New Route to Aryl–Gold σ-Bonded Complexes

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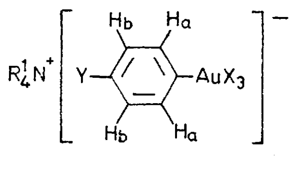
Summary A new reaction for the direct formation of aryl–gold σ-bonded complexes is described; characterization by i.r., Raman, and ^{1}H n.m.r. spectroscopy indicates a square-planar structure with the generalized formula $(R^1_4N)^+(R^2AuCl_3)^-$.

Until now, the aryl–gold(III) compounds known were obtained by 'direct auration' of an aromatic hydrocarbon by anhydrous $AuCl_3$.[1] These compounds, $(RAuX_2)_2$ (where R=aryl, X=halogen), are unstable but were used by Liddle and Parkin[2] to prepare trichloroarylgold(III), $RAuCl_3^-$, and dichloroarylgold(III), $RAuCl_2L$, complexes.

We found that the reaction of phenyl- (or substituted-phenyl)-hydrazine hydrochloride with the tetraethyl- or tetra-n-butyl-ammonium salts of tetrachloro- or tetrabromo-aurate(III) afforded the corresponding gold(I) di-



(I) - (VIII)

TABLE

Compound	R^1	Y	X	M.p. (°)	^{1}H N.m.r., δ
(I)	Et	H	Cl	154	7·03 (m)
(II)	Bu^n	H	Cl	99	
(III)	Et	H	Br	122	
(IV)	Bu^n	H	Br	87	
(V)	Bu^n	H	I	78—79	
(VI)	Et	Cl	Cl	160	7·12 (s)
(VII)	Et	Br	Cl	178	7·17
(VIII)	Et	NO_2	Cl	168	7·50 (d, H_a), 7·97 (d, H_b) $J_{a,b}$ 8·6 Hz

halide and an arylgold(III) complex, according to reaction (1).[3]

$$2\,R^1_4N^+(AuX_4)^- + R^2NHNH_2{,}HCl \longrightarrow R^1_4N^+(R^2AuX_3)^- + R^1_4N^+(AuX_2)^- + N_2 + 4HCl \quad (1)$$

R^1 = Et, Bu^n

R^2 = Ph, p-ClC_6H_4, p-BrC_6H_4, p-$O_2NC_6H_4$

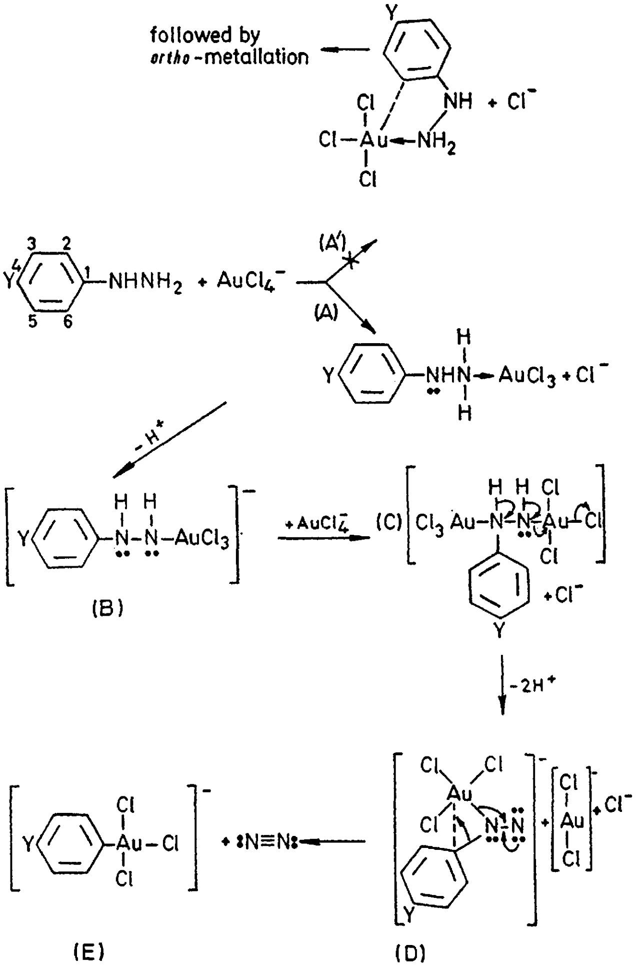
X = Cl, Br

The compounds prepared are listed in the Table; compound (V) was obtained by the metathetical reaction with Bu^n_4NI. The aromatic protons of (VIII) give a typical A_2B_2 pattern which is characteristic of *para*-disubstitution, whereas the similarity of shielding effects in (VI) and (VII) does not produce any H splitting. The increasing order of δ values is (I) < (VI) < (VII) < C_6H_6 < (VIII), and parallels the increase in electron-withdrawing properties of the substituents.

The detailed i.r. and Raman spectroscopic studies emphasize the strong *trans*-influence of the phenyl group.[4] The present report is restricted to the presentation of the mechanism and ^{1}H n.m.r. interpretation. The use of *para*-substituted phenylhydrazines establishes which carbon atom is bonded to the gold after migration of the phenyl group.

Since the ^{1}H n.m.r. and the i.r. spectra[4] show that reaction (A) (see Scheme) always terminates with a *para*-substituted phenylgold complex, we conclude that there is a nucleophilic attack of gold(III) by C-1 instead of an *ortho*-metallation reaction (A').[6] The following mechanism is suggested: (i) co-ordination of the primary nitrogen of one molecule of phenylhydrazine to the gold centre (A)[5] with the resulting increase of proton acidity is followed by proton loss (B); (ii) co-ordination of the other nitrogen to another $AuCl_4^-$ ion (C); (iii) elimination of two HCl molecules, reduction of the first Au^{III} into Au^I, and production of a postulated *N*-nitrene intermediate (D); (iv) migration of the phenyl group to the gold(III) and liberation of N_2 (E).

The last step is known to occur when $R^1R^2\ddot{N}$–$\ddot{N}$: rearranges to $R^1R^2 + N_2$ as described in the 'abnormal oxidation' of 1,1-disubstituted-hydrazines.[7] To our knowledge, this is the first example of this mechanism in organometallic reactions.



SCHEME.

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