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PREPARATION OF PENTAHALOPHENYL *p*-TOLYLISOCYANIDE COMPLEXES OF GOLD(I) AND THEIR REACTIONS WITH AMINES, AMMONIA AND ALCOHOLS

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Summary

(Pentahalophenyl) (*p*-tolylisocyanide)gold(I) complexes were prepared by treating $Au(C_6X_5)$ (tetrahydrothiophen) (X = F, Cl or Br) with *p*-MeC_6H_4NC. Their reactivity toward nucleophiles was studied and found to decrease in the sequence: primary amines > ammonia > secondary amines > aromatic amines > alcohols; the effects of the various C_6X_5 groups were less pronounced, but decreased according to $C_6F_5 > C_6Cl_5 > C_6Br_5$.

Twenty-five novel gold(I) carbene derivatives were isolated.

Introduction

Although a very large number of pentafluorophenyl-gold(I) and -gold(III) complexes have been reported, relatively few pentachlorophenyl- [1] and only five pentabromophenyl-gold complexes [2] have so far been described. The latter are the only hitherto known organotransition metal compounds containing this group. The influence which the respective pentahalophenyl group exerts upon the properties and reactivity of the various complexes has not been studied previously.

On the other hand, following the initial reports by Schoellkopf [3] and Richards [4] many papers have been published [5,6] dealing with the addition of nucleophiles, such as alcohols and amines, to isocyanide groups attached to transition metal ions (e.g. gold(I) [7—12]), which leads to the formation of carbene complexes. It has been proposed [7,13] that these reactions proceed via the nucleophilic attack of amines and alcohols upon the carbon atom of the isocyanide group, so that the rate of the addition should depend not only on the basic character of the nucleophile and the reactivity of the respective isocyanide (aromatic isocyanides are more reactive than aliphatic isocyanides) but also upon the electronegativity of the other ligands in the complex, which modify the electrophilic character of the carbon atom of the isocyanide.

In the present paper we describe the preparation of gold(I) isocyanide complexes of the general formula $Au(C_6X_5)(CNTo)$ (X = F, Cl or Br; To = *p*-tolyl) which was accomplished by replacing the tht group of $Au(C_6X_5)(tht)$ (tht = tetrahydrothiophen) by *p*-tolylisocyanide. Their reactions with various aliphatic amines (primary and secondary), aromatic amines, ammonia and alcohols have been studied and the corresponding carbenes isolated.

Discussion and results

Recently, we showed that the tht group in $Au(C_6F_5)(tht)$ can readily be replaced by other neutral ligands [14], especially isocyanide [12]. This makes pentafluorophenyltetrahydrothiophengold(I) a very useful precursor for the synthesis of gold(I) isocyanide complexes. Pentachloro- and pentabromo-tetrahydrothiophengold(I) complexes can be prepared according to eq. 1, in a similar way to that described for $Au(C_6F_5)(tht)$ [15]:

$$AuCl(tht) + LiR \dashrightarrow AuR(tht) + LiCl \qquad (1)$$

$(R = C_6F_5, C_6Cl_5 \text{ or } C_6Br_5)$

However, since the compounds with $R = C_6Cl_5$ and C_6Br_5 are less stable than those with $R = C_6F_5$ they cannot be isolated as pure solids, but their ether solutions are stable. Thus, the addition of a small excess of *p*-tolylisocyanide to the filtered ether solutions (obtained according to eq. 1) leads to the corresponding pentahalophenylisocyanide complex (eq. 2):

$$Au(C_6X_5)(tht) + CNTo \dashrightarrow Au(C_6X_5)(CNTo) + tht \qquad (2)$$

These can be isolated as white air- and moisture-stable solids, which are nonconducting in acetone.

The absorption due to $\nu(CN)$ for the C_6F_5, C_6Cl_5 and C_6Br_5 derivatives are located at decreasing frequencies, viz. 2220(vs), 2210(vs) and 2205(vs) cm^{-1}. This may be attributed to the decreasing electronegativity ($C_6F_5 > C_6Cl_5 > C_6Br_5$) which causes the backbonding to the π^* orbitals of the isocyanide group to increase in the same order [7].

Primary amines (aliphatic and aromatic), secondary amines as well as alcohols react with the isocyanide complexes to give the corresponding gold(I) carbenes. The addition of ammonia takes place in a similar way (see Scheme 1).

