the resulting arylgold(III) complexes, 2,6-lutidine (lut) was used as a stabilizing ligand and arylgold(III) complexes were isolated as mononuclear species $[AuArCl_2(lut)]$. In this way mononuclear arylgold(III) complexes $[AuArCl_2(lut)]$ **1**–**9** (Ar = phenyl, **1**; 4-tolyl, **2**; 3,4-xylyl, **3**; 2,4-xylyl, **4**; 2,5-xylyl, **5**; mesityl, **6**; 4-cumenyl, **7**; 4-methoxyphenyl, **8**; 4-chlorophenyl, **9**) were isolated from the reactions of $[AuCl_3]_2$ with the corresponding aromatic hydrocarbons, *i.e.*, benzene, toluene, xylenes (*o*-, *m*- and *p*-), mesitylene, cumene, methoxybenzene and chlorobenzene (Scheme 1). When diethyl ether was used as a solvent, these reactions proceeded not heterogeneously but homogeneously, and 2,5-xylyl- and 4-methoxyphenyl-gold(III) complexes **5** and **8** were obtained. However in diethyl ether $[AuCl_3]_2$ did not react with benzene and toluene (see below).

Arylgold(III) complexes **1**–**9** are fairly stable and can be handled in air without any difficulty. Yields, melting points and IR data of the arylgold(III) complexes **1**–**9** are described in the Experimental section, while the ^1H NMR data, assigned with the aid of ^1H–^1H correlation spectroscopy, are summarized in Table 1. The far-IR spectra of **1**–**9** exhibited only one band in the range 360–373 cm^{-1} attributable to ν(Au–Cl),[5,6] indicating a *trans* configuration for the two chloro ligands. The single-crystal X-ray analysis of $[Au(2,5\text{-}Me_2C_6H_3)Cl_2(lut)]$ **5** confirmed the *trans* configuration of the arylgold(III) complexes **1**–**9** (see below).

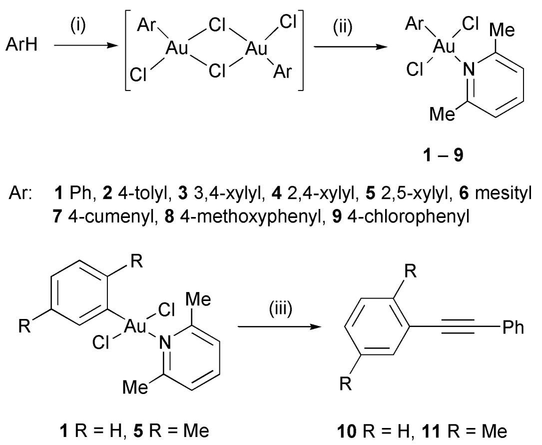
Concerning the yield of arylgold(III) complexes **1**–**9**, the theoretical maximum yield of this reaction is calculated to be

DOI: 10.1039/b102527a

Table 1 Proton NMR spectral data of the new aryl gold(III) complexes[a]

