

Preliminary communication

UNUSUAL STERIC EFFECT OF AN ALKENYL OR ARYL GROUP ON THE DISSOCIATIVE REDUCTIVE ELIMINATION FROM *cis*-ALKENYL(OR -ARYL)DIMETHYL(TRIPHENYLPHOSPHINE)GOLD(III)

SANSHIRO KOMIYA*, AKIRA SHIBUE and SATOSHI OZAKI

*Department of Applied Chemistry for Resources, Tokyo University of Agriculture and Technology,
 2-24-16 Nakamachi, Koganei, Tokyo 184 (Japan)*

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Summary

A sterically bulky aryl or alkenyl group directly bonded to gold suppresses the rate of dissociation of the triphenylphosphine ligand from *cis*-alkenyl(or -aryl)dimethyl(triphenylphosphine)gold(III) leading to selective reductive elimination.




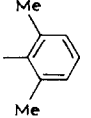
The coordination of suitable tertiary phosphine ligands in organotransition metal complexes plays an important role in stabilizing the metal-carbon bond, since the dissociation of the stabilizing ligands frequently leads to scission of the bond giving rise to a reductive elimination or β -elimination [1]. We previously reported the steric and electronic effects of the stabilizing ligand on the dissociative reductive elimination in triorganogold(III) complexes [2]. Here we report the preparation and the unexpected steric effect of alkenyl and aryl groups on the dissociative process.

A series of *cis*-alkenyl(or -aryl)dimethyl(triphenylphosphine)gold(III) complexes, AuRMe₂(PPh₃) (R = *cis*-CH=CHMe (**1a**), *trans*-CH=CHMe (**1b**), *E*-CMe=CHMe (**1c**), Ph, (**2a**), *o*-tolyl; (**2b**), 2,6-dimethylphenyl, (**2c**)) has been prepared by the reaction of AuMe₂I(PPh₃) with corresponding Grignard reagents [2] *. The rates of dissociation (k_1) of the triphenylphosphine ligand from the complexes **1** and **2** were

* The compounds used were characterized by ¹H and ¹³C NMR as well as by elemental analyses [2]. Selected NMR data for **1a** and **1b** in CDCl₃ (chemical shifts are referred to internal standard TMS in ppm and coupling constants are in Hz). ¹H NMR: **1a**, H_α: 6.34 (1H, ddq, *J*(H-H) 10.4, *J*(H-P) 2.9, *J*(H-H) 1.0); H_β: 6.56 (1H, ddq, *J*(H-H) 10.4, *J*(H-P) 3.5, *J*(H-H) 6.2); Me: 1.41 (3H, ddd, *J*(H-H) 1.0, 6.2, 1.0); Au-Me: 0.04 (3H, d, *J*(H-P) 7.3), 1.11 (3H, d, *J*(H-P) 9.0). **1b**, H_α: 6.20 (1H, ddq, *J*(H-H) 16.8, *J*(H-P) 8.3, *J*(H-H) 1.5); H_β: 5.41 (1H, ddq, *J*(H-H) 16.8, *J*(H-P) 1.2, *J*(H-H) 6.0); Me: 1.50 (3H, ddd, *J*(H-H) 1.5, 6.0, 1.0); Au-Me: 0.04 (3H, d, *J*(H-P) 7.3), 1.18 (3H, d, *J*(H-P) 9.0). ¹³C NMR: **1a**, Au-Me: *cis* to P, 9.5 (d, 6.1), *trans* to P, 11.62 (d, 118.4); Me: 20.87 (s); C_α, 153.93 (d, 9.8). **1b**, Au-Me: *cis* to P, 7.5 (d, 6.1), *trans* to P, 15.22 (d, 118.4); Me, 24.08 (s); C_α, 156.30 (d, 11.0).

TABLE 1

SELECTED ^1H NMR AND ANALYTICAL DATA FOR *cis*-ALKENYL(OR -ARYL)DIMETHYL-(TRIPHENYLPHOSPHINE)GOLD(III) ^a

R	Analyses (Found (calc) (%))		^1H NMR $\delta(\text{Au-Me})$ (in ppm from ext. TMS in CDCl_3)	
	C	H	<i>cis</i> to PPh_3	<i>trans</i> to PPh_3
 (1a)	52.5 (52.1)	5.2 (4.9)	0.04	1.11
 (1b)	52.1 (52.1)	4.8 (4.9)	0.04	1.18
 (1c)	52.6 (53.0)	4.9 (5.2)	-0.01	1.02
Ph (2a)	54.3 (55.1)	4.6 (4.6)	0.18	1.18
<i>o</i> -tolyl (2b)	55.3 (55.9)	4.6 (4.9)	0.18	1.11
 (2c)	56.0 (56.6)	5.0 (5.1)	0.20	1.07

^a A part of the data was taken from Ref. 2.

estimated by examining the dependence of the pseudo first order rate constant, k_{obs} in the thermolysis of these organogold(III) complexes in benzene at 70°C , on the concentration of triphenylphosphine ligand as reported previously [2].

