Journal of Organometallic Chemistry, 352 (1988) C37–C41
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Interaction of organogold(I) compounds with tetraalkylthiuram disulfides

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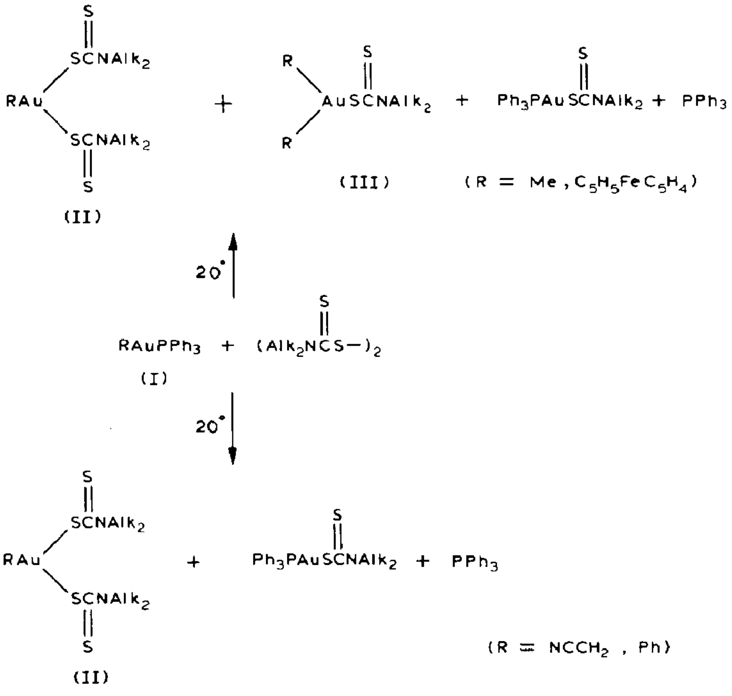
(Received May 25th, 1988)

Abstract

Reactions of tetraalkylthiuram disulfides with $RAuPPh_3$ complexes (R = alkyl, phenyl, ferrocenyl) lead by oxidation to gold(III) dialkyldithiocarbamates. The products formed gaves satisfactory elemental analysis.

Examples of oxidative addition of disulfides to organometallic derivatives of univalent gold are rare [1,2]. Nevertheless disulfides are very promising in this respect owing to the ability of heavy metals and particularly gold, to form bonds with sulfur.



0022-328X/88/$03.50

Table 1

Dithiocarbamates of trivalent gold (II–IV)

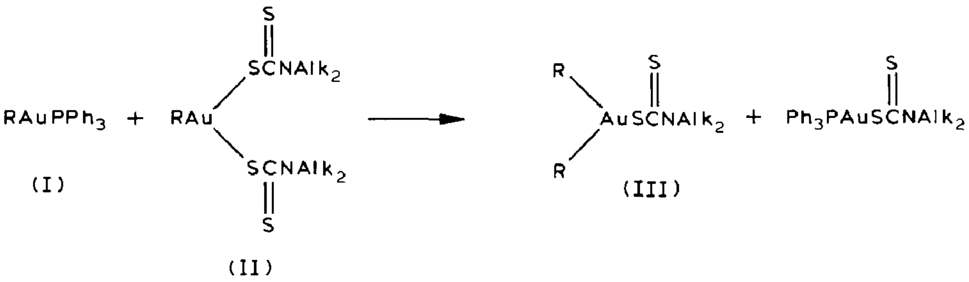
Compound	Colour	Yield (%)	M.p. (decomp.) (°C)	Elemental analysis (found (calcd.) (%))				
				C	H	N	Au	S
$MeAu(SC(S)NMe_2)_2$	yellow	30	> 120	18.59	3.30	6.10	43.77	
				(18.58)	(3.34)	(6.19)	(43.54)	
$NCCH_2Au(SC(S)NMe_2)_2$	red	92	148–151	20.30	2.47	8.98	41.49	26.87
				(20.13)	(2.96)	(8.80)	(41.25)	(26.86)
$NCCH_2Au(SC(S)NEt_2)_2$	red	65	137–138	26.95	3.93	7.83	36.55	24.02
				(27.00)	(4.15)	(7.91)	(36.90)	(24.03)
$C_5H_5FeC_5H_4Au(SC(S)NMe_2)_2$	deep-red	28	181–183	31.18	3.40	4.54	–	20.52
				(30.88)	(3.40)	(4.50)		(20.61)
$C_5H_5FeC_5H_4Au(SC(S)NEt_2)_2$	red	32	144–145	35.11	4.06	4.37	–	18.84
				(35.40)	(4.31)	(4.13)		(18.90)
$PhAu(SC(S)NMe_2)_2$	yellow	20	142–144	28.30	3.13	5.36	38.22	24.49
				(28.01)	(3.32)	(5.44)	(38.29)	(24.93)
$(C_5H_5FeC_5H_4)_2AuSc(S)NMe_2$	yellow	32 [a]	> 150	40.17	3.41	2.15	–	9.36
				(40.20)	(3.52)	(2.04)		(9.33)
$(C_5H_5FeC_5H_4)_2AuSC(S)NEt_2$	yellow	32 [a]	> 150	42.10	3.64	1.97	–	9.19
		100 [b]		(41.98)	(3.95)	(1.96)		(8.97)
$(C_5H_5FeC_5H_4)(Ph)AuSC(S)NMe_2$	yellow	100	139–140	39.19	3.49	2.46	–	10.70
				(39.39)	(3.48)	(2.42)		(11.07)
$(Me)(Ph)AuSC(S)NMe_2$	white	70	93.5–94.5	29.55	3.46	3.36	48.43	15.76
				(29.34)	(3.45)	(3.42)	(48.12)	(15.67)

