

# Solid-State Photochemical *diag*–*lat* Isomerization of $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Re}(\text{CO})(\text{L})\text{X}_2$ on the Surface of Silica Gel

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Room-temperature visible illumination (200 W light source) of *diag*– $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Re}(\text{CO})(\text{L})\text{X}_2$  (R = H, alkyl; L = CO, P(OR)<sub>3</sub>; X = Br, I) adsorbed on silica gel results in isomerization of the complexes into the corresponding lateral isomers in good yield (typically >80%). For L = CO, the isomerization reactions occurred in the direction reverse to that found in solution in which *lat*-to-*diag* isomerization was observed. It was found that the ratio of diagonal to lateral isomers established on the surface of silica gel was influenced by both X and L, *viz.*  $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Re}(\text{CO})[\text{P}(\text{OR})_3]\text{Br}_2 > (\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Re}(\text{CO})_2\text{Br}_2 > (\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Re}(\text{CO})_2\text{I}_2$ . Chemical removal of surface hydroxyl groups with Me<sub>2</sub>SiCl<sub>2</sub> revealed that only a monolayer of the rhenium complex chemically adsorbed on the surface of the silica gel underwent isomerization. A mechanism to rationalize the role of the silica surface hydroxyl groups is described.

## Introduction

Compared to the development of synthetic chemistry in the solution state, synthetic chemistry employing solid-state reactivity has been less developed.<sup>1</sup> Indeed, a survey of the organometallic chemistry literature reveals that little exploration of the use of the solid phase in the synthesis of new molecules has been reported. From what has been reported, the reactions can be divided into three types.<sup>2</sup>

Firstly, solid-state reactions can occur within a solid. For example, a range of isomerization reactions have been carried out both thermally and photochemically in the solid-state. Reactions include nitrito to nitro isomerization<sup>3</sup> and *cis* to *trans* isomerization of chromium,<sup>4</sup> ruthenium,<sup>5</sup> platinum,<sup>6</sup> and rhenium<sup>7</sup> complexes.

Second, reactions can occur *between* solid particles. Here the intimacy and method of interaction (heating, shaking, grinding, *etc.*) become critical and particle size typically plays a dominant role in determining the reaction rate. This methodology has been exploited in organic chemistry<sup>1</sup> and materials science<sup>8</sup> but appears

to be little developed in the synthesis of organometallic compounds.

Finally, the surfaces of solids can be used as reagents for carrying out reactions. Thus, reagents can be added to a surface and the surface–reagent interaction used to induce reactivity such that the reagent is converted into a product which can be extracted from the surface in a later step. In these reactions the product is formed in a solid-state reaction and is to be differentiated from the use of the heterogeneous complexes to bring about reactions in the solution phase.<sup>9,10</sup> Studies of surface–organometallic complexes have been directed at the production of well-controlled heterogeneous materials, e.g. Mo(CO)<sub>n</sub> on a range of surfaces,<sup>11</sup> for use in gas- and liquid-phase catalytic reactions.<sup>12</sup> The use of the surface as a reagent for the synthesis of new organometallic complexes has been less extensively exploited.<sup>7a,13</sup>

In this publication we wish to report on a novel example of the third type of solid-state reaction. We<sup>7a</sup> and others<sup>14</sup> have reported that *lat*– $(\eta^5\text{-C}_5\text{R}_4\text{R}')\text{Re}(\text{CO})_2\text{X}_2$  isomerizes to *diag*– $(\eta^5\text{-C}_5\text{R}_4\text{R}')\text{Re}(\text{CO})_2\text{X}_2$  (R = H, Me; R' = H, alkyl group, X = halogen) in the solution phase. Herein we report that surface-supported  $(\eta^5\text{-}$

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(1) (a) Toda, F. *Acc. Chem. Res.* **1995**, *28*, 480. (b) West, A. *Solid State Chemistry and its Applications*; Wiley: Chichester, U.K., 1994.

(2) Reactions in matrices, e.g. matrix isomerization reactions, have been excluded from this discussion since the matrix molecules/atoms can be regarded as frozen “solvent” molecules.

(3) (a) Boldyreva, E. V. *Mol. Cryst. Liq. Cryst.* **1994**, *242*, 17. (b) Grenthe, I.; Nordin, E. *Inorg. Chem.* **1979**, *18*, 1869. (c) Dulepov, V. E.; Boldyreva, E. V. *React. Kinet. Catal. Lett.* **1994**, *53*, 289. (d) Masciocchi, N.; Kolyshev, A.; Dulepov, V.; Boldyreva, E.; Sironi, A. *Inorg. Chem.* **1994**, *33*, 2579.

(4) Sedova, G. N.; Demchenko, L. N. *Zh. Neorg. Khim.* **1981**, *26*, 435.

(5) (a) Katsuki, K.; Ooyama, Y.; Okamoto, M.; Yamamoto, Y. *Inorg. Chim. Acta* **1994**, *217*, 181. (b) Krassowski, W. D.; Lemay, H. E., Jr.; Nelson, J. H. *Inorg. Chem.* **1988**, *27*, 4307.