SCHEME 1

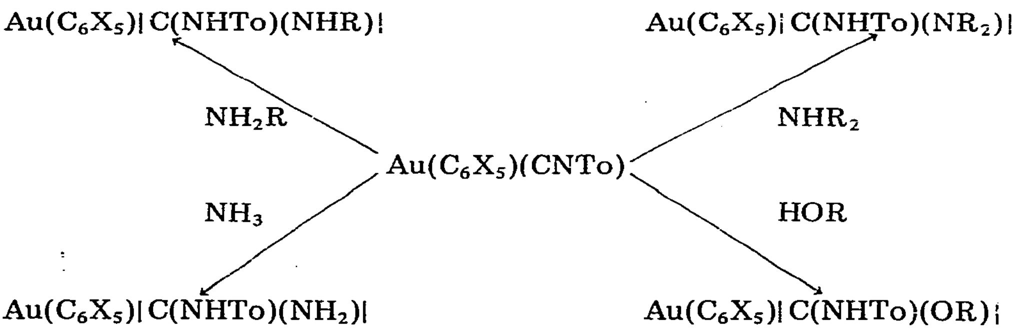

TABLE 1

REACTIONS OF $Au(C_6X_5)(CNTo)$ WITH NUCLEOPHILES

Reaction times (h)

Reagent	C_6X_5 =		
	C_6F_5	C_6Cl_5	C_6Br_5
Primary aliphatic amines			
$MeNH_2$	$1\frac{1}{2}$	2	$3\frac{1}{2}$
$t\text{-}BuNH_2$	3	—	—
$CyNH_2$	3	3	4
$C_6H_5CH_2NH_2$	2	3	4
$C_6H_5CH_2CH_2NH_2$	3	—	—
Ammonia			
NH_3	10	24	48
Secondary amines			
Et_2NH	15	—	—
Pr_2NH	24	24	72
$(C_6H_5CH_2)_2NH$	[a]	[a]	[a]
Primary aromatic amines			
$C_6H_5NH_2$	96	—	[a]
$p\text{-}FC_6H_4NH_2$	96	96	[a]
$p\text{-}CH_3OC_6H_4NH_2$	96	—	[a]
$p\text{-}NO_2C_6H_4NH_2$	[a]	[a]	[a]
Alcohols [b]			
MeOH	72	—	[a]
EtOH	72	96	[a]

[a] No reaction could be observed. [b] The reaction was carried out in refluxing alcohol.

The reactions with ammonia and amines were carried out in dichloromethane or chloroform at room temperature and with a 1 : 2 isocyanide/nucleophile ratio. Alcohols do not react under these conditions, and the corresponding carbene can only be obtained by using refluxing alcohol solutions.

The course of the reactions was monitored by IR spectroscopy until the ν(CN) vibration of the coordinated isocyanide was no longer observed. The times required for each reaction to go to completion are listed in Table 1. It can be seen that the reactivity depends mainly on the nucleophile, and decreases in the sequence: primary aliphatic amines > ammonia > secondary aliphatic amines > aromatic amines > alcohols. Electronegative substituents (e.g. $p\text{-}O_2NC_6H_4NH_2$) prevent the reaction with aromatic amines.

The reactivity also perceptibly depends upon the respective pentahalophenyl group, and decreases in the sequence $C_6F_5 > C_6Cl_5 > C_6Br_5$. Thus, whilst $Au(C_6F_5)(CNTo)$ reacts with all the nucleophiles used except for $p\text{-}O_2NC_6H_4\text{-}NH_2$ and $(C_6H_5CH_2)_2NH$, the pentabromophenyl derivative react with the primary aliphatic amines, NH_3 and Pr_2NH.

The isolated carbenes are air- and moisture-stable solids, which are moderately soluble in most organic solvents, though insoluble in hexane. They are non-conducting in acetone. Along with the absorptions due to the C_6F_5 [16], C_6Cl_5 [17] and C_6Br_5 [2] groups, the complexes show an intense, frequently broad and asymmetric band at ca. 1550 cm^{-1} which is assignable to a C—N stretching vibration with a bond order between 1 and 2.

