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Thermally-induced Production of Hydrogen by Dinuclear Rhodium(I) Complexes [1]

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There has been considerable recent interest in dinuclear isocyanide complexes in which direct metal–metal interactions are present [2–5]. The dinuclear isocyanide complexes exhibit unusual spectroscopic and chemical properties. Gray *et al.* reorted that a windmill-shaped complex, $[Rh_2(bridge)_4]^{2+}$ *1a* (bridge = 1,3-diisocyanopropane) produced hydrogen by 546 nm irradiation in an aqueous 12 *M* HCl solution [2b, e]. The following scheme has been proposed for the hydrogen production [1e, h].

$$\underset{1a}{[Rh_2(bridge)_4]^{2+}} + HCl \xrightarrow[12M\ HCl]{} \underset{2a}{\tfrac{1}{2}[Rh_2(bridge)_4Cl]_2^{4+}} + \tfrac{1}{2}H_2 \qquad (1)$$

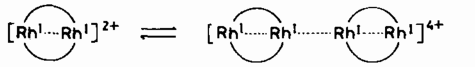
$$\underset{2a}{\tfrac{1}{2}[Rh_2(bridge)_4Cl]_2^{4+}} + HCl \xrightarrow[12M\ HCl]{} \underset{3a}{[Rh_2(bridge)_4Cl_2]^{2+}} + \tfrac{1}{2}H_2 \qquad (2)$$

This system is particularly interesting in connection with solar energy storage. It is now desired to examine the effect of altering the diisocyanide ligands. In this respect we synthesized structurally similar complexes, $[Rh_2(CYCLO\text{-}bridge)_4]^{2+}$ *1b* and $[Rh_2(Me\text{-}bridge)_4]^{2+}$ *1c* (CYCLO-bridge = meso-1,3-diisocyanocyclohexane, Me-bridge = meso-2,4-diisocyanopentane) [1]. The present communication describes the characterization of these complexes: oligomerization of the dinuclear species and evolution of hydrogen by thermal or photochemically accelerated process in the reaction with HCl. The results are compared with that of $[Rh_2(bridge)_4]^{2+}$.

TABLE I. Electronic Spectra of Rhodium(II) Complexes in MeOH.

Complex		λ_{max} (nm)	
		monomer	dimer
$[Rh_2(bridge)_4]^{2+}$	*1a*	555	778
$[Rh_2(CYCLO\text{-}bridge)_4]^{2+}$	*2a*	561	800
$[Rh_2(Me\text{-}Bridge)_4]^{2+}$	*3a*	556	827

Windmill-shaped isocyanide complexes (*1b* and *1c*) were obtained by the reaction of $[Rh(cod)Cl]_2$ with the bidentate isocyanide such as CYCLO-bridge or Me-bridge. The electronic absorption spectra of *1b* and *1c* are listed in Table I together with that of *1a****. The dimerization constant in methanol decreases in the order *1a* > *1b* > *1c* as judged from the absorption band of dimers near 800 nm (eqn. 3)†.



(3)

The molecular models suggest that the environment of the two inner rhodium atoms in the dimer species becomes more sterically crowded in the above-mentioned sequence. Thus the difference in dimerization constants arises from the steric hindrance of diisocyanide ligands.

When *1b* was treated with an aqueous 12 *M* HCl solution under dark conditions, hydrogen evolved readily together with formation of the oxidized blue species $[Rh_2(CYCLO\text{-}bridge)_4Cl]^{4+}$ *2b* (λ_{max} = 590 nm, ϵ/Rh_2 = 5.9 × 10^4), and then evolution of hydrogen proceeded slowly to give the final yellow product $[Rh_2(CYCLO\text{-}bridge)_4Cl_2]^{2+}$ *3b** (λ_{max} = 338 nm, ϵ/Rh_2 = 6.2 × 10^4) (Fig. 1, curve b). Evolution of hydrogen in the present dark reaction exceeded 0.5 in a molar ratio of $[H_2]/[Rh_2]$. If the reaction (eqn. 2) does not take place by a thermal energy, a ratio of $[H_2]/[Rh_2]$ for the dark reaction cannot be greater than 0.5**. The curve a shows that hydro-

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***Four coordinated ligands were abbreviated for clarity.

†The ϵ value of the dimer species was assumed to be similar.

*Elemental analyses were in agreement with the calculated values. Gray *et al.* determined the structure of yellow species, $[Rh_2(bridge)_4Cl_2]^{2+}$, by an X-ray crystal analysis (ref. 1g).