(6) (a) Macdonald, F. M.; Sadler, P. J. *Polyhedron* **1991**, *10*, 1443. (b) Louw, W. J. *Inorg. Chem.* **1977**, *16*, 2147. (c) Favez, R.; Roulet, R.; Pinkerton, A. A.; Schwarzenbach, D. *Inorg. Chem.* **1980**, *19*, 1356.

(7) (a) Cheng, L.; Coville, N. J. *Organometallics* **1996**, *15*, 867. (b) Palmer, B. J.; Becalska, A.; Hader, R.; Hill, R. H. *Polyhedron* **1991**, *10*, 877.

(8) (a) Moore, J. J.; Feng, H. J. *Prog. Mater. Sci.* **1995**, *39*, 243. (b) Thadhani, N. N. *Prog. Mater. Sci.* **1993**, *37*, 117.

(9) Gates, B. C. *J. Mol. Catal.* **1994**, *86*, 95.

(10) (a) Mayo, P.; Nakamura, A.; Tsang, P. W. K.; Wong, K. S. *J. Am. Chem. Soc.* **1982**, *104*, 6824. (b) Mayo, P.; Ramnath, N. *Can. J. Chem.* **1986**, *64*, 1293.

(11) (a) Reddy, K. P.; Brown, T. L. *J. Am. Chem. Soc.* **1995**, *117*, 2845. (b) Ang, H. G.; Chan, K. S.; Chuah, G. K.; Jaenicke, S.; Neo, S. K. *J. Chem. Soc., Dalton Trans.* **1995**, 3753. (c) Nakamura, R.; Pioch, D.; Bowman, G.; Burwell, R. L. *J. Catal.* **1985**, *93*, 388, 399. (d) Brenner, A.; Hucul, D. A.; Hardwick, S. J. *Inorg. Chem.* **1979**, *18*, 1487. (e) Gonzales, P. N.; Villa Garcia, M. A.; Brenner, A. *J. Catal.* **1989**, *118*, 360.

(12) *Chem. Rev.* **1995**, *95*. Issue 3 of this volume contains numerous articles on solid-state reactions.

(13) (a) Roberto, D.; Cariati, E.; Ugo, R.; Psaro, R. *Inorg. Chem.* **1996**, *35*, 2311. (b) Roberto, D.; Cariati, E.; Psaro, R.; Ugo, R. *J. Organomet. Chem.* **1995**, *488*, 109. (c) Theolier, A.; Smith, A. K.; Leconte, M.; Basset, J. M.; Zanderighi, G. M.; Psaro, R.; Ugo, R. *J. Organomet. Chem.* **1980**, *191*, 415.

(14) (a) King, R. B.; Reimann, R. H. *Inorg. Chem.* **1976**, *12*, 183. (b) Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53. (c) Hill, R. H.; Palmer, B. J. *Organometallics* **1989**, *8*, 1651.

$C_5H_4R)Re(CO)(L)X_2$  ( $L = CO$ , phosphite) undergoes a solid-state photochemical isomerization reaction in the direction reverse to that observed in the solution phase, a reaction which indicates the influence of the surface as a ligand in the overall reaction. This reaction provides for a facile synthesis of *lat*-( $\eta^5$ - $C_5H_4R)Re(CO)(L)X_2$ .

### Experimental Section

The diagonal and lateral ( $\eta^5$ - $C_5H_4R)Re(CO)(L)Br_2$  ( $R = Me$ , Et,  $t$ Bu,  $Si(CH_3)_3$ ,  $L = CO$ ;  $R = H$ ,  $L = CO$ ,  $P(OMe)_3$ ,  $P(OPh)_3$ ) complexes were prepared by the literature methods.<sup>7a,14a</sup> Kieselgel PF<sub>254</sub> (Merck) silica gel for preparative thin-layer chromatography was used as the support for most of the reactions. Dichlorodimethylsilane (98%) was obtained from Merck. Solvents were dried by conventional methods, distilled under nitrogen, and used immediately. Irradiation was carried out with two 200 W incandescent lamps. The BET surface area measurements of the inorganic solids were performed using the  $N_2$  adsorption method with classical gas-phase surface area equipment constructed in our department.<sup>15</sup> Melting points were recorded on a Kofler hot stage melting point apparatus. Infrared spectra were measured on a Midac FTIR spectrometer, usually in KBr cells (solutions). NMR spectra were measured on a Bruker AC200 spectrometer operating at 200 MHz. Microanalyses were carried out at the CSIR, Pretoria, South Africa.

