

Leaving Group Selectivity in Reductive Elimination from Organogold(III) Complexes

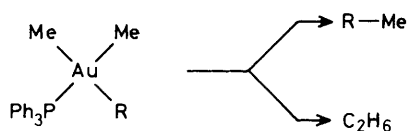
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Selective reductive elimination of Me-R from *cis*-AuMe₂(R)(PPh₃) takes place when R is alkenyl, aryl, and furyl, whereas only ethane is reductively eliminated when R is an alkynyl or electron-withdrawing alkyl group.

Reductive elimination from organotransition metal complexes is a most important step in various transition metal-promoted reactions. Although recent mechanistic studies¹ on reductive elimination from isolated organotransition metal complexes show that various pathways exist for the C-C coupling process, the selectivity of the leaving group is not well

understood. We previously reported dissociative reductive elimination from triorganogold(III) complexes having a triphenylphosphine ligand.² These compounds should also provide a suitable model for estimating the relative ease of reductive elimination, since reductive elimination of two alkyl groups during the thermolysis of these compounds will



Scheme 1

compete with that of another two alkyl groups to give a mixture of RMe and ethane. Thus examination of the reaction products will indicate the relative ease of reductive elimination of the alkyl groups involved (Scheme 1). We now report the intramolecular competitive reductive elimination from organodimethylgold(III) complexes.†

A series of *cis*-organodimethylgold(III) complexes having a triphenylphosphine ligand was prepared by the method previously reported.² Table 1 summarizes the ratio of the thermolysis products for these complexes. In the thermolysis of *cis*-alkyldimethylgold(III) complexes (runs 1–4), electron donating alkyl groups are preferentially eliminated as predicted theoretically.¹ In contrast, thermolysis of (*cis*- or *trans*-propenyl)dimethylgold(III) complexes cleanly liberated *cis*- or *trans*-but-2-ene stereoselectively. The selective coupling of alkenyl and methyl groups rather than the formation of ethane is noteworthy, since alkenyl groups are considered to be weaker donors than methyl. Similar coupling reactions were observed when R is aryl, alkenyl, or furyl, in which an sp² carbon atom is directly bonded to gold (runs 5–11). Participation of π -orbitals in the concerted reductive elimination process should decrease the activation energy.³ Such a ready coupling involving sp² carbon is known⁴ for the thermolysis of arylmethyl[1,2-bis(dimethylphosphino)ethane]nickel(II).

The results may relate to the selective cross-coupling reaction of aryl or alkenyl halides with Grignard reagents prompted by nickel or palladium complexes.⁵ The results for the aryldimethylgold(III) complexes (runs 5–7), however, show a slight enhancement of reductive elimination also if the more electron donating aryl group was employed.

In contrast, ethane became the dominant thermolysis product for an (alkynyl)dimethylgold(III) complex in which an sp carbon atom was bonded directly to gold (run 12), possibly owing to the fairly strong gold–sp carbon bond. This result

† The results of the thermolysis were obtained at the initial stages of the reactions in order to avoid the further decomposition of the gold(I) products and intermolecular processes. Further detailed studies are necessary.

Table 1. Reductive elimination products from *cis*-AuMe₂(R)(PPh₃).^a

Run	R	Molar ratio Me–Me : R–Me
1 ^b	Et	33 : 67
2	PhCH ₂	78 : 32
3	PhCH ₂ CH ₂	62 : 38
4	2-Pyridylmethyl	89 : 11
5	<i>p</i> -FC ₆ H ₄	10 : 90
6	Ph	5 : 95
7	<i>p</i> -Me ₂ NC ₆ H ₄	1 : 99
8 ^c	2-Furyl	4 : 96
9	<i>trans</i> -PhCH=CH	0 : 100
10	<i>trans</i> -MeCH=CH	2 : 98
11	<i>cis</i> -MeCH=CH	3 : 97
12	PhC≡C	96 : 4

^a In benzene at 70 °C for 60–200 min. Product ratios were estimated by g.c. when the yield was 10–30%.[†] ^b Data from ref. 7. ^c At 120 °C in Ph₂O.

may be relevant to the selective C–C bond formation in the reaction of organo(alkynyl)cuprate with organic halides.⁶

The observed trend concerning the concerted reductive elimination seems to be general and further kinetic aspects of the leaving group selectivity are under investigation.

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