**The value of $[H_2]/[Rh_2]$ for $[Rh_2(bridge)_4]^{2+}$ is 0.19–0.42 under the dark reaction (ref. 2h).

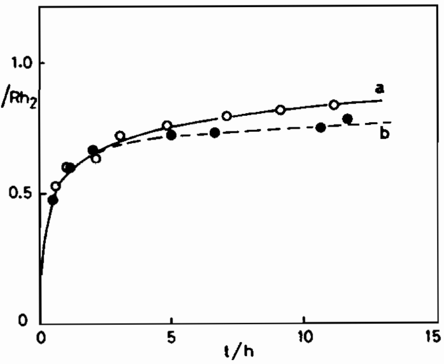
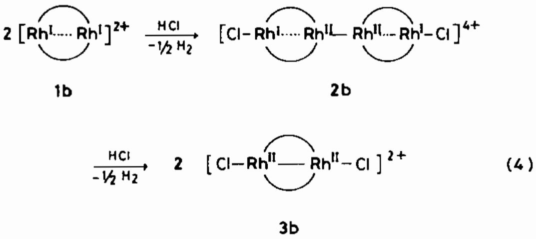


Fig. 1. Evolution of hydrogen by thermal and photo-assisted reaction of $[Rh_2(CYCLO\text{-bridge})_4][BPh_4]_2$ in a 12 *M* HCl solution at 45 °C. a (○) irradiated by a 100W W-lamp. b (●) under the dark reaction.

gen evolution is accelerated by the irradiation. However, photons are not essential for the evolution of hydrogen under our experimental condition. Apparent difference between *1a* and *1b* is that the second path (eqn. 2) in the latter complex proceeds even by a thermal energy.

This may be responsible for stabilization of the dimer species *2*, and shows that the inner Rh^{II}–Rh^{II} bond of $[Rh_2(CYCLO\text{-bridge})_4Cl]_2^{4+}$ *2b* is more labile than that of $[Rh_2(bridge)_4Cl]_2^{4+}$ *2a*, arising from facile dissociation of *2b* to *3b* by the steric hindrance of bulkier cyclohexane rings than propane moieties.



It is substantiated by the fact that the evolution of hydrogen in the preliminary reaction with *1c* having bulkier Me-bridge than CYCLO-bridge occurs more easily than other complexes (*1a*and *1b*)*.

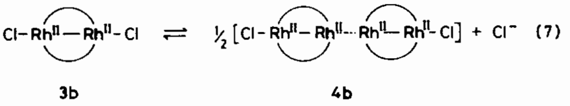
The reverse reaction (eqn. 5) was observed when *3b* was stored in the presence of 1 atm of H_2 at room temperature for several days. An equilibrium as shown in eqn. 5 exists and lies on a right-hand side under the experimental condition.

$$\underset{2b}{\tfrac{1}{2}[Rh_2(CYCLO\text{-bridge})_4Cl_2]_2^{4+}} + HCl \underset{\Delta}{\overset{\Delta\,(h\nu)}{\rightleftharpoons}} \underset{3b}{[Rh_2(CYCLO\text{-bridge})_4Cl_2]^{2+}} + \tfrac{1}{2}H_2 \qquad (5)$$

In an attempt to examine a possibility of a water splitting reaction by the final yellow complex *3b* (eqn. 6), the reaction of *3b* with H_2O was carried out.

$$\underset{3b}{[Rh_2(CYCLO\text{-bridge})_4Cl_2]_2^{4+}} + H_2O \rightarrow \underset{2b}{\tfrac{1}{2}[Rh_2(CYCLO\text{-bridge})_4Cl]_2^{4+}} + \tfrac{1}{2}H_2O_2\ (\tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O) + HCl \qquad (6)$$

The solution color changed from yellow to blue (λ_{max} = 590 nm, $\epsilon/Rh_2 \geqslant 2.6 \times 10^4$). The blue solution again turns back to yellow on radiation. Thus, the reaction is reversible. The precipitate obtained by the addition of methanol solution of $NaBPh_4$ to the blue solution is not *2b*, but is formulated as $Rh_4(CYCLO\text{-bridge})_8Cl_4(BPh_4)_4$ *4b* by elemental analysis. Neither H_2O_2 nor O_2 was produced through the color change. In addition, no production of hydrogen was observed when the aforementioned blue species *4b*, prepared freshly, was irradiated in an aqueous 12 *M* HCl solution. These results suggest that *4b* exists in a similar oxidation state to that of *3b*. The species *4b* may be tentatively assigned to a tetranuclear complex (eqn. 7)**.



The reaction in our system was ascertained to occur with thermal or photo-accelerated process. This is due to the fact that the thermal equilibrium of eqn. 5 lies on the right-hand side for $[Rh_2(CYCLO\text{-bridge})_4]^{2+}$ and $[Rh_2(Me\text{-bridge})_4]^{2+}$.

Finally, it is of interest to note that no hydrogen evolution occurred in the reaction of [Rh(C_6-

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*A relative ratio of hydrogen evolution between *2* and *3* was *ca.* 1.3.

**An accurate structure of *4b* remains unknown, but a blue color of *4b* can rule out a structure having a metal–metal σ bond *e.g.* $[Cl{-}Rh^{II}{-}Rh^{II}{-}Cl][BPh_4]_2$.

$H_{11}NC)_4]Cl$ with an aqueous HCl, suggesting an importance of dinuclear complexes of isocyanide. Further studies are now in progress.

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