Hydrogen Abstraction from Transition Metal Hydrides by Gold Alkoxides Giving Gold-Containing Heterodinuclear Complexes

Yoko Usui, Masafumi Hirano, Atsushi Fukuoka,[†] and Sanshiro Komiya*
Department of Applied Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology,
2-24-16 Nakacho, Koganei, Tokyo 184

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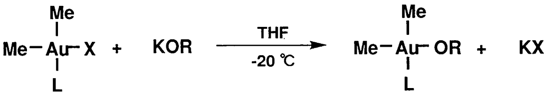
Gold(I) alkoxides, Au(OR)L (L = PPh_3, PCy_3; R = $CH(CF_3)_2$, CH_2CF_3, Ph) smoothly abstract a hydrogen from transition metal hydrides (MH = $CoH(CO)_4$, $MoHCp(CO)_3$, $WHCp(CO)_3$, $MnH(CO)_5$, $WHCp(CO)_2(PPh_3)$) to give corresponding dinuclear complexes LAu-M with liberation of equimolar amount of ROH. Similar reactions of gold(III) alkoxides, *cis*-$AuMe_2$-(OR)L also give dinuclear intermediates LMe_2Au-M, from which preferential reductive elimination of ethane takes place when M is more electron withdrawing.

Alkoxides of late transition metals have attracted growing interests in relation to not only catalysts and synthetic tools in organic syntheses but also their possible use as new materials, and considerable efforts have been devoted for their synthesis in recent years.[1] In general, they are considered to be highly reactive due to possible electronic repulsion between filled metal d-orbitals and oxygen lone pair electrons, giving an inherently reactive Au-O bond. We have recently isolated series of gold(I or III) fluoroalkoxides and aryloxides stabilized by a tertiary phosphine ligand *via* simple metathetical reaction.[2]

$$\text{AuClL} + \text{KOR} \xrightarrow[-20\ ^\circ\text{C}]{\text{THF}} \text{Au(OR)L} + \text{KCl} \qquad (1)$$



$$\text{Me}-\underset{\text{L}}{\overset{\text{Me}}{\text{Au}}}-\text{X} + \text{KOR} \xrightarrow[-20\ ^\circ\text{C}]{\text{THF}} \text{Me}-\underset{\text{L}}{\overset{\text{Me}}{\text{Au}}}-\text{OR} + \text{KX} \qquad (2)$$

X = I, NO_3 L = PPh_3, PCy_3; R = $CH(CF_3)_2$, CH_2CF_3, Ph

They are in fact highly basic to show hydrogen bonding with free alcohol and to act as catalysts for Knoevenagel reactions under neutral and ambient conditions.[3] We now report the selective hydrogen abstraction reaction from transition metal hydrides by the gold alkoxides resulting in the formation of heterodinuclear complexes having a Au-M bond.[4]

When gold(I) alkoxide, $Au[OCH(CF_3)_2]L$ (L = PPh_3 (**1a**), PCy_3 (**1b**)) was treated with transition metal hydrides MH (MH = $CoH(CO)_4$, $MoHCp(CO)_3$, $WHCp(CO)_3$, $WHCp(CO)_2(PMe_3)$, $ReH(CO)_5$), the hydride was cleanly abstracted by the alkoxo ligand to form Au(I) heterodinuclear complexes, LAu-M, with liberation of the corresponding alcohol.

$$\text{Au[OCH(CF}_3)_2]\text{L} + \text{MH} \longrightarrow \text{LAu}-\text{M} + (\text{CF}_3)_2\text{CHOH} \qquad (3)$$

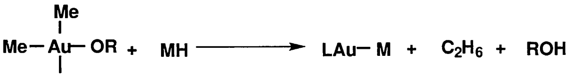
L = PPh_3, PCy_3
MH = $CoH(CO)_4$, $MoHCp(CO)_3$, $WHCp(CO)_3$, $ReH(CO)_5$, $WHCp(CO)_2(PMe_3)$

