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1-Chloro-2,3,4,5-Tetraphenylaura-Cyclopentadiene Dimer and Its Derivatives

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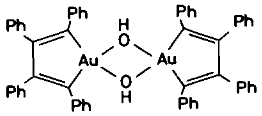
Only few carbocyclic complexes containing Au as heteroatom are known [1]. Thus, for example, the reaction of [$AuCl_3py$] with the di-Grignard compound derived from 1,5-dibromopentane and successive treatment of the resulting product with ethylenediamine and HBr gives the pentamethylene gold complex [$(CH_2)_5AuBr]_2$ in low yields [2] whilst the reaction between $AuCl_3$ and 1,4-dilithium-1,2,3,4-tetraphenylbutadiene gives low yields of 1-hydroxy-2,3,4,5-tetraphenylaura-cyclopentadiene dimer [3]. The structure of the latter shows the two Au atoms bridged by OH-groups [4]:

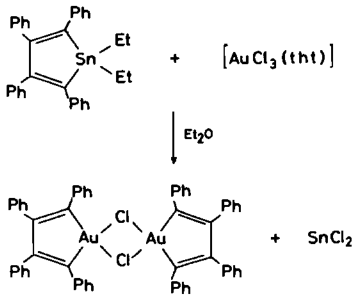


Other tetraphenyl-substituted heterocycles with different heteroatoms have also been described: *e.g.* with Hg, Tl, Zr, N, Se, Te [3], B [3,5], Si [3,6], Sn, P, As, Sb, S [3,7], Ge [6,7], Ni [8], Rh [9–12], Fe [13], Ti [14], Co [15] or Ir [10]. Most of these complexes are obtained by two essentially different routes: a) by the reaction of the above-mentioned dilithium compound with a dihalocompound or b) by the reaction of diphenylacetylene with a complex of a transition metal in low oxidation state. Furthermore, in some cases the Ph_4C_4 group has been transferred by means of a metallole [5, 13].

In the present paper we show that also stannole compounds can be used for transferring the Ph_4C_4 group to Au(III) complexes. We think that the synthesis of novel complexes of this type may be of interest since the intermediacy of metallole or metallole-like systems has been demonstrated or inferred for the cyclotrimerization of alkynes [8, 15, 16].

Results and Discussion

The reaction of 1,1-diethyl-2,3,4,5-tetraphenylstannole (obtained similarly to the 1,1-dimethyl derivative [7]) with [$AuCl_3(tht)$] (tht = tetrahydrothiophen) [17] in Et_2O solution gives rise to the precipitation of complex (I) in 75% yield, according to eqn. (1):



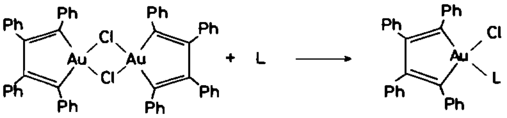
(1)

(I)

Complex (I) can also be obtained, though in lower yields, by reacting the stannole complex with n-$Bu_4N[AuCl_4]$ in CH_2Cl_2 solution, whereas reactions of 1,4-dilithium-1,2,3,4-tetraphenylbutadiene with [$AuCl_3(tht)$] or with n-$Bu_4N[AuCl_4]$ lead to the formation of metallic gold or, respectively, metallic gold, n-$Bu_4N[AuCl_2]$, $Ph_4C_4H_2$ and unchanged n-$Bu_4N[AuCl_4]$.

The structure of complex (I) should be analogous to that of the above mentioned hydroxocomplex, since this is obtained by reacting complex (I) with NaOH in acetone solution.

Several novel derivatives were prepared by the cleavage of the Cl bridge, according to eqn. (2):



(2)

L = py(II), PPh_3(III), phen(IV)

Thus, the addition of py, PPh_3 or phen leads to the complexes (II), (III) or (IV) which were obtained in *ca.* 80% yields. In acetone solution the complexes (II) and (III) are non-conducting whilst (IV) shows a low conductivity (Λ_M = 13 Ω^{-1} cm^2 mol^{-1}). Their I.R. spectra show the absorption due to ν(Au–Cl) at 308, 300 or, respectively, 280 cm^{-1}.

