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Preliminary communication

REACTIONS OF ANHYDROUS GOLD(III) CHLORIDE WITH ORGANIC NITRILES CONTAINING AROMATIC GROUPS

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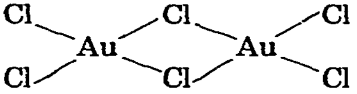
Summary

When moisture is excluded, gold(III) chloride reacts with nitriles containing aromatic groups to give products of the type $AuCl_3L$ (e.g. L = PhCN, p-$CH_3C_6H_4CN$, $PhCH_2CN$), not ring metallated products as previously reported.

Aliphatic nitriles were reported [1] to react with anhydrous gold(III) chloride with bridge cleavage according to eqn. 1. We have confirmed this result [2]. In contrast, the reactions of organic nitriles containing aromatic groups were reported [1] to result in substitution in the aromatic ring yielding compounds of general formula $AuCl_2NC(ArH)$, presumably arising from an electrophilic attack of gold(III). In view of the fact that auration of benzene itself was described [3] as a rather facile reaction, and since we are interested in the general problem of metalation of aromatic rings by transition elements [4], we decided to reinvestigate the reactions of anhydrous gold(III) chloride with some organic nitriles containing aromatic groups.



$$+ 2\,RCN \rightarrow 2\,AuCl_3NCR \qquad (1)$$

We wish to report that, by working under conditions approaching the complete exclusion of moisture, the only products isolated from the reaction mixtures were those resulting from the bridge-splitting reaction 1. As it can be seen from the data in Table 1, products of formula $AuCl_3L$ (L = benzonitrile, p-tolunitrile, phenylacetonitrile) were obtained. The nature of the products was established by elemental analysis, by ^1H NMR spectra measured in CH_2Cl_2 at 60 MHz (L = p-tolunitrile: AB quartet centred at τ 2.33 from TMS (four protons), singlet at τ 7.47 (three protons); L = phenylacetonitrile: asymmetric singlet at τ 2.53, singlet at τ 5.65), by infrared spectra measured in CH_2Cl_2 (L = benzonitrile, ν(CN) 2297 cm^{-1}, corresponding to a 68 cm^{-1} increase with respect to

TABLE 1

SYNTHESES OF NITRILE DERIVATIVES OF GOLD(III)

Compound	Formula	Method of preparation [a]	Yield (%)
$AuCl_3 \cdot C_6H_5CN$ (I)	$C_7H_5AuCl_3N$	A	47.2
$AuCl_3 \cdot C_6H_4(CH_3)CN$ (II)	$C_8H_7AuCl_3N$	B	76.2
$AuCl_3 \cdot C_6H_4(CH_3)CN$ (II)	—	A	86.5
$AuCl_3 \cdot C_6H_5CH_2CN$ (III)	$C_8H_7AuCl_3N$	A	83.5
$AuCl_3 \cdot C_6H_5CH_2CN$ (III)	—	C	66.7

[a] A, in CH_2Cl_2, initially at Dry-Ice temperature, with the stoicheiometric amount of the nitrile; B, in CH_2Cl_2 at room temperature with the stoicheiometric amount of the nitrile; C, initially in the neat liquid at room temperature, then addition of CCl_4.

the uncomplexed nitrile, L = *p*-tolunitrile, ν(CN) 2291 cm^{-1}, corresponding to a 63 cm^{-1} increase with respect to the uncomplexed nitrile, L = phenylacetonitrile ν(CN) 2329 cm^{-1}, corresponding to a 77 cm^{-1} increase with respect to the uncomplexed nitrile), and by displacement reaction of the coordinated nitrile by pyridine (eqn. 2). The shift to higher wavenumbers of the CN stretching vibration is typical of nitrogen-coordinated nitriles [5].

$$AuCl_3 \cdot p\text{-}NCC_6H_4CH_3 + C_5H_5N \rightarrow AuCl_3NC_5H_5 + p\text{-}NCC_6H_4CH_3 \qquad (2)$$

The compounds reported in this paper are all bright-yellow crystalline solids, soluble in halogenated solvents and nitrobenzene. Cryoscopic measurements on the *p*-tolunitrile derivative in nitrobenzene have shown that the compound is monomeric (mol. wt. found 434; calcd. 420.5). The experimental evidence presented here suggest that the compounds are nitrogen-bonded nitrile derivatives of planar d^8 gold(III).

There is likewise no metalation in the reaction between anhydrous gold(III) chloride and azobenzene or 4,4′-azotoluene. As recently reported independently by Hüttel and Konietzny [6], we also have obtained 1/1 adducts with these nitrogen donor ligands.

The experimental conditions which promote metalation are now under investigation, and will be reported in a forthcoming publication. Reaction times for the preparations range from 30 minutes to two hours. All the operations were carried out under dry nitrogen.

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References

1 M.S. Kharasch and T.M. Beck, J. Amer. Chem. Soc., 56 (1934) 2057.
2 D. Belli Dell'Amico and F. Calderazzo, Gazz. Chim. Ital., in press.
3 M.S. Kharasch and H.S. Isbell, J. Amer. Chem. Soc., 53 (1931) 3035.
4 G.W. Parshall, Accounts Chem. Res., 3 (1970) 139.
5 T.L. Brown and M. Kubota, J. Amer. Chem. Soc., 83 (1961) 4175.
6 R. Hüttel and A. Konietzny, Chem. Ber., 106 (1973) 2098.