Similar reactions of trivalent gold alkoxides, *cis*-$AuMe_2[OCH(CF_3)_2](PPh_3)$ (**2a**) with metal hydrides (MH = $CoH(CO)_4$, $MoHCp(CO)_3$, $MnH(CO)_5$, $WHCp(CO)_3$, $WHCp(CO)_2(PPh_3)$) also proceeded to liberate $(CF_3)_2CHOH$ to gain $(Ph_3P)Au$-M accompanied by evolution of an equimolar amount of ethane within experimental error. Results for **2a** are summarized in Table 1. Analogous reactions of $AuMe_2(OR)(PPh_3)$ (R = CH_2CF_3 (**2b**), Ph (**2c**)) with $MoHCp(CO)_3$ or $WHCp(CO)_3$ gave similar results.

Table 1. Reactions of *cis*-$AuMe_2RL$[a] with transition metal hydrides

MH	pKa[b]	Products (%/Au)						
		LAu-M[c]	M-Me[d]	AuMeL[e]	$AuMe_3L$[e]	ROH[e]	C_2H_6[f]	CH_4[f]
$CoH(CO)_4$[g]	7.2	91	0	0	0	83	85	0
$MoHCp(CO)_3$[h]	13.9	83	0	0	0	80	105	0
$MnH(CO)_5$[h]	15.1	81	0	0	0	86	100	0
$WHCp(CO)_3$[h]	16.1	93	0	0	0	95	101	0
$WHCp(CO)_2(PPh_3)$[h]	—	89	0	0	0	97	94	0
$ReH(CO)_5$[i]	21.1	82	9.5	0	18	99	35	45
$WHCp(CO)_2(PMe_3)$[j]	26.6	20	19	22	8	66	4	9

[a] R = $OCH(CF_3)_2$, L = PPh_3. [b] pKa values in acetonitrile at 25°C were taken from ref. 4. [c] characterized spectroscopic comparison with authentic samples (ref. 6). [d] characterized spectroscopic comparison with authentic samples (ref. 7). [e] estimated by ^1H NMR. [f] estimated by GLC. [g] in CH_2Cl_2 at -50°C within 10 min. [h] in toluene at -50°C within 10 min. [i] in benzene at r.t. for 150 min. [j] in benzene at 50°C for 96 hr.



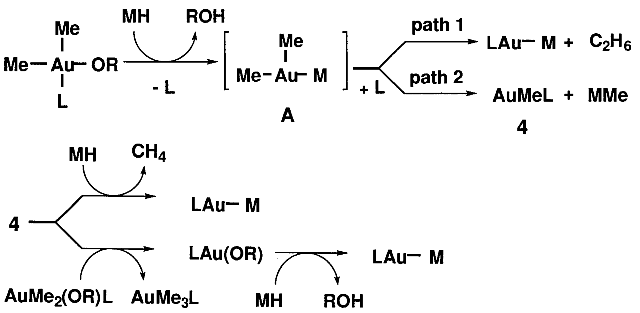
$$\text{Me}-\underset{\text{L}}{\overset{\text{Me}}{\text{Au}}}-\text{OR} + \text{MH} \longrightarrow \text{LAu}-\text{M} + \text{C}_2\text{H}_6 + \text{ROH} \qquad (4)$$

R = $CH(CF_3)_2$, CH_2CF_3, Ph

In contrast, reactions of **2a** with $ReH(CO)_5$ under the same conditions are very slow, giving $AuMe_3(PPh_3)$, $ReMe(CO)_5$ and methane in addition to ethane, alcohol and bimetallic complexes. Reaction with $WHCp(CO)_2(PMe_3)$ also gave similar results.

As shown in Scheme 1, the formation of these products can be consistently interpreted by assuming the initial hydrogen abstraction by the gold alkoxide to form a common trivalent heterobimetallic complex, Me_2Au-M (**A**), from which

Scheme 1.



competitive reductive elimination of ethane (path 1) and methylmetal species (path 2) takes place giving bimetallic compound $(Ph_3P)Au$-M and $AuMe(PPh_3)$, respectively.

