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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)

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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 phoshine ligands in organotransition metal complexes plays an important role in stabilizing the metal–carbon bond, since the dissociation of the stabilizing ligands frequency leads to scission of the bond giving rise to a reductive elmination 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, $AuRMe_2(PPh_3)$ (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 $AuMe_2I(PPh_3)$ 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 ^{13}C NMR as well as by elemental analyses [2]. Selected NMR data for **1a** and **1b** in $CDCl_3$ (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). ^{13}C NMR: **1a**, Au-Me: *cis* to P, 9.5 (d, 6.1), *trans* to P, 11.62 (d, 1184.); 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).

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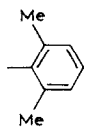
TABLE 1

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

R	Analyses (Found (calc) (%))		^{1}H NMR δ(Au-Me) (in ppm from ext. TMS in $CDCl_3$)	
	C	H	*cis* to PPh_3	*trans* 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
o-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].

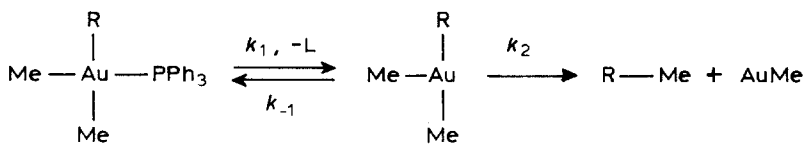


Figure 1 demonstrates the relationship between the first order dissociation rate constant, k_1, and the effective ligand angle θ *, which can be estimated by means of a space-filling model as in Fig. 2 and can be taken as an index of their two dimensional steric bulkiness. The dissociation rate constant, 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°.

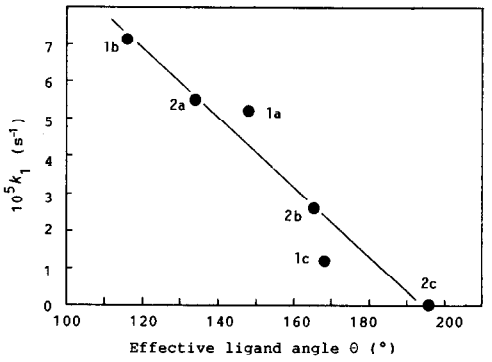


Fig. 1. Relationship between k_1 and effective ligand angle θ of the alkenyl and aryl groups.

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 ^{1}H 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 H_α–C_α–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 $p\pi^\star$ orbital of alkenyl or aryl group,

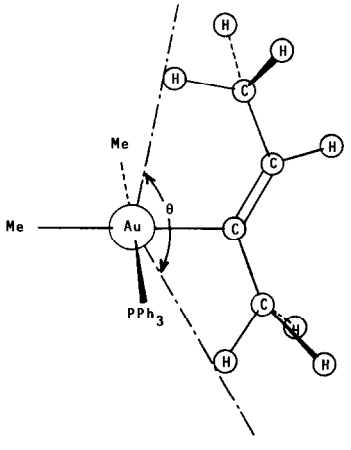


Fig. 2. Effective ligand angle θ.

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

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