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Synthesis and Reactivity of Dichloro 2-(phenylazo)phenyl gold(III)

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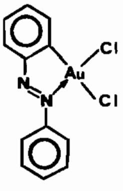
Since the report of Kharasch [1] that anhydrous gold(III) chloride reacted easily with benzene to give $[Au(C_6H_5)Cl_2]_2$ the so-called auration reactions have been a subject of considerable interest. However, this type of reaction is inhibited by the presence of a coordinating substituent in the aromatic ring [2]. This behaviour contrasts with the ease with which palladium(II) and platinum(II) compounds react with this type of aromatic compounds such as azobenzene to give *ortho*-metallated complexes [3]. In fact, three different authors reported separately reactions between azobenzene and gold(III) halides trying to get *ortho*-metallated compounds but only the adducts $[AuX_3(PhN_2Ph)]$ were isolated [4–6]. Decomposition of these adducts was thought likely to occur through the intermediacy of dichloro[2-(phenylazo)phenyl]gold(III). We report here the synthesis of this complex using chloro[2-phenylazo)phenyl]mercury(II) which has been used previously in the preparation of other [2-(phenylazo)phenyl] complexes [7].

Results and Discussion

The reaction of $[AuCl_3(tht)]$ (tht = tetrahydrothiophene] with [Hg(Az)Cl] (Az = 2-(phenylazo)phenyl) gives, after stirring for 24 hr in Cl_2CH_2 at room temperature, a greyish precipitate and an orange solution containing $[Au(Az)Cl_2]$ (I). The precipitate has not been fully identified but seems to be $[HgCl_2(tht)_n]$ (by i.r. spectroscopy) mixed with some metallic mercury. Better results can be reached by adding Me_4NCl to the above reaction mixture in acetone in which case 96% of the mercury is recovered as the very insoluble $Me_4N[HgCl_3]$.

$$[AuCl_3(tht)] + [Hg(Az)Cl] + Me_4NCl \rightarrow [Au(Az)Cl_2] + Me_4N[HgCl_3] + tht$$



(I)

I.r. spectrum, analytical data, conductivity and molecular weight determined by osmometry allow the formulation of complex (I) such as had been postulated previously [4] as an intermediate in the decomposition of $[AuCl_3(PhN_2Ph)]$.

The i.r. spectrum of complex (I) shows two strong bands at 305 and 370 cm^{-1} that can be assigned to ν(Au–Cl) *trans* to the phenyl ring and to the nitrogen of the azo-group, respectively. Such a great difference in position of the bands is in accordance with the stronger *trans*-influence of phenyl with respect to N-donor ligands. In the related complex of palladium(II), $NEt_4[Pd(\widehat{CN})Cl_2]$ ($\widehat{CN}$ = acetophenone hydrazone) two strong quite separate bands (263, 346 cm^{-1}) are also observed [8].

When a suspension of complex (I) in acetone is treated with PPh_3 or $AsPh_3$, solutions are immediately obtained from which the complexes of formula $[Au(Az)Cl_2L]$ [L = PPh_3 (II), $AsPh_3$ (III)] precipitate after 10 min stirring even when 1:2 ratios of complex to ligand are used. The i.r. spectrum of complex (II) has two strong bands at 290 and 315 cm^{-1}. The main difference with complex (I) is the shift of the band at 370 cm^{-1} to a lower wavenumber. This band can be assigned to ν(Au–Cl) *trans* to PPh_3 [9] hence the complex could be formulated as the result of the cleavage of the N–Au bond as has been observed with other similar complexes of palladium(II) and platinum(II) [10], although a pentacoordination is not excluded. The i.r. spectrum of complex (III) also shows two strong bands at 297 and 312 cm^{-1} but the presence of other bands in this region due to the ligand $AsPh_3$ makes the assignment difficult.

Experimental

[Au(Az)Cl₂] (I)

To a solution of $[AuCl_3(tht)]$ in acetone [Hg(Az)Cl] and Me_4NCl (molar ratio 1:1:1) are added. After 24 hr stirring at room temperature, the solvent is evaporated, the resulting solid extracted with dichloromethane, the solution concentrated and diethyl ether added to precipitate yellow complex (I).

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Yield 64%; m.p., 218 °C (d). $\Lambda_M = 4\ \Omega^{-1}\ cm^2\ mol^{-1}$ (5×10^{-4} *M* solution in acetone). *Anal.* Found (calculated)%: C, 32.59(32.09); H, 2.12(2.02); N, 6.03(6.24); Au, 44.59(43.86). Molecular weight (by osmometry in chloroform) 490(449).

[Au(Az)Cl$_2$L] (II)–(III)

To a suspension of (I) in acetone PPh_3 (1:1 or 1:2 molar ratio complex (I):PPh_3) or $AsPh_3$ (1:2) are added. Clear red solutions are immediately obtained and after 10 min brick-red solids [L = PPh_3 (II), $AsPh_3$ (III)] precipitate. From the mother liquor additional amounts of the complexes can be obtained by adding diethyl ether. Yields %: 84(II), 69(III). M.p. °C: 181(d) (II), 175(d) (III). Λ_M: 2.2(II), 1.7(III) $\Omega^{-1}\ cm^2\ mol^{-1}$. *Anal.* Found (calculated) %, (II): C, 50.99(50.65); H, 3.97(3.40); N, 3.83(3.94); Au, 27.13(27.69). (III): C, 48.41(47.70); H, 3.57 (3.20); N, 3.74(3.71); Au, 27.26(26.08).

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