The amount of $AuMe(PPh_3)$ once formed diminished at the final stage of the reaction. Further reactions of the $AuMe(PPh_3)$ with the hydride and alkoxide would give methane and resultant gold products. The processes are supported by the following independent experiments using $ReH(CO)_5$: Methane and bimetallic compound $(Ph_3P)AuRe(CO)_5$ were smoothly formed by the reaction of $AuMe(PPh_3)$ with $ReH(CO)_5$. Reaction of $AuMe(PPh_3)$ with *cis*-$AuMe_2[OCH(CF_3)_2](PPh_3)$ gave $AuMe_3(PPh_3)$ and $Au[OCH(CF_3)_2](PPh_3)$, the latter being further converted to $(Ph_3P)AuRe(CO)_5$ with liberation of alcohol by the reaction with the hydride.

The smaller the p*K*a value of the hydride, the faster the reaction. In fact, the reaction of gold alkoxides with hydrides having p*K*a value less than 16 took place instantaneously even at -50 °C, while the reaction of $ReH(CO)_5$ with *cis*-$AuMe_2(OCH(CF_3)_2)(PPh_3)$ (**2a**) took for few hours at room temperature. On the other hand, the reactions of gold(I) alkoxides are faster than those of gold(III), reflecting higher basicity of gold(I) alkoxides. These trends suggest that the hydride of MHL_n is abstracted as a proton by the highly basic gold alkoxides.

In order to obtain further mechanistic insight of the reaction, the time-course of the reaction of *cis*-$AuMe_2[OCH(CF_3)_2](PPh_3)$ (**2a**) with $ReH(CO)_5$ was followed by GLC. Addition of an equimolar amount of triphenylphosphine lowered the initial rate approximately to the half. The retardation effect suggests the involvement of the dissociation of tertiary phosphine ligand prior to the rate-determining hydrogen abstraction process. Such a transition state may have highly polarized interaction between hydride and gold alkoxides, since the apparent reaction rate was larger in the polar solvent such as DMSO.

Another interesting feature of the reaction is the relative preference of paths 1 and 2. Thus the ratios of ethane to the total other methyl groups ($AuMe(PPh_3)$, MMe, methane and $AuMe_3(PPh_3)$), which were taken as an index of selectivity in the reductive elimination at intermediate **A**, are constant (2.1 and 11.5 for the reactions with $HRe(CO)_5$ and $WHCp(CO)_3$, respectively) regardless of reaction time, solvent, and concentration of the metal hydride. These results suggest that the subsequent reductive elimination process from the common intermediate **A** is very fast and non-ionic concerted one. Quantitative formation of ethane in the reactions of gold alkoxides with $CoH(CO)_4$, $MoHCp(CO)_3$, $MnH(CO)_5$, $WHCp(CO)_3$ and $WHCp(CO)_2(PPh_3)$ indicates the occurrence of selective reductive elimination of two methyl groups at Au-containing heterodinuclear intermediate **A**. Whereas the reactions with $ReH(CO)_5$ and $WHCp(CO)_2(PMe_3)$ gave a mixture of products including methane, alcohol, $AuMe_3(PPh_3)$, and MMe, which are considered to be derived from the competitive reductive elimination among methyls and transition metal moiety. The more electron rich transition metal tends to be reductively eliminated. Similar but selective alkyl transfer at the heterodinuclear organoplatinum complexes L_nRPt-ML_m giving RML_m has been reported by us.[8]

It is concluded that the condensation between gold alkoxide and transition metal hydride provides a convenient method making a heterobimetallic bond. The reductive elimination of ethane from the dimethyl(metal)gold(III) intermediate **A** takes place when the metal is more electron deficient, whereas alkyl transfer from gold to M (reductive elimination of Me and M at Au) becomes a preferred pathway when M is more electron rich. Such a trend is consistent with the previous report concerning selectivity in reductive elimination from $Au(^1R)(^2R)(^3R)L$ as well as theoretical calculations on d^8-organotransition metal complexes.[9] These results may model the selectivity and mobility of the surface alkyl groups on the heterogeneous catalysts.

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† Present address: Catalysis Research Center, Hokkaido University, Kita-ku, Sapporo, 060.

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