	Aryl moiety		2,6-Lutidine		
Complex	Aromatic protons	Others	β-H	γ-H	Me
1 $[AuCl_2Ph(lut)]$	7.1–7.25 (5H, c)	—	7.28 (1H, d)[b]	7.74 (1H, t)[b]	3.06 (6H, s)
2 $[Au(4\text{-}MeC_6H_4)Cl_2(lut)]$	6.97 (2H, d, H^3, H^5)[c] 7.12 (2H, d, H^2, H^6)[c]	2.33 (3H, s, Me)	7.28 (1H, d)[b]	7.73 (1H, t)[b]	3.06 (6H, s)
3 $[Au(3,4\text{-}Me_2C_6H_3)Cl_2(lut)]$	6.76 (1H, d, H^5)[c] 6.88 (1H, d, H^6)[c] 6.92 (1H, s, H^2)	2.24 (3H, s, Me) 2.26 (3H, s, Me)	7.27 (1H, d)[b]	7.73 (1H, t)[b]	3.06 (6H, s)
4 $[Au(2,4\text{-}Me_2C_6H_3)Cl_2(lut)]$	6.82 (1H, dd, H^5)[c,d] 6.86 (1H, s, H^3)	2.31 (3H, s, 4-Me) 2.61 (3H, s, 2-Me) 6.97 (1H, d, H^6)[c]	7.29 (1H, d)[b]	7.73 (1H, t)[b]	3.08 (6H, s)
5 $[Au(2,5\text{-}Me_2C_6H_3)Cl_2(lut)]$	6.82 (1H, d, H^4)[b] 6.90 (1H, d, H^3)[b] 6.92 (1H, s, H^6)	2.32 (3H, s, 5-Me) 2.60 (3H, s, 2-Me)	7.29 (1H, d)[b]	7.73 (1H, t)[b]	3.08 (3H, s) 3.10 (3H, s)
6 $[Au(2,4,6\text{-}Me_3C_6H_2)Cl_2(lut)]$	6.69 (2H, s, H^2, H^4)	2.28 (3H, s, 4-Me) 2.64 (6H, s, 2,6-Me_2)	7.27 (1H, d)[b]	7.72 (1H, t)[b]	3.09 (6H, s)
7 $[Au(4\text{-}Me_2CHC_6H_4)Cl_2(lut)]$	7.01 (2H, d, H^3, H^5)[e] 7.15 (2H, d, H^2, H^6)[e]	1.24 (6H, d, Me)[b] 2.87 (3H, h, CH)[b]	7.28 (1H, d)[b]	7.74 (1H, t)[b]	3.06 (6H, s)
8 $[Au(4\text{-}MeOC_6H_4)Cl_2(lut)]$	6.77 (2H, d, H^3, H^5)[f] 7.16 (2H, d, H^2, H^6)[f]	3.05 (3H, s, OMe)	7.29 (1H, d)[b]	7.74 (1H, t)[b]	3.06 (6H, s)
9 $[Au(4\text{-}ClC_6H_4)Cl_2(lut)]$	7.16 (2H, d, H^3, H^5)[f] 7.21 (2H, d, H^2, H^6)[f]	—	7.27 (1H, d)[b]	7.76 (1H, t)[b]	3.05 (6H, s)

[a] Measured in $CDCl_3$ at 270 MHz and at 23 °C; δ in ppm with respect to $SiMe_4$; s = singlet, d = doublet, dd = double doublet, t = triplet, h = heptet. [b] $^3J(HH) = 7.6$ Hz. [c] $^3J(HH) = 8.3$ Hz. [d] $^4J(HH) = 2.0$ Hz. [e] $^3J(HH) = 8.5$ Hz. [f] $^3J(HH) = 8.8$ Hz.



Scheme 1 (i) $[AuCl_3]_2$; (ii) 2,6-lutidine; (iii) phenylacetylene.

50% based upon $[AuCl_3]_2$ because hydrogen chloride generated during the auration reaction consumes starting $[AuCl_3]_2$ by producing $H[AuCl_4]$.[6] To improve the yield of this reaction, several experiments were performed in the presence of organic and inorganic bases. The reaction between $[AuCl_3]_2$ and *p*-xylene in diethyl ether was carried out in the presence of 2,6-di-*tert*-butylpyridine or 1,8-bis(dimethylamino)naphthalene. These bases are believed not to co-ordinate to metal ions owing to the bulky substituents so that generated hydrogen chloride is effectively removed from the reaction mixture as the pyridinium or ammonium salt, respectively, but in both cases an isolable amount of arylgold(III) complex, **5**, could not be obtained. On the other hand, in the heterogeneous reaction between $[AuCl_3]_2$ and *p*-xylene in hexane, addition of alkali metal carbonate such as Li_2CO_3, Na_2CO_3, $NaHCO_3$ or K_2CO_3 increased the average yield of **5** up to ≈50%. Li_2CO_3 and Na_2CO_3 were most effective, the yield of **5** reaching 67 and 69%, respectively.