**Irradiation Experiments.** Experiments were performed as follows. Pyrex cylinders (22 mm  $\times$  90 mm) were used as reactors and were loaded with *diag*- or *lat*-( $\eta^5$ - $C_5H_4R)Re(CO)(L)X_2$  (0.038 mmol) dissolved in  $CH_2Cl_2$  (3 mL). Silica gel (300 mg) was added to the reactor, the reagents were well-mixed, and the  $CH_2Cl_2$  was removed under vacuum. The cylinders were sealed under nitrogen (atmospheric pressure) and rotated with a motor (8 rpm) with the cylinder axis in a horizontal position. Two 200 W incandescent lamps ( $\lambda > 370$  nm) were located 30 cm from the cylinder, and the whole experimental apparatus was set up in a ventilated fume hood; this ensured minimum local heating from the lamp at the sample.<sup>16</sup> A thermometer placed next to the sample cylinder indicated that the temperature of the reaction vessel never exceeded 25 °C. A control experiment was performed in the dark by completely wrapping a cylinder, containing the silica-supported *diag*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2Br_2$ , in aluminum foil. After completion of the irradiation, the products were extracted from the surface of the silica gel with  $CH_2Cl_2$ , separated on a silica gel column ( $CH_2Cl_2$ /hexane), weighed, and identified by IR and NMR spectroscopy.

The photochemical isomerization reaction of the pure amorphous solid *diag*- or *lat*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2Br_2$  was carried out in the same manner as described above. The irradiation of *diag*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2Br_2$  on other inorganic solids was also performed in the same way as described above, except that two or more Pyrex cylinders were sometimes used in order to irradiate the large quantities of material required in the study.

**Syntheses of *diag*- and *lat*-( $\eta^5$ - $C_5H_4Me)Re(CO)[P(OPh)_3]Br_2$ .** A solution of *diag*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2Br_2$  (100 mg, 0.208 mmol) and  $P(OPh)_3$  (212 mg, 0.683 mmol) in toluene (25 mL) was refluxed under  $N_2$  for 20 h. IR spectra indicated that all the starting material had reacted. After solvent removal under reduced pressure, the red residue was dissolved in dichloromethane and chromatographed on a silica gel column prepared in hexane. Successive elution with dichloromethane/hexane (1:1) and dichloromethane gave *diag*-( $\eta^5$ - $C_5H_4Me)Re(CO)[P(OPh)_3]Br_2$  (48 mg, 30% yield) from a red band and *lat*-( $\eta^5$ -

$C_5H_4Me)Re(CO)[P(OPh)_3]Br_2$  (92 mg, 58% yield) from a brown band, respectively.

**Syntheses of *diag*- and *lat*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2I_2$ .** To a solution of ( $\eta^5$ - $C_5H_4Me)Re(CO)_3$  (730 mg, 2.09 mmol) in 50 mL of dimethyl sulfoxide, a solution of  $I_2$  (530 mg, 2.09 mmol) in 20 mL of dimethyl sulfoxide was added dropwise. After the reaction mixture was stirred for an additional 1.0 h at room temperature, the reaction was quenched by adding 100 mL of water at 25 °C. The resulting brown precipitate, which contained unreacted ( $\eta^5$ - $C_5H_4Me)Re(CO)_3$  and both isomers of ( $\eta^5$ - $C_5H_4Me)Re(CO)_2I_2$ , was filtered and dried at 25 °C (0.1 mmHg). This solid was dissolved in dichloromethane and chromatographed on a silica gel column prepared in hexane. Successful elution with hexane, hexane/dichloromethane (1:1), and dichloromethane gave unreacted ( $\eta^5$ - $C_5H_4Me)Re(CO)_3$  (350 mg, 48% recovery), *diag*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2I_2$  (245 mg, 20% conversion, 39% yield) from a red band, and *lat*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2I_2$  (106 mg, 9% conversion, 17% yield) from a brown band, respectively.

**Syntheses of *diag*- and *lat*-( $\eta^5$ - $C_5H_4^iPr)Re(CO)_2Br_2$ .** A solution of  $Br_2$  (136 mg, 0.85 mmol) in 2 mL of trifluoroacetic acid was added dropwise at 25 °C to a solution of ( $\eta^5$ - $C_5H_4^iPr)Re(CO)_3$  (304 mg, 0.81 mmol) in 3 mL of trifluoroacetic acid. After the reaction mixture was stirred for an additional 1.0 h at room temperature, the reaction was quenched by pouring the mixture into 100 mL of water at 25 °C. The resulting brown precipitate, which contained unreacted ( $\eta^5$ - $C_5H_4^iPr)Re(CO)_3$  and both isomers of ( $\eta^5$ - $C_5H_4^iPr)Re(CO)_2Br_2$ , was filtered and dried at 25 °C (0.1 mmHg). This solid was dissolved in dichloromethane and chromatographed on a silica gel column prepared in hexane. Successive elution with hexane, hexane/dichloromethane (1:1), and dichloromethane gave unreacted ( $\eta^5$ - $C_5H_4^iPr)Re(CO)_3$  (171 mg, 56% recovery), *diag*-( $\eta^5$ - $C_5H_4^iPr)Re(CO)_2Br_2$  (66 mg, 16% conversion, 37% yield) from a red band, and *lat*-( $\eta^5$ - $C_5H_4^iPr)Re(CO)_2Br_2$  (60 mg, 12% conversion, 33% yield) from a brown band, respectively.