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TABLE 2

ANALYTICAL DATA FOR COMPLEXES I—XXVIII

		Yield (%)	M.p. (°C)	Anal. (found (calcd.) (%))				ν(CN) (cm^{-1})
				C	H	N	Au	
I	Au(C_6F_5)(CNTo)	56	178(dec.)	34.46 (34.94)	1.50 (1.46)	2.87 (2.91)	41.12 (40.94)	2220vs
II	Au(C_6Cl_5)(CNTo)	50	171	29.42 (29.84)	1.38 (1.25)	2.51 (2.48)	34.22 (34.95)	2210vs
III	Au(C_6Br_5)(CNTo)	42	160(dec.)	21.24 (21.40)	1.04 (0.89)	1.71 (1.68)	25.60 (25.07)	2204vs
IV	Au(C_6F_5)[C(NHTo)(NHMe)]	56	146(dec.)	34.99 (35.17)	2.28 (2.36)	5.50 (5.46)	38.00 (38.45)	1150vs
V	Au(C_6F_5)[C(NHTo)(NH-t-Bu)]	66	128(dec.)	39.65 (39.00)	3.46 (3.27)	5.36 (5.05)	34.89 (35.53)	1530vs
VI	Au(C_6F_5)[C(NHTo)(NHCy)]	65	151(dec.)	41.70 (41.38)	3.62 (3.47)	4.90 (4.82)	34.22 (33.94)	1554vs
VII	Au(C_6F_5)[C(NHTo)(NHCH$_2$C$_6$H$_5$)]	60	102(dec.)	43.28 (42.86)	3.12 (2.74)	4.90 (4.76)	33.92 (33.48)	1545vs
VIII	Au(C_6F_5)[C(NHTo)(NHCH$_2$CH$_2$C$_6$H$_5$)]	69	107(dec.)	44.12 (43.86)	3.17 (3.01)	4.52 (4.65)	33.10 (32.70)	1560vs
IX	Au(C_6Cl_5)[C(NHTo)(NHMe)]	48	174(dec.)	30.09 (30.30)	2.15 (2.03)	4.82 (4.71)	33.04 (33.13)	1568vs
X	Au(C_6Cl_5)[C(NHTo)(NHCy)]	64	164(dec.)	37.10 (36.25)	3.10 (3.04)	4.19 (4.22)	29.12 (29.72)	1549vs
XI	Au(C_6Cl_5)[C(NHTo)(NHCH$_2$C$_6$H$_5$)]	63	167(dec.)	37.56 (37.61)	2.64 (2.40)	4.15 (4.17)	29.74 (29.37)	1560vs
XII	Au(C_6Br_5)[C(NHTo)(NHMe)]	41	157(dec.)	22.01 (22.05)	1.34 (1.48)	3.04 (3.42)	24.26 (24.11)	1550vs
XIII	Au(C_6Br_5)[C(NHTo)(NHCy)]	46	149(dec.)	27.62 (27.14)	2.15 (2.27)	3.36 (3.16)	21.98 (22.16)	1562vs

XIV	$Au(C_6Br_5)[C(NHTo)(NHCH_2C_6H_5)]$	49	117(dec.)	28.99 (28.24)	1.81 (1.80)	3.06 (3.13)	22.12 (22.06)	1546vs
XV	$Au(C_6F_5)[C(NHTo)(NH_2)]$	75	169(dec.)	33.39 (33.75)	1.97 (2.02)	5.64 (5.62)	39.12 (39.53)	1580vs
XVI	$Au(C_6Cl_5)[C(NHTo)(NH_2)]$	68	168(dec.)	28.74 (28.96)	1.63 (1.73)	4.63 (4.82)	32.49 (33.93)	1568vs
XVII	$Au(C_6Br_5)[C(NHTo)(NH_2)]$	70	180(dec.)	20.91 (20.94)	1.21 (1.25)	3.37 (3.48)	23.87 (24.53)	1568vs
XVIII	$Au(C_6F_5)[C(NHTo)(NEt_2)]$	56	87(dec.)	39.33 (39.00)	3.30 (3.27)	5.09 (5.05)	35.80 (35.53)	1545vs
XIX	$Au(C_6F_5)[C(NHTo)(NPr_2)]$	68	127(dec.)	41.90 (41.24)	3.74 (3.80)	5.02 (4.81)	34.10 (33.82)	1540vs
XX	$Au(C_6Cl_5)[C(NHTo)(NPr_2)]$	65	131(dec.)	36.94 (36.14)	3.75 (3.33)	4.27 (4.21)	29.55 (29.63)	1530vs
XXI	$Au(C_6Br_5)[C(NHTo)(NPr_2)]$	47	130(dec.)	26.94 (27.08)	2.51 (2.49)	3.07 (3.15)	22.41 (22.21)	1553vs
XXII	$Au(C_6F_5)[C(NHTo)(NHC_6H_5)]$	56	174(dec.)	41.72 (41.82)	2.40 (2.41)	4.86 (4.87)	34.82 (34.30)	1542vs
XXIII	$Au(C_6F_5)[C(NHTo)(p\text{-}NHC_6H_4F)]$	50	132(dec.)	40.10 (40.55)	2.41 (2.21)	4.98 (4.73)	33.85 (33.25)	1550vs
XXIV	$Au(C_6F_5)[C(NHTo)(p\text{-}NHC_6H_4OCH_3)]$	46	178(dec.)	42.31 (41.73)	2.55 (2.66)	4.78 (4.63)	32.08 (32.59)	1540vs
XXV	$Au(C_6Cl_5)[C(NHTo)(p\text{-}NHC_6H_4F)]$	26	180(dec.)	36.45 (35.65)	2.02 (1.94)	4.18 (4.15)	29.36 (29.20)	1560vs
XXVI	$Au(C_6F_5)[C(NHTo)(OMe)]$	40	126(dec.)	35.54 (35.10)	2.02 (2.16)	2.80 (2.72)	38.50 (38.38)	1535vs
XXVII	$Au(C_6F_5)[C(NHTo)(OEt)]$	38	98(dec.)	36.19 (36.45)	2.26 (2.45)	2.65 (2.65)	37.54 (37.36)	1542vs
XXVIII	$Au(C_6Cl_5)[C(NHTo)(OEt)]$	30	133(dec.)	32.15 (31.52)	2.21 (2.14)	2.34 (2.29)	32.46 (32.32)	1575vs