Single-crystal X-ray structural analysis of $[Au(2,5\text{-}Me_2C_6H_3)Cl_2(lut)]$

The structure of $[Au(2,5\text{-}Me_2C_6H_3)Cl_2(lut)]$ **5** was established by X-ray diffraction and ORTEP views of the molecule are shown in Fig. 1. Selected bond distances and angles are summarized in Table 2. The gold atom has essentially square-planar

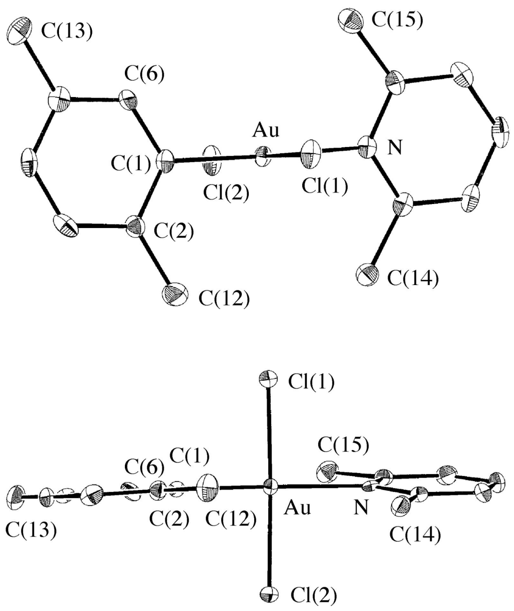


Fig. 1 ORTEP[31] views of $[Au(2,5\text{-}Me_2C_6H_3)Cl_2(lut)]$. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for **5**

Au–C(1)	2.013(4)	Au–N	2.160(4)
Au–Cl(1)	2.286(1)	Au–Cl(2)	2.275(1)
C(1)–C(2)	1.402(6)	C(1)–C(6)	1.382(6)
C(2)–C(3)	1.392(7)	C(3)–C(4)	1.386(7)
C(4)–C(5)	1.379(7)	C(5)–C(6)	1.390(6)
C(2)–C(12)	1.500(7)	C(5)–C(13)	1.510(7)
N–C(7)	1.355(6)	N–C(11)	1.353(5)
C(7)–C(8)	1.375(7)	C(8)–C(9)	1.383(7)
C(9)–C(10)	1.387(8)	C(10)–C(11)	1.386(6)
C(7)–C(15)	1.498(7)	C(11)–C(14)	1.502(7)
C(1)–Au–Cl(1)	89.2(1)	C(1)–Au–Cl(2)	88.7(1)
N–Au–Cl(1)	91.92(10)	N–Au–Cl(2)	90.16(10)
Cl(1)–Au–Cl(2)	177.79(4)	C(1)–Au–N	177.6(1)
Au–C(1)–C(2)	120.8(3)	Au–C(1)–C(6)	118.1(3)
Au–N–C(7)	118.6(3)	Au–N–C(11)	121.2(3)

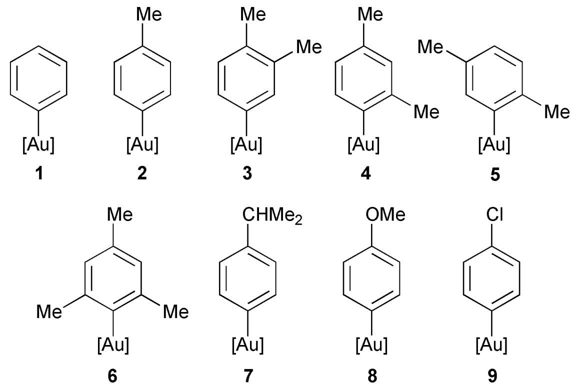


Fig. 2 Regiospecific auration positions of the aromatic hydrocarbons. [Au] denotes the AuCl$_2$(lut) moiety.

AuCNCl$_2$ co-ordination with the mean deviation from the best plane of 0.0213 Å. The Au–C bond distance 2.013(4) Å is normal for gold(III) complexes[7–17] and the Au–Cl bond lengths [2.286(1) and 2.275(1) Å] are very similar to those found in *trans*-[AuCl$_2$(C$_3$H$_2$N$_2$C$_6$H$_5$)(3,5-Me$_2$C$_5$H$_3$N)].[15] The Au–N bond distance, 2.160(4) Å, is long but typical for an Au–N bond *trans* to an atom having a high *trans* influence {2.121(5) Å in *trans*-[AuCl$_2$(C$_3$H$_2$N$_2$C$_6$H$_5$)(3,5-Me$_2$C$_5$H$_3$N)]}.[15] Both the benzene and pyridine rings stand nearly upright towards the gold square-planar plane [Au–C(1)–Cl(1)–Cl(2)–N], forming dihedral angles of 95.8 and 95.8°, respectively. Accordingly, the benzene ring is nearly parallel to the pyridine ring, making a dihedral angle of 9.8°.