**Syntheses of *diag*- and *lat*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2BrI$ .** (i) A solution of *diag*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2Br_2$  (57 mg, 0.118 mmol) and *diag*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2I_2$  (68 mg, 0.118 mmol) in benzene (25 mL) was refluxed under nitrogen for 20 h. After solvent removal with a rotary evaporator, the red solid was dissolved in dichloromethane and chromatographed on a silica gel column (1.5 cm  $\times$  60 cm) prepared in hexane. Careful elution with hexane/dichloromethane (4:1) and hexane/dichloromethane (1:1) gave *diag*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2I_2$  (35.8 mg, 53% recovery), *diag*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2BrI$  (48.5 mg, 39% conversion, 67% yield), *diag*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2Br_2$  (18.0 mg, 32% recovery), *lat*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2I_2$  (2.4 mg, 1.8% conversion, 3.0% yield), *lat*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2BrI$  (7.1 mg, 5.7% conversion, 9.8% yield), and *lat*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2Br_2$  (8.9 mg, 7.8% conversion, 13% yield).

(ii) Silica gel (900 mg) was added to a solution of NaI (17.1 mg, 0.114 mmol) in water (2 mL). The slurry was well stirred and dried in an oven at 120 °C. This pretreated silica gel was then added to a solution of *diag*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2Br_2$  (55 mg, 0.114 mmol) in dichloromethane (3 mL), the reagents were well mixed, and the  $CH_2Cl_2$  was removed under vacuum. The reaction mixture was placed into three Pyrex cylinders (22 mm  $\times$  90 mm) and sealed. After irradiation with two 200 W incandescent lamps at room temperature for 48 h, the reaction products were extracted from silica gel with dichloromethane and chromatographed on a silica gel column prepared in hexane. Elution with hexane/dichloromethane (1:1) gave first a mixture of *diag*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2I_2$ , *diag*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2BrI$ , and *diag*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2Br_2$  (14.7 mg, 24% yield) and then *lat*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2I_2$  (7.5 mg, 11% yield), *lat*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2BrI$  (12.0 mg, 20% yield), and *lat*-( $\eta^5$ - $C_5H_4Me)Re(CO)_2Br_2$  (12.0 mg, 22% yield), respectively.

All new complexes were characterized by elemental analysis and by IR and NMR spectroscopy (Table 1).

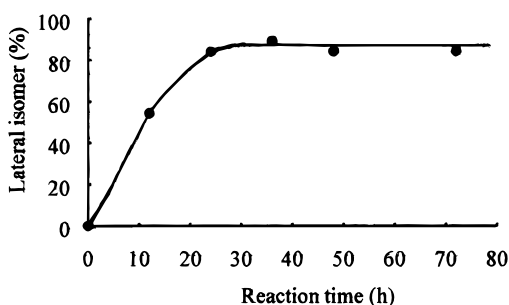
(15) Duvenhage, D. J. Ph.D. Thesis, University of the Witwatersrand, Johannesburg, South Africa, 1993.

(16) Abdel-Malik, M. M.; De Mayo, P. *Can. J. Chem.* **1984**, *62*, 1275.

**Table 1. Spectroscopic and Analytical Data for ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)Re(CO)(L)X<sub>2</sub> Complexes**

compd	mp (°C)	$\nu_{\text{co}}^a$ (cm <sup>-1</sup> )	<sup>1</sup> H NMR <sup>b</sup> (ppm)			anal (%)	
			Cp ring	R	L	C	H
<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO)[P(OPh) <sub>3</sub> ] <sub>2</sub> Br <sub>2</sub>	164–166	1988	4.53 (t, 2H), 4.65 (t, 2H) <sup>c</sup>	1.64 (s, 3H) <sup>c</sup>	6.88–7.56 (m, 15H) <sup>c</sup>	calcd 39.33 found 39.39	2.90 2.68
<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> <sup>i</sup> Pr)Re(CO) <sub>2</sub> Br <sub>2</sub>	112–114	1997, 2062	5.38 (t, 2H) 5.71 (t, 2H)	1.29 (d, 6H), 2.83 (m, 1H)		calcd 23.59 found 23.35	2.18 1.88
<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> I <sub>2</sub>	142–144	1982, 2048	5.29 (t, 2H), 5.71 (t, 2H)	2.44 (s, 3H)		calcd 16.71 found 16.54	1.23 1.04
<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> BrI	125–127	1989, 2054	5.52 (t, 2H), 5.70 (t, 2H)	2.36 (s, 3H)		calcd 18.19 found 18.08	1.34 1.15
<i>lat</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO)[P(OPh) <sub>3</sub> ] <sub>2</sub> Br <sub>2</sub>	183–185	1959	4.62 (d, 1H), 4.72 (d, 1H), 4.77 (d, 1H), 5.07 (d, 1H) <sup>c</sup>	1.73 (s, 3H) <sup>c</sup>	6.75–7.55 (m, 15H) <sup>c</sup>	calcd 39.33 found 39.38	2.90 2.69
<i>lat</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> <sup>i</sup> Pr)Re(CO) <sub>2</sub> Br <sub>2</sub>	127–129	1978, 2054	5.88 (d, 2H), 5.92 (d, 2H)	1.28 (d, 6H), 2.88 (m, 1H)		calcd 23.59 found 23.36	2.18 1.92
<i>lat</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> I <sub>2</sub>	127–129	1972, 2040	5.78 (m, 4H)	2.58 (s, 3H)		calcd 16.71 found 16.54	1.23 1.04
<i>lat</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> BrI	135–137	1974, 2043	5.76 (m, 2H), 5.81 (m, 1H), 5.88 (m, 1H)	2.39 (s, 3H)		calcd 18.19 found 17.95	1.34 1.14