The analytical results, yields, melting points and ν(CN) vibrations for the twenty-eight novel complexes are listed in Table 2.

Experimental

IR spectra were recorded (over the range 4000—200 cm^{-1}) on a Perkin—Elmer 577 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured on 5×10^{-4} *M* acetone solutions with a Philips PW 9501/01 conductimeter. C, H and N analyses were carried out with a Perkin—Elmer 240 microanalyzer. Au was determined by ashing the samples in a crucible together with an aqueous solution of hydrazine.

Preparation of Au(C_6X_5) (CNTo)

A small excess of *p*-tolylisocyanide was added to a solution of Au(C_6X_5) (tht) (prepared by addition of AuCl (tht) to an ether solution of LiC_6X_5 at —78°C and slowly warmed to —10°C) and the mixture was allowed to warm to room temperature. After 1 h of stirring the solvent was evaporated, and the resulting colourless oil was stirred with hexane for several hours to yield a white product, which was recrystallized from dichloromethane/hexane (complexes I—III).

(a) Reactions with aliphatic amines (primary and secondary). Two mmol of amines were added to a solution of 1 mmol of Au(C_6X_5) (CNTo) in 30 ml of dichloromethane. The solution was stirred at room temperature until the ν(CN) band of the isocyanide was no longer present. (The reaction times are listed in Table 1.) The solvent was then evaporated, and the resulting oil was stirred with hexane for several hours to give the white carbene, which was recrystallized from ether/hexane (complexes IV—XIV and XVIII—XXI).

(b) Reactions with aromatic amines. The addition of 2 mmol of amine to a solution of 1 mmol of Au(C_6X_5) (CNTo) in 30 ml of chloroform leads after several days' stirring at room temperature (IR spectrum) to the precipitation of the required carbenes as white solids. Evaporation of the solvent gives more of the product. The obtained carbenes were recrystallized from dichloromethane/hexane (complexes XXII—XXV).

(c) Reactions with ammonia. An aqueous solution of ammonia (201 g/l) was added in excess (3 : 1 molar ratio) to a solution of 1 mmol of Au(C_6X_5) (CNTo) in 30 ml of dichloromethane and the mixture was stirred at room temperature. When the reaction was complete (IR spectrum) the solution was dried with anhydrous magnesium sulphate and evaporated under reduced pressure. The residue was washed with hexane and recrystallized from ether/hexane to give the white carbene (complexes XV—XVII).

(d) Reactions with alcohols. A suspension of 1 mmol of Au(C_6X_5) (CNTo) in 50 ml of alcohol was refluxed until the vibrations due to ν(CN) of the isocyanide could no longer be observed. A small quantity of metallic gold was filtered off and the filtrate was evaporated to dryness. The residue was recrystallized from dichloromethane/hexane to give a white solid (complexes XXVI—XXVIII).

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