Nature of auration by anhydrous gold(III) chloride

As described above, aromatic hydrocarbons having electron-donating substituents such as alkyl and methoxy groups produced arylgold(III) complexes **1**–**8**. Concerning the aromatic hydrocarbons bearing an electron-withdrawing group, chlorobenzene afforded **9**, but *o*-, *m*- and *p*-dichlorobenzene, acetophenone and nitrobenzene did not react with [AuCl$_3$]$_2$. These results clearly indicate that C–H bond activation by gold(III) proceeds in an electrophilic manner. Lowered activity of [AuCl$_3$]$_2$ towards benzene and toluene in diethyl ether (see above) also supports the electrophilic mechanism, the electrophilicity of the adduct formed in diethyl ether [AuCl$_3$(OEt$_2$)] seems to be lower than that of [AuCl$_3$]$_2$.

Moreover, it was found that complexes **2**–**4**, **7**–**9**, are composed of only one isomer. In each ^{1}H NMR spectrum of **2**, **7**, **8** and **9**, aromatic protons appeared as a typical A$_2$B$_2$ pattern [**2**, δ 6.97 (2H, d) and 7.12 (2H, d); **7**, δ 7.01 (2H, d) and 7.15 (2H, d); **8**, δ 6.77 (2H, d) and 7.16 (2H, d); **9**, δ 7.16 (2H, d) and 7.21 (2H, d)], confirming that auration occurs at the 4-position of the four aromatic hydrocarbons (toluene, cumene, methoxybenzene and chlorobenzene) (Fig. 2). In the cases of **3** and **4**, aromatic protons of the xylyl moiety were observed as ABC patterns at δ 6.76 (d), 6.88 (d) and 6.92 (s) for **3**, and 6.82 (dd), 6.86 (s) and 6.97 (d) for **4**, suggesting that auration of both *o*-xylene and *m*-xylene takes place at the 4-position.

Especially in **4**, deshielding of the 2-methyl resonance (δ 2.61) in the 2,4-xylyl group also supported the 4-metallation. Such a deshielding of the methyl resonance *ortho* to the metal atom was also found in *trans*-[Ni(2-MeC$_6$H$_4$)(CCl=CCl$_2$)(PEt$_3$)$_2$][18] and was ascribed to paramagnetic anisotropy of the metal ion.[19] These results clearly indicate that auration proceeds regiospecifically in the C–H bond activation by gold(III) species which is in sharp contrast to the results obtained in the aromatic C–H bond activation by the palladium(II) acetate–dialkyl sulfide[20] or–dialkyl selenide systems[21] which afforded arylpalladium(II) complexes composed of several isomers. The difference in the reactivity between gold(III) and palladium(II) is probably caused by the reaction temperatures. In other words, metallation reactions by gold(III) carried out at lower temperature (0–20 °C) produced kinetically controlled products, while those by palladium(II), performed at higher temperature (90–95 °C), gave thermodynamically controlled products. Considering that 1,3,5-triisopropylbenzene did not react with [AuCl$_3$]$_2$, auration sites are further restricted by the steric hindrance of the substituents, establishing regiospecificity. In summary, the auration reaction studied here proceeded *via* an electrophilic mechanism and produced kinetically and sterically controlled highly regiospecific products.

Reactions of arylgold(III) complexes with unsaturated organic molecules

It is well established that the Fujiwara reaction proceeds *via* formation of an arylpalladium(II) complex followed by alkene insertion and β-hydrogen elimination affording the final arylated alkene.[3,22] Moreover, very recently it was reported that hydroarylation of alkynes takes place smoothly using the palladium(II) acetate and trifluoroacetic acid system.[23] It is interesting to investigate how the arylgold(III) complexes behave towards alkenes or alkynes.