<sup>a</sup> Recorded in CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> Recorded in CDCl<sub>3</sub>, relative to TMS: s, singlet; d, doublet; t, triplet; m, multiplet. <sup>c</sup> Recorded in C<sub>6</sub>D<sub>6</sub>.

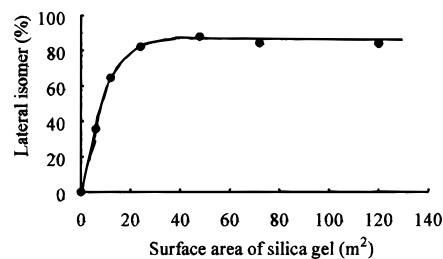


**Figure 1.** Solid-state photochemical isomerization reaction of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> after different times.

## Results and Discussion

*diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> was loaded onto silica as described in the Experimental Section and irradiated with two 200 W lamps. A series of experiments were performed in which the reaction was terminated after different reaction times (1–72 h; Figure 1). The products were extracted from the silica (>85%), separated on a chromatographic column, weighed, and analyzed by IR and NMR spectroscopy. The data indicated that after 24 h a photostationary state of the isomers had formed with a [*lat*]/[*diag*] ratio of ~7. Thus, an isomerization reaction takes place on irradiation of silica in the solid-state which favors the lateral isomer. This ratio is different from that achieved in the thermal solid-state isomerization reaction.<sup>7a</sup> Further, Hill and co-workers have reported that photoisomerization of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Re(CO)<sub>2</sub>Br<sub>2</sub> on Si(111) at 77 K gave a reaction in which the diagonal isomer was formed from the lateral isomer.<sup>7b</sup> We have further observed that irradiation of either pure amorphous solid *diag*- or *lat*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> in the absence of silica resulted in no photoisomerization activity.

A series of experiments were performed using a varying *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub>/SiO<sub>2</sub> ratio achieved by changing the amount of SiO<sub>2</sub>. BET surface areas for the loaded and unloaded SiO<sub>2</sub> samples were determined, and a plot of the SiO<sub>2</sub> surface area against the percentage of lateral isomer formed (after 48 h reaction) is shown in Figure 2. Clearly a photostationary state is established when the SiO<sub>2</sub> surface area is >29 m<sup>2</sup> for 0.038 mmol of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub>. This corresponds to less than a monolayer coverage of the SiO<sub>2</sub><sup>17</sup>



**Figure 2.** Solid-state photochemical isomerization reaction of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> as a function of silica gel surface area.

and suggests that only ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> in physical contact with the SiO<sub>2</sub> will undergo the photoisomerization reaction. A plot of SiO<sub>2</sub> surface area against the percentage of lateral isomer formed for *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)Re(CO)<sub>2</sub>Br<sub>2</sub> (R = Me, <sup>i</sup>Pr) gave similar results, suggesting that the substituents on the cyclopentadienyl ring ligand had little effect on the solid-state photochemical isomerization reaction. This result was further confirmed by the similar isomerization yields obtained for ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)Re(CO)<sub>2</sub>Br<sub>2</sub> (R = H, Me, Et, <sup>i</sup>Pr, <sup>t</sup>Bu, Si(CH<sub>3</sub>)<sub>3</sub>) at a fixed complex loading (Table 2). All the above reactions were terminated after 48 h; by this time a photostationary state had been established, as revealed by studying the isomerization reactions of both the lateral and diagonal isomers. The photostationary ratio [*lat*]/[*diag*] increased as follows: ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)(L)Br<sub>2</sub> > ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> > ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>I<sub>2</sub> (Table 2). As can be seen from Table 2, most of the product was extractable from silica (generally 90–95%) and suggests that the method provides a facile procedure for isomerization of the rhenium complexes.