[a] Reaction of ferrocenyl(triphenylphosphine)gold with thiuram disulfide. [b] Reaction of ferrocenyl(triphenylphosphine)gold with ferrocenylgold-bis(dimethyldithiocarbamate).

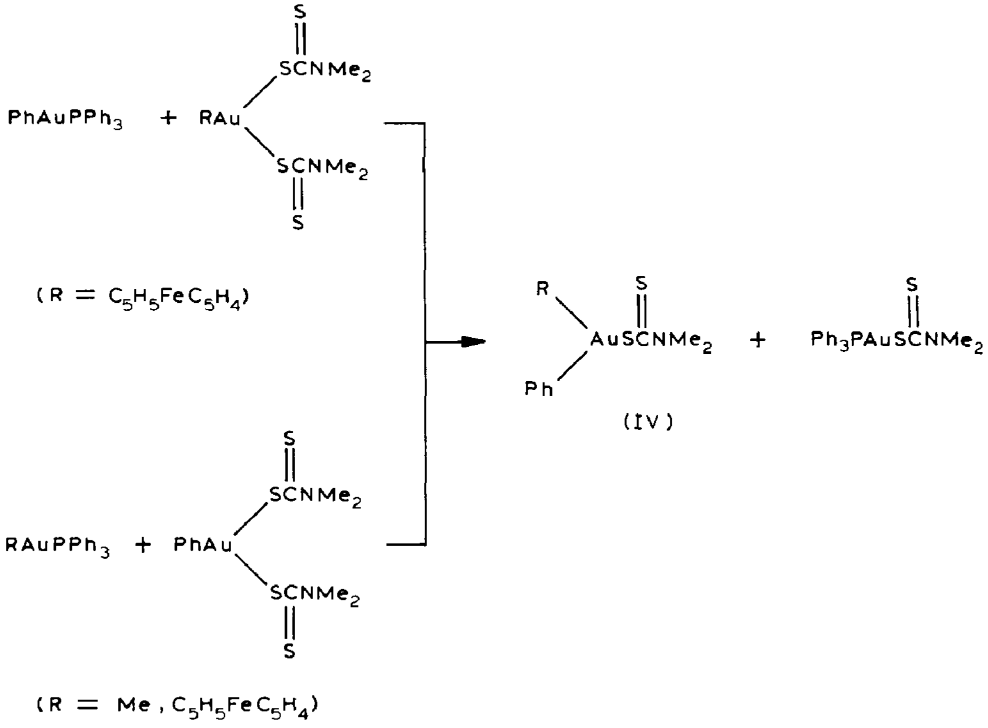
We have studied the reactions of tetraalkylthiuram disulfides with organogold complexes $RAuPPh_3$ (I) that differ from each other in the nature of the σ-bonded organic moiety (R-alkyl, phenyl, ferrocenyl). We have found that our organogold compounds react with thiuram disulfides by oxidative addition to give trivalent gold dialkyldithiocarbamates.

In this way we have obtained the novel bis-dithiocarbamates of trivalent gold, $RAu[SC(S)NAlk_2]_2$ (II). Yields, melting points and elemental analysis data are listed in Table 1. IR and ^1H NMR spectra are consistent with the structure proposed.

Reaction of the methyl- and ferrocenyl-(triphenylphosphine)gold with the gold dithiocarbamates, leads to the formation of $R_2AuSC(S)NAlk_2$ (III) having two σ-bonded R groups along with bis(dithiocarbamates). Dithiocarbamates III arise from a reaction of initially formed II with starting organogold compounds I as we have shown in a specific experiment. In this reaction a σ-bonded R group is transferred from univalent to the trivalent gold.