Reaction of complex **5** with styrene did not afford any arylated styrene even at the reflux temperature of THF, only recovering starting material **5**. Internal alkynes such as diphenylacetylene and dimethylacetylenedicarboxylate also did not react with **5** at all, but the terminal acetylene, phenylacetylene did react with **1** and **5** to give arylated alkynes, diphenylacetylene **10** and 1,4-dimethyl-2-(phenylethynyl)benzene (2,5-xylylphenylacetylene) **11**, respectively, in high yields. It is interesting that such arylation of a alkyne occurred even in the presence of acetic acid or trifluoroacetic acid, from where no hydroarylation products were obtained. Arylation of alkynes [Sonogashira reaction in the absence of copper(I) compound] was recently reported by Herrmann and co-workers using cyclopalladated complexes[24] and *N*-heterocyclic carbene palladium(II) compounds[25] in triethylamine. It is assumed that the difference in the reactivity among alkenes, internal acetylenes and terminal acetylenes depends upon the relative difficulty towards π co-ordination of the substrates to the metal centre in the *z*-axis direction: methyl groups in 2,6-lutidine ligand disturb the co-ordination of bulky alkene and internal acetylenes, whereas less bulky, linear terminal acetylenes ligate more easily along the *z*-axis. Further investigation concerning the reactivity of arylgold(III) complexes towards unsaturated hydrocarbons are in progress.

Experimental

General

The IR spectra were measured on a JASCO FT/IR-420 spectrophotometer, and ^{1}H NMR spectra were recorded on a JEOL JNM-GX-270 spectrometer using tetramethylsilane as an internal standard. Melting points were determined on a Yanaco MP-500D micro melting-point apparatus and are uncorrected. The GC analysis was performed on a Shimadzu GC-14A using a BP-1 (50 m × 0.25 mm) capillary column. The GC/MS was performed at the Faculty of Engineering of Kyushu University. Anhydrous gold(III) chloride [AuCl$_3$]$_2$ was prepared by the action of thionyl chloride upon H[AuCl$_4$]·4H$_2$O.[26] Other reagents were obtained commercially and used without purification.

General procedure for the synthesis of mononuclear arylgold(III) complexes [AuArCl$_2$(lut)] 1–9 in hexane

Under a dinitrogen atmosphere a hexane solution (2 cm^3) of the arene (6.0 mmol) was added to a hexane suspension (5 cm^3) of [AuCl$_3$]$_2$ (0.15 mmol) at 20 °C (benzene, toluene and chlorobenzene) or 0 °C (xylene, mesitylene, cumene and methoxybenzene). The initial red colour of the anhydrous gold(III) chloride changed immediately to brown, accompanied by the generation of white fumes of hydrogen chloride. Stirring was continued for 30 min, and then diethyl ether (2 cm^3) was added. The resulting suspension was filtered and the filtrate was treated with a diethyl ether solution (2 cm^3) of 2,6-lutidine (lut) (0.30 mmol), whereupon a pale yellow precipitate appeared. After the suspension was stirred at room temperature for 1 h, the volatile materials were removed *in vacuo*. The residue was chromatographed on a silica gel (18 mm × 110 mm) to give a pale yellow fraction by eluting with benzene–hexane (2 : 3). The pale yellow fraction was recrystallized from dichloromethane–hexane to give the arylgold(III) complexes **1**–**9**.

[AuPhCl$_2$(lut)] 1. Yield 30%; mp 157 °C (decomp.) (Found: C, 34.5; H, 3.15; N, 3.05. $C_{13}H_{14}AuCl_2N$ requires C, 34.5; H, 3.1; N, 3.1%); ν_{max}/cm^{-1} (KBr) 366 (Au–Cl).

[Au(4-MeC$_6$H$_4$)Cl$_2$(lut)] 2. Yield 10%; mp 167 °C (decomp.) (Found: C, 36.2; H, 3.45; N, 3.0. $C_{14}H_{16}AuCl_2N$ requires C, 36.05; H, 3.45; N, 3.0%); ν_{max}/cm^{-1} (KBr) 370 (Au–Cl).

[Au(3,4-Me$_2$C$_6$H$_3$)Cl$_2$(lut)] 3. Yield 17%; mp 166 °C (decomp.) (Found: C, 37.35; H, 3.85; N, 2.9. $C_{15}H_{18}AuCl_2N$ requires C, 37.5; H, 3.8; N, 2.9%); ν_{max}/cm^{-1} (KBr) 366 (Au–Cl).