In contrast, the solution isomerization reaction for ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)Re(CO)<sub>2</sub>Br<sub>2</sub> (R = H, Me, Et, <sup>i</sup>Pr, <sup>t</sup>Bu, Si(CH<sub>3</sub>)<sub>3</sub>) has been reported<sup>7a</sup> and indicated that the diagonal isomer was the dominant isomer formed in the equilibrium reaction. We have now also established that *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)[P(OPh)<sub>3</sub>]<sub>2</sub>Br<sub>2</sub> isomerizes completely into the lateral isomer in CHCl<sub>3</sub> after several days at

(17) The "footprint"<sup>18</sup> of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> was calculated from its X-ray structure<sup>19</sup> as 22.5 Å<sup>2</sup>. Thus, 0.038 mmol of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> will cover an area of 5.2 m<sup>2</sup>.

(18) Matsuishi, T.; Shimada, T.; Morihara, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 748.

(19) Boeyens, J. C. A.; Cheng, L.; Coville, N. J.; Levendis, D. C.; McIntosh, K. S. Manuscript in preparation.

**Table 2. Solid-State Photochemical *diag*-*lat* Isomerization of ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R) Re(CO)(L)X<sub>2</sub> on the Surface of Silica Gel<sup>a</sup>**

entry no	complex	<i>diag</i> (%) <sup>b</sup>	<i>lat</i> (%) <sup>b</sup>	total recovery (%) <sup>c</sup>
1	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Re(CO) <sub>2</sub> Br <sub>2</sub>	23.4	76.6	86.5
2	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> Br <sub>2</sub>	15.7	84.3	94.0
3	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Et)Re(CO) <sub>2</sub> Br <sub>2</sub>	12.2	87.8	87.2
4	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> <sup>i</sup> Pr)Re(CO) <sub>2</sub> Br <sub>2</sub>	10.1	89.9	76.7 <sup>d</sup>
5	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> <sup>t</sup> Bu)Re(CO) <sub>2</sub> Br <sub>2</sub>	10.3	89.7	87.9
6	<i>diag</i> -[ $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Si(CH <sub>3</sub> ) <sub>3</sub> ]Re(CO) <sub>2</sub> Br <sub>2</sub>	18.6	81.4	89.3
7	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> I <sub>2</sub>	71.1	28.9	93.2
8	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Re(CO)[P(OMe) <sub>3</sub> ]Br <sub>2</sub>	0.0	100.0	79.4
9	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Re(CO)[P(OPh) <sub>3</sub> ]Br <sub>2</sub>	0.0	100.0	84.2
10	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO)[P(OPh) <sub>3</sub> ]Br <sub>2</sub>	0.0	100.0	82.4
11	<i>lat</i> -( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Re(CO) <sub>2</sub> Br <sub>2</sub>	11.7	88.3	91.6
12	<i>lat</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> Br <sub>2</sub>	11.0	89.0	89.1
13	<i>lat</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Et)Re(CO) <sub>2</sub> Br <sub>2</sub>	15.9	84.1	87.2
14	<i>lat</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> <sup>i</sup> Pr)Re(CO) <sub>2</sub> Br <sub>2</sub>	13.7	86.3	72.0
15	<i>lat</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> <sup>t</sup> Bu)Re(CO) <sub>2</sub> Br <sub>2</sub>	13.3	86.7	98.5
16	<i>lat</i> -[ $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Si(CH <sub>3</sub> ) <sub>3</sub> ]Re(CO) <sub>2</sub> Br <sub>2</sub>	11.5	88.5	89.3
17	<i>lat</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO)[P(OPh) <sub>3</sub> ]Br <sub>2</sub>	0.0	100.0	90.3

<sup>a</sup> Conditions: ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)Re(CO)(L)X<sub>2</sub>, 0.038 mmol; silica gel, 300 mg; reaction time, 48 h; room temperature. <sup>b</sup> Isolated yields. <sup>c</sup> Based on starting materials used. <sup>d</sup> Silica gel 200 mg.

**Table 3. Solid-State Photochemical *diag*-*lat* Isomerization of ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me) Re(CO)<sub>2</sub>Br<sub>2</sub> on Various Inorganic Solids<sup>a</sup>**

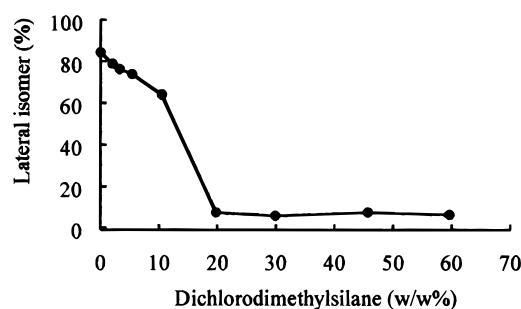
entry no.	inorganic solid	surface		<i>diag</i> (%)	<i>lat</i> (%)	total recovery (%)
		area (m <sup>2</sup> /g)	amt (mg)			
1	ZnO	29.7	300	99.4	0.6	90.2
2	ZnO	29.7	2400	99.0	1.0	29.0
3	CaSO <sub>4</sub>	28.1	300	94.3	5.7	95.6
4	CaSO <sub>4</sub>	28.1	2400	92.0	8.0	68.3
5	Al <sub>2</sub> O <sub>3</sub> (neutral)		300	15.8	84.2	10.4
6	MgO	62.5	300	83.6	16.4	33.3
7	TiO <sub>2</sub>	108	300	66.9	33.1	69.4
8	TiO <sub>2</sub>	108	750	10.0	90.0	6.0
9	zeolite <sup>b</sup>	271	300	56.3	43.7	95.1
10	Nil			100.0	0.0	100.0
11	amorphous SiO <sub>2</sub>	258	300	9.5	90.5	80.9
12	Silica gel	240	300	15.7	84.3	94.0