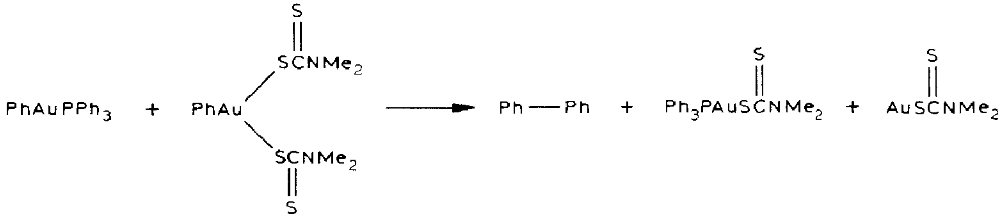


(R = Me, $C_5H_5FeC_5H_4$)



Interaction between the univalent and trivalent gold compounds containing different R moieties, leads to novel trivalent gold compounds, the mixed dithiocarbamates (IV).

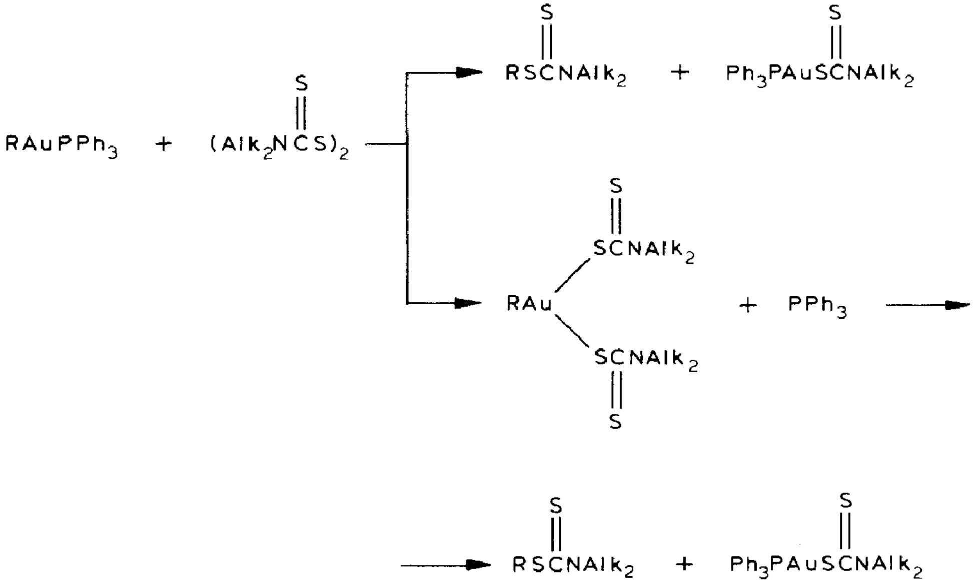
The dithiocarbamates, $R_2AuSC(S)NAlk_2$, are not formed in the reactions of I ($R = CH_2CN$, Ph) with thiuram disulfides, which is due to the absence of any interaction between the compounds I and II ($R = CH_2CN$) under the reaction conditions; the reaction of $PhAuPPh_3$ with $PhAu[SC(S)NMe_2]_2$ leads to biphenyl.



Previous attempts to obtain $Ph_2AuSC(S)NAlk_2$ starting from phenylmagnesium bromide and $Br_2AuSC(S)NAlk_2$ [3] also failed.

In the reactions of $MeAuPPh_3$ and $NCCH_2AuPPh_3$ with thiuram disulfides we observed the formation of the dithiocarbamic acid methyl and cyanomethyl esters. There are two possible reaction pathways leading to these esters: electrophilic substitution or oxidative addition followed by reductive elimination.

We have found that $MeAu[SC(S)NMe_2]_2$ is stable in solution under our reaction conditions with thiuram disulfide. However, in the presence of triphenylphosphine $MeAu[SC(S)NMe_2]_2$ undergoes reductive elimination. It is one of the few examples of the reductive elimination from trivalent gold that leads to formation of a



carbon–heteroatom bond. In most of the reactions of this type, a C–C bond is formed [4].

The cyanomethyl derivative $NCCH_2Au[SC(S)NEt_2]_2$ is stable towards reductive elimination both pure and in the presence of triphenylphosphine. So we presume that Au–C bond cleavage in $NCCH_2AuPPh_3$ under the action of thiuram disulfide proceeds independently of oxidative addition. For $MeAuPPh_3$ the cleavage that proceeds via oxidative addition and subsequent reductive elimination plays a significant role.

The dithiocarbamic acid ferrocenyl esters have not been detected in the reactions of $C_5H_5FeC_5H_4AuPPh_3$ with thiuram disulfides. Consequently electrophilic substitution and reductive elimination do not take place in this case.

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