[Au(2,4-Me$_2$C$_6$H$_3$)Cl$_2$(lut)] 4. Yield 26%; mp 166 °C (decomp.) (Found: C, 37.35; H, 3.8; N, 2.95. $C_{15}H_{18}AuCl_2N$ requires C, 37.5; H, 3.8; N, 2.9%); ν_{max}/cm^{-1} (KBr) 366 (Au–Cl).

[Au(2,5-Me$_2$C$_6$H$_3$)Cl$_2$(lut)] 5. Yield 39%; mp 168 °C (decomp.) (Found: C, 37.6; H, 3.85; N, 2.95. $C_{15}H_{18}AuCl_2N$ requires C, 37.5; H, 3.8; N, 2.9%); ν_{max}/cm^{-1} (KBr) 361 (Au–Cl).

[Au(2,4,6-Me$_3$C$_6$H$_2$)Cl$_2$(lut)] 6. Yield 12%; mp 167 °C (decomp.) (Found: C, 38.35; H, 3.9; N, 2.8. $C_{16}H_{20}AuCl_2N$ requires C, 38.9; H, 4.1; N, 2.85%); ν_{max}/cm^{-1} (KBr) 369 (Au–Cl).

[Au(4-Me$_2$CHC$_6$H$_4$)Cl$_2$(lut)] 7. Yield 39%; mp 157 °C (decomp.) (Found: C, 38.4; H, 4.05; N, 2.9. $C_{16}H_{20}AuCl_2N$ requires C, 38.9; H, 4.1; N, 2.85%); ν_{max}/cm^{-1} (KBr) 360 (Au–Cl).

[Au(4-MeOC$_6$H$_4$)Cl$_2$(lut)] 8. Yield 6%; mp 156 °C (decomp.) (Found: C, 34.95; H, 3.4; N, 2.85. $C_{14}H_{16}AuCl_2NO$ requires C, 34.9; H, 3.35; N, 2.9%); ν_{max}/cm^{-1} (KBr) 373 (Au–Cl).

[Au(4-ClC$_6$H$_4$)Cl$_2$(lut)] 9. Yield 20%; mp 179 °C (decomp.) (Found: C, 32.05; H, 2.7; N, 2.85. $C_{13}H_{13}AuCl_3N$ requires C, 32.1; H, 2.7; N, 2.9%); ν_{max}/cm^{-1} (KBr) 372 (Au–Cl).

Synthesis of [Au(2,5-Me$_2$C$_6$H$_3$)Cl$_2$(lut)] 5 in hexane in the presence of alkali metal carbonates

The synthetic procedure used was similar to that described above except for adding alkali metal carbonates (3.0 mmol) to the initial suspension of [AuCl$_3$]$_2$ (0.15 mmol). When Li_2CO_3, Na_2CO_3, $NaHCO_3$ and K_2CO_3 were used, the yields of **5** were 67, 69, 47 and 46%, respectively.

Synthesis of [Au(2,5-Me$_2$C$_6$H$_3$)Cl$_2$(lut)] 5 and [Au(4-MeOC$_6$H$_4$)-Cl$_2$(lut)] 8 in diethyl ether

Under a dinitrogen atmosphere a diethyl ether solution (2 cm^3) of the arene (6.0 mmol) was added to a solution of [AuCl$_3$]$_2$ (0.15 mmol) in the same solvent (4 cm^3) at 0 °C. The colour of the solution gradually changed to orange. Stirring was continued for 30 min at 0 °C, and then a diethyl ether solution (1 cm^3) of lut (0.30 mmol) was added. The resulting yellow suspension was stirred for another hour and then the mixture was evaporated to dryness. The residue was recrystallized from dichloromethane–hexane to give yellow crystals of the arylgold(III) complexes, **5** and **8**, in 11 and 58% yields, respectively.

Reactions of arylgold(III) complexes of 1 and 5 with unsaturated hydrocarbons

Reaction of 5 with styrene. A THF solution (2 cm^3) of styrene (0.048 g, 0.457 mmol) was added to a solution of **5** (0.092 g, 0.187 mmol) in the same solvent (10 cm^3). The reaction mixture was refluxed for 12 h. GC analysis of the resulting mixture showed absence of the arylated styrene. The volatile materials of the reaction mixture were removed under reduced pressure, and then the residue was recrystallized from dichloromethane–hexane to give **5** (0.036 g, 39%).