<sup>a</sup> Conditions: *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub>, 0.038 mmol; reaction time, 48 h; room temperature. <sup>b</sup> HZSM-5.

room temperature. The isomerization reaction was much slower (>2 weeks) when benzene was used as solvent. In contrast, *lat*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)Re(CO)<sub>2</sub>I<sub>2</sub> (R = H, Me) converted (>90%) into the diagonal isomer after several hours at room temperature in CHCl<sub>3</sub>; the *diag* to *lat* isomerization did not occur under these conditions.

The *diag*-*lat* isomerization reaction of ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)-Re(CO)<sub>2</sub>Br<sub>2</sub> was also performed in the dark (no reaction) and by irradiation with sunlight and UV light. The latter reactions also yielded photoisomerized products with conversions little different from that obtained with the 200 W lamp. This suggests that the solid-state isomerization reactions on the surface of silica gel can be achieved by a range of wavelengths.

Other inorganic solids were also tested as potential supports for the photoisomerization reaction of ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub>, and the data are shown in Table 3. In general only the silica supports gave good conversions to the lateral isomer. ZnO, MgO, Al<sub>2</sub>O<sub>3</sub>, and CaSO<sub>4</sub> were found to be poor supports; they either caused complex decomposition or resulted in low conversions. Increasing the product by increasing the amount (surface area) of the supports which gave poor results was also found to be unsuccessful. It should be pointed out that the quality of the surface coating, which depends on the preparation method used, could also perturb the efficiency of the photochemical isomerization reaction.

**Figure 3.** Solid-state photochemical isomerization reaction of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> on silica gel containing different amounts of surface hydroxyl groups.

**Reaction Mechanism.** The solid-state photochemical isomerization reactions of ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> were carried out on a series of silica gels containing different amounts of surface hydroxyl groups (obtained by pretreatment of the surface with different amounts of dichlorodimethylsilane). The results showed that the yield of isomerized product increased with the amount of surface hydroxyl groups (Figure 3). Clearly, the surface hydroxyl groups play a crucial role in the solid-state photochemical isomerization reaction.

The solid-state photochemical isomerization reactions of an equimolar mixture of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(CO)-[P(OMe)<sub>3</sub>]Br<sub>2</sub> and *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)[P(OPh)<sub>3</sub>]Br<sub>2</sub> were carried out, and no intermolecular exchange between P(OMe)<sub>3</sub> and P(OPh)<sub>3</sub> ligands was found (Table 4). The intermolecular exchange between CO and P(OPh)<sub>3</sub> ligands was also not observed for the solid-state isomerization reaction of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> in the presence of excess P(OPh)<sub>3</sub> ligand (Table 4). This suggests that the solid-state photochemical *diag*-*lat* isomerization reactions of ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)Re(CO)(L)X<sub>2</sub> do not proceed via intermolecular exchange of CO, L, or cyclopentadienyl ligands.

The solid-state photochemical isomerization reaction of an equimolar mixture of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> and *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>I<sub>2</sub> was carried out, and a mixture of dibromide and diiodide complexes, as well as 48% ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>BrI (Table 1), was formed in the reaction (Table 4). Facile exchange of Br and I (ions, free radicals) is possible on photolysis. This was also indicated by the formation of molecular iodine on

**Table 4. Solid-State Photochemical Isomerization of Mixed Rhenium Complexes<sup>a</sup>**

entry no	reacn mixture	diag (%)	lat (%)	total recovery (%)
1	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> Br <sub>2</sub> <i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> I <sub>2</sub>	38.6 <sup>b</sup>	(A) 19.6 <sup>c</sup> (B) 48.0 <sup>c</sup> (C) 32.4 <sup>c</sup>	82.2
2 <sup>b</sup>	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> Br <sub>2</sub> <i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> I <sub>2</sub>	(H) 29.7 <sup>j</sup> (I) 40.2 <sup>j</sup> (J) 14.9 <sup>j</sup>	(A) 2.0 <sup>c</sup> (B) 5.9 <sup>c</sup> (C) 7.4 <sup>c</sup>	96.6
3 <sup>i</sup>	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> Br <sub>2</sub> <i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> I <sub>2</sub>	(H) 34.1 <sup>j</sup> (I) 0.0 <sup>j</sup> (J) 57.3 <sup>j</sup>	(A) 1.3 <sup>c</sup> (B) 1.4 <sup>c</sup> (C) 6.0 <sup>c</sup>	72.6
4	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> Br <sub>2</sub> 20-fold NaI	14.2 <sup>e</sup>	85.8 <sup>e</sup>	84.7
5	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> Br <sub>2</sub> 20-fold NaCl	70.2 <sup>f</sup>	29.8 <sup>f</sup>	78.1
6	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> I <sub>2</sub> 20-fold NaCl	15.0 <sup>e</sup>	85.0 <sup>e</sup>	90.5 <sup>e</sup>
7	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> Br <sub>2</sub> 5-fold P(OPh) <sub>3</sub>	0.0	(F) 45.3 <sup>g</sup> (G) 54.7 <sup>g</sup>	75.4
8	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Re(CO)[P(OMe) <sub>3</sub> ]Br <sub>2</sub> <i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO)[P(OPh) <sub>3</sub> ]Br <sub>2</sub>			

