Gold(I) Ketenide

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Summary The preparation and some properties of gold(I) ketenide and its co-ordination complexes with some heterocyclic bases are described.

THE feasibility of substituting metal atoms for the hydrogen atoms of keten was recently demonstrated by the formation of silver(I) ketenide[1] and copper(I) ketenide.[2] We now report the formation of the new compound gold(I) ketenide, Au_2C_2O (I), by reaction of keten with a solution of chloro-(1,4-oxathian)gold(I)[3] in acetonitrile in the presence of an excess of 2,6-dimethylpyridine and triethylamine under argon at −10°. N.m.r. evidence shows that the chloro gold(I) precursor undergoes ligand exchange [equation (1)].

$$AuCl{\cdot}C_4H_8OS + L \rightleftharpoons AuCl{\cdot}L + C_4H_8OS \qquad (1)$$

$$2AuCl{\cdot}L + CH_2{=}C{=}O + 2NEt_3 \rightleftharpoons Au_2C_2O{\cdot}L + 2(Et_3NH)^+Cl^- + L \qquad (2)$$

(L = 2,6-dimethylpyridine)

The initial insoluble yellow product is a gold(I) ketenide 2,6-dimethylpyridine complex, $Au_2C_2O{\cdot}C_7H_9N$ (II), which readily loses the ligand to give (I) on warming to 25°. Loss of the ligand is accompanied by a marked deepening in colour.

The use of a less sterically hindered heterocyclic tertiary base *e.g.* pyridine, mono-methylpyridines, or quinoline gives complexes analogous to (II), having the same stoicheiometry $Au_2C_2O{\cdot}(L)$, from which complete removal of the ligand has not proved to be possible. Although the presence of triethylamine (or other strong tertiary base) is essential in the preparations, no complex of triethylamine with (I) is obtained; presumably the function of the strong base is to remove the HCl from the system [equation (2)].

Omission of a heterocyclic base gives (I) directly but usually in a less pure state than when prepared *via* (II). In equation (2) acetic anhydride may serve as an *in situ* source of keten if a large excess of triethylamine is used, although the rate of formation of the gold(I) ketenide complex is slower and the yields are low, except where L = pyridine.

Gold(I) ketenide (I) and its complexes with tertiary heterocyclic bases explode when heated above 100° (in the dry state (I) is also shock sensitive). Explosion of (I) under argon at reduced pressure gives carbon suboxide, C_3O_2, as the major gaseous product.[1,2] Controlled thermal decomposition of (I) on a glass support at 100° under propylene gives tightly adhering films of gold which catalyse the air-oxidation of propylene at 215°, giving propylene oxide as the major organic product (yields up to 50%), and minor amounts of acrolein; the conversions per pass are $<1\%$. This catalytic behaviour contrasts with that previously reported for gold.[4]

Reaction of (I) with phenylacetylene in the presence of aniline gives gold(I) phenylacetylide and acetanilide. This reaction is best carried out in pyridine, in which gold(I) phenylacetylide is soluble.

The i.r. spectrum of gold(I) ketenide (I) closely resembles those of silver(I) and copper(I) ketenides.[1,2] Between 250—4000 cm^{-1} it shows absorption bands at 428 m(νAu–C) 562 w (δ CCO), and 2015 vs (ν_{as}CCO) cm^{-1}. In the pyridine complex these bands are shifted to 420, 552, and 1980 cm^{-1} respectively.

The spectroscopic properties and reactions of (I) together with good elemental analyses indicate that it is correctly represented as $Au_2C=C=O$. The total insolubility of (I) and its complexes with heterocyclic bases in all common solvents suggests that they are polymers (*cf.* silver ketenide[1]), but their poor crystallinity has precluded confirmation of this by *X*-ray powder diffraction.

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