Reactions of 5 with diphenylacetylene and dimethyl acetylenedicarboxylate. A THF solution (2 cm^3) of diphenylacetylene (0.029 g, 0.160 mmol) and then acetic acid (2 cm^3) was added to a solution of **5** (0.066 g, 0.134 mmol) in the same solvent (10 cm^3). The reaction mixture was refluxed for 12 h. GC analysis of the resulting mixture showed the absence of hydroarylation product. The volatile materials of the reaction mixture were removed under reduced pressure, and then the residue was recrystallized from dichloromethane and hexane to give **5** (0.053 g, 80%). The reaction of **5** with dimethyl acetylenedicarboxylate was similarly carried out, but only **5** was recovered (31%).

Reactions of 1 and 5 with phenylacetylene. A THF solution (2 cm^3) of phenylacetylene (0.022 g, 0.217 mmol) was added to a solution of **1** (0.048 g, 0.103 mmol) in the same solvent (10 cm^3). The reaction mixture was heated at 50 °C for 5 h, and then the volatile materials were removed *in vacuo*. The residue was chromatographed on a silica gel column (18 mm × 60 mm) by eluting with hexane. This fraction was evaporated to dryness to give diphenylacetylene **10** (0.015 g, 82%). The ^{1}H NMR spectrum was identical with the authentic sample. GC/MS: *m*/*z* 178 (M$^+$).

In a similar way, by the reaction of **5** with phenylacetylene 1,4-dimethyl-2-(phenylethynyl)benzene (2,5-xylylphenylacetylene) **11** was obtained in 94% yield; mp 85 °C (Found: C, 93.0; H, 7.0. $C_{16}H_{14}$ requires C, 93.15; H, 6.85%); GC/MS: *m*/*z* 204 (M$^+$); ^{1}H NMR (CDCl$_3$): 2.31 (3H, s, Me), 2.47 (3H, s, Me), 7.04 [1H, d, ^3J(HH) = 7.7 Hz, H^4], 7.05 (1H, s, H^6), 7.11 [1H, d, ^3J(HH) = 7.7 Hz, H^3], 7.25–7.4 (3H, m, *m*-, *p*-H), 7.5–7.6 (2H, m, *o*-H).

X-Ray crystallography

Suitable crystals of [Au(2,5-Me$_2$C$_6$H$_3$)Cl$_2$(lut)] **5** were grown from dichloromethane–hexane.

Crystal data. $C_{15}H_{18}AuCl_2N$, $M = 480.19$, monoclinic, space group $P2_1/c$, $a = 8.3765(4)$, $b = 24.270(1)$, $c = 8.5809(5)$ Å, $\beta = 116.865(1)$ °, $U = 1556.2(1)$ Å^3, $D_c = 2.049$ g cm^{-3}, $F(000) = 912.00$, $Z = 4$, μ(Mo-Kα) = 98.15 cm^{-1}, Mo-Kα radiation, $\lambda = 0.71069$ Å.

A yellow prismatic crystal having approximate dimensions of 0.30 × 0.50 × 0.30 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of −180 ± 1 °C and processed by the PROCESS-AUTO program package.[27] Of the 11552 reflections measured 3482 were unique ($R_{int} = 0.036$). An asymmetry-related absorption correction using the program ABSCOR[28] was applied. The data were corrected for Lorentz-polarization effects. The structure was solved by direct methods[29] and expanded using Fourier-techniques.[30] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 2757 observed reflections ($I > 3.00\sigma(I)$) and 245 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.022$ and $R' = 0.026$.

CCDC reference number 165244. See http://www.rsc.org/suppdata/dt/b1/b102527a/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank Professor Teruo Shinmyozu of the Institute for Fundamental Reseach of Organic Chemistry, Kyushu University for the use of the crystallographic facility. This work is partially supported by a Grand-in-Aid for Scientific Research (12640541) from the Ministry of Education, Science, Sports and Culture.