The phenanthroline complex (IV) is noteworthy, since its low conductivity along with the significant shift of the band due to ν(Au–Cl) towards lower energies points to a pentacoordination of the gold atom in the complex and not to a square planar structure, as in complexes (II) and (III). Complex (IV) might therefore well be the first pentacoordinated organometallic gold(III) complex.

The few hitherto known pentacoordinated Au(III) complexes are of the general formula [$AuCl_3(LL)$]

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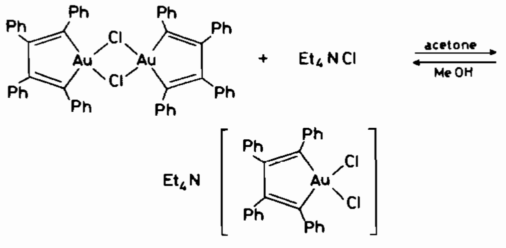
(LL = 2,2'-biquinolyl [18], 2,9-dimethyl-1,10-phenanthroline [19] or 2-(2'-pyridyl)quinoline [20]). It has been postulated that the unusual five-coordinated gold(III) environment can be forced by the choice of sterically hindered ligands. Hence, although 1,10-phenanthroline and 2,2'-bipyridyl form compounds of the $AuX_3(LL)$ type, these complexes are not believed to possess a five-coordinated molecular structure, but rather to contain $[AuX_2(LL)]^+$ species [21]. Therefore, the presence of the two phenyl groups next to the Au atom [4] could in our case have a steric effect which is similar to that caused by the bidentated N-donors in the aforementioned complexes. In fact, if complexes of the type $[AuMe_2X]_2$, containing not very bulky substituents, are reacted with 1,10-phenanthroline $[AuMe_2(phen)]^+ [AuMe_2X_2]^-$ are obtained [22]. This formulation does, however, not agree with the experimental results (analyses, I.R. spectra, conductivity) for complex (IV).

The addition of $NaClO_4$ to the phenanthroline complex (IV) leads, according to eqn. (3), to the

$$[Au(Ph_4C_4)Cl(phen)] + NaClO_4 \rightarrow NaCl + \underset{(V)}{[Au(Ph_4C_4)(phen)]ClO_4} \qquad (3)$$

precipitation of NaCl, whereupon complex (V) can be crystallized from the filtrate (conductivity in acetone $\Lambda_M = 117\ \Omega^{-1}\ cm^2\ mol^{-1}$). A small amount of elemental gold is formed during the crystallization of (V).

The addition of Et_4NCl to an acetone solution of complex (I) yields the anionic complex (VI) ($\Lambda_M = 107\ \Omega^{-1}\ cm^2\ mol^{-1}$ in acetone), according to eqn. (4):



(4)

(VI)

The reaction can be reversed by addition of MeOH. Complex (VI) shows two bands assignable to ν(Au–Cl) at 298 and 275 cm^{-1}, which are in good agreement with those observed for other *cis*-dichloro complexes [23]. We think that the differences between the I.R. spectra of complexes (IV) and (VI), especially in the region 300–200 cm^{-1}, show conclusively that the phenanthroline complex (IV) cannot be formulated as $[Au(Ph_4C_4)(phen)]^+[Au(Ph_4C_4)Cl_2]^-$.

The use of the stannole compound offers a clear advantage over that of 1,4-dilithium-1,2,3,4-tetraphenylbutadiene since not only are the obtained yields higher, but also the reactions are more straightforward; thus, $SnEt_2Cl_2$ can easily be removed from the reaction products and the lower reactivity of the stannole compound allows a more selective attack upon the two mutually *cis* halogen groups.

At present we are studying further reactions with this stannole and other heterocyclic tin compounds in order to prepare heterocyclic complexes of gold and other transition metals.

All the novel complexes have been characterized by C, H, N and Au analyses, conductivities and I.R. spectra.

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