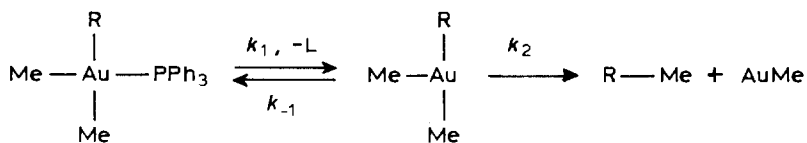


Figure 1 demonstrates the relationship between the first order dissociation rate constant, k_1 , and the effective ligand angle θ^* , which can be estimated by means of a space-filling model as in Fig. 2 and can be taken as an index of their two dimensional steric bulkiness. The dissociation rate constant, k_1 , decreases with an increase in the effective ligand angle in spite of the increase of steric repulsion between the triphenylphosphine ligand and the aryl or alkenyl group. The results are

* Normal bond lengths and angles were used for calculation: *cis*-CH=CHMe 148, *trans*-CH=CHMe 116, *E*-CMe=CHMe 168, Ph 134, *o*-tolyl 165, 2,6-dimethylphenyl 196°.

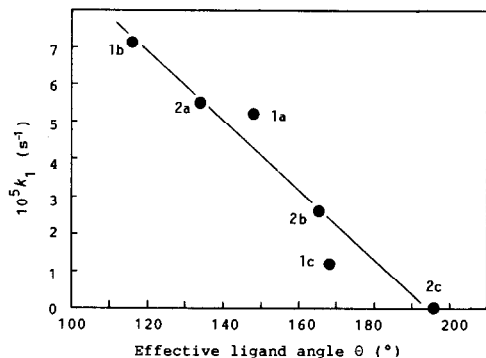


Fig. 1. Relationship between k_1 and effective ligand angle θ of the alkenyl and aryl groups.

also in sharp contrast to the fact that the electron donation from the aryl group enhances the ligand dissociation from aryldimethylgold(III) complexes [2].

On the other hand, a sterically bulky alkenyl or aryl group is considered to remain perpendicular to the coordination plane. In the ^1H NMR of complexes **1a** and **1b**, the coupling constant between H_α and P nuclei in **1a** (J 2.9 Hz) is found to be considerably smaller than that in **1b** (J 8.3 Hz). Since the dihedral angle in $\text{H}_\alpha\text{-C}_\alpha\text{-Au-P}$ can reflect the coupling constant between H and P according to the well-known Karplus equation, **1a** is considered to keep an alkenyl group more perpendicular to the coordination plane than **1b**, in reducing their steric hindrance. In fact a large upfield shift due to the steric influence in the ^{13}C NMR spectrum is observed between the methyl carbon *trans* to the P nucleus and the methyl carbon of *cis*-propenyl group. A similar upfield shift of the signal of Me-Au *trans* to P is also observed in *ortho*-substituted arylgold(III) complexes **2b** and **2c**. (^{13}C NMR and Me-Au *trans* to P (ppm in CDCl_3): **1a**, 11.62; **1b**, 15.22; **1c**, 11.16; **2a**, 15.08; **2b**, 12.37; **2c**, 10.36) Such a perpendicular geometry possibly compels the effective interaction of the occupied d -orbital with the $p\pi^*$ orbital of alkenyl or aryl group,

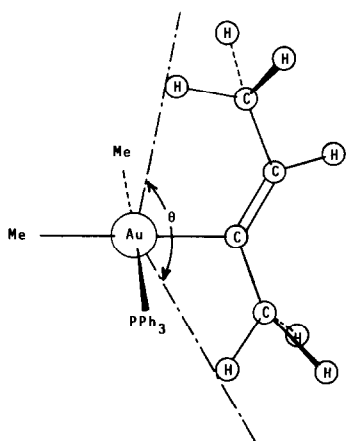


Fig. 2. Effective ligand angle θ .

thus increasing π back-donation. However, at present, further structural and theoretical investigations are required to complete the study.

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References

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