References

1 A. E. Shilov and G. B. Shul'pin, *Chem. Rev.*, 1997, **97**, 2879; A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403; R. H. Crabtree, *Chem. Rev.*, 1985, **85**, 245.
2 S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda and N. Chatani, *Nature*, 1993, **366**, 529; N. Chatani and S. Murai, *J. Synth. Org. Chem. Jpn.*, 1998, **56**, 443.
3 I. Moritani and Y. Fujiwara, *Tetrahedron Lett.*, 1967, 1119; I. Moritani and Y. Fujiwara, *Synthesis*, 1973, 524.
4 M. S. Kharasch and H. S. Isbell, *J. Am. Chem. Soc.*, 1931, **53**, 3053.
5 K. S. Liddle and C. Parkin, *J. Chem. Soc., Chem. Commun.*, 1972, 26.
6 P. W. J. de Graaf, J. Boerasma and G. J. M. van der Kerk, *J. Organomet. Chem.*, 1976, **105**, 399.
7 C. W. Chan, W. T. Wong and C. M. Che, *Inorg. Chem.*, 1994, **33**, 1266.
8 M. A. Cinellu, A. Zucca, S. Stoccoro, G. Minghetti, M. Manassero and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1995, 2865.
9 M. A. Cinellu, A. Zucca, S. Stoccoro, G. Minghetti, M. Manassero and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1996, 4217.
10 Y. Fuchita, H. Ieda, Y. Tsunemune, J. Kinoshita-Kawashima and H. Kawano, *J. Chem. Soc., Dalton Trans.*, 1998, 791.
11 Y. Fuchita, H. Ieda, A. Kayama, J. Kinoshita-Kawashima, H. Kawano, S. Kameda and M. Mikuriya, *J. Chem. Soc., Dalton Trans.*, 1998, 4095.
12 P. A. Bonnardel, R. V. Parish and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1996, 3185.
13 J. Vicente, M. D. Bermudez, F. J. Carrion and P. G. Jones, *Chem. Ber.*, 1996, **129**, 1301.
14 J. Vicente, M. D. Bermudez, M. P. Carrillo and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1992, 1975.
15 G. Minghetti, M. A. Cinellu, M. V. Pinna, S. Stoccoro, A. Zucca and M. Manassero, *J. Organomet. Chem.*, 1998, **568**, 225.
16 Y. Fuchita, H. Ieda, S. Wada, S. Kameda and M. Mikuriya, *J. Chem. Soc., Dalton Trans.*, 1999, 4431.
17 Y. Fuchita, H. Ieda and M. Yasutake, *J. Chem. Soc., Dalton Trans.*, 2000, 271.
18 R. G. Miller, R. D. Stauffer, D. R. Fahey and D. R. Parnell, *J. Am. Chem. Soc.*, 1976, **92**, 1511.
19 A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 1964, 4583.
20 Y. Fuchita, M. Kawakami and K. Shimoke, *Polyhedron*, 1991, **10**, 2037.
21 Y. Fuchita, H. Oka and M. Okamura, *Inorg. Chim. Acta.*, 1992, **194**, 213.
22 Y. Fuchita, K. Hiraki, Y. Kamogawa and M. Suenaga, *J. Chem. Soc., Chem. Commun.*, 1987, 941; Y. Fuchita, K. Hiraki, Y. Kamogawa, M. Suenaga, K. Tohgoh and Y. Fujiwara, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 1081.
23 C. Jia, D. Piao, J. Oyamada, W. Lu, T. Kitamura and Y. Fujiwara, *Science*, 2000, **287**, 1992; C. Jia, W. Lu, J. Oyamada, T. Kitamura, K. Matsuda, M. Irie and Y. Fujiwara, *J. Am. Chem. Soc.*, 2000, **122**, 7252.
24 W. A. Herrmann, C.-P. Reisinger, K. Ôfele, C. Broβmer, M. Beller and H. Fischer, *J. Mol. Catal. A*, 1996, **108**, 51.
25 W. A. Herrmann, C.-P. Reisinger and M. Spiegler, *J. Organomet. Chem.*, 1998, **557**, 93.
26 D. B. Dell'amico and F. Calderazzo, *Gazz. Chim. Ital.*, 1973, **103**, 1099.
27 PROCESS-AUTO, Automatic Data Acquisition and Processing Package for Imaging Plate Diffractometer, Rigaku Corporation, Tokyo, 1998.
28 T. Higashi, Program for Absorption Correlation, Rigaku Corporation, Tokyo, Japan, 1995.
29 A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacpvazzp, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435.
30 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. De Gelder, R. Israel, J. M. M. Smits, the DIRDIF-94 program system, Technical Report of Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.
31 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.