<sup>a</sup> Two equimolar complexes were mixed together and coadsorbed on silica in the impregnation method. Reaction conditions were the same as those recorded in Table 2. <sup>b</sup> The mixture consisted of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub>, *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>BrI, and *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>I<sub>2</sub>. <sup>c</sup> Legend: (A) *lat*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>I<sub>2</sub>; (B) *lat*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>BrI; (C) *lat*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub>. <sup>d</sup> Legend: (D) *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>I<sub>2</sub>; (E) *lat*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>I<sub>2</sub>. <sup>e</sup> Only ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> was found in the product. <sup>f</sup> Only ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>I<sub>2</sub> was found in the product. <sup>g</sup> Legend: (F) *lat*-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(CO)[P(OMe)<sub>3</sub>]Br<sub>2</sub>; (G) *lat*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)[P(OPh)<sub>3</sub>]Br<sub>2</sub>. <sup>h</sup> The complexes were refluxed in the dark in benzene for 20 h without silica gel. <sup>i</sup> Silica gel was treated with 30% dichlorodimethylsilane. <sup>j</sup> Legend: (H) *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>I<sub>2</sub>; (I) *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>BrI; (J) *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub>.

**Table 5. Solid-State Photochemical Isomerization in the Presence of a Free-Radical Scavenger<sup>a</sup>**

entry no.	complex	diag (%)	lat (%)	total recovery (%)
1	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> Br <sub>2</sub> + equimolar NaI	31.8 <sup>b</sup>	(A) 23.8, <sup>c</sup> (B) 38.1 <sup>c</sup> (C) 38.1 <sup>c</sup>	76.7
2	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> Br <sub>2</sub> + 3-fold galvinoxyl	78.3	21.7	83.1
3	<i>diag</i> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)Re(CO) <sub>2</sub> Br <sub>2</sub> + equimolar NaI + 3-fold galvinoxyl	81.2 <sup>b</sup>	(A) 1.1, <sup>c</sup> (B) 6.1, <sup>c</sup> (C) 11.6 <sup>c</sup>	90.2

<sup>a</sup> Reaction conditions were the same as those recorded in Table 2. <sup>b</sup> The mixture of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub>, *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>BrI, and *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>I<sub>2</sub>. <sup>c</sup> Legend: (A) *lat*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>I<sub>2</sub>; (B) *lat*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>BrI; (C) *lat*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub>.

irradiation of silica-supported *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>I<sub>2</sub>.<sup>20</sup> Irradiation of a mixture of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> and excess NaI on SiO<sub>2</sub> gave exclusively a photostationary mixture of *diag*- and *lat*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>I<sub>2</sub> (Table 4). No halogen exchange between NaCl and *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>X<sub>2</sub> (X = Br, I) took place under the irradiation conditions. This may be related to the ease of formation of the halogen radical X.<sup>21</sup>

Further experiments were performed to correlate solid-state photochemical isomerization reactions with a halogen dissociation–association reaction. The solid-state photochemical isomerization reaction of an equimolar mixture of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> and *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>I<sub>2</sub> was carried out on a completely dehydroxylated surface of silica gel. Neither isomerization activity nor any Br and I exchange was detected (Table 4). The solid-state photochemical isomerization reaction of an equimolar mixture of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> and NaI in the presence of the free-radical scavenger galvinoxyl was also carried out, and it was observed that galvinoxyl greatly suppressed both Br and I ligand exchange and the isomerization reaction (Table 5). Because the photochemical reactions were carried out in the solid-state and not in solution, the role of galvinoxyl is not completely clear. It is possible that

competitive light absorption by galvinoxyl or surface occupation by galvinoxyl molecules reduced the efficiency of the photochemical reactions. However, the results clearly suggest that a close relationship exists between the halogen dissociation–association reaction and the solid-state photochemical isomerization reaction.

The Br and I ligand exchange was also observed when an equimolar mixture of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>Br<sub>2</sub> and *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>I<sub>2</sub> was refluxed in benzene in the dark (Table 4), which indicated that the halogen dissociation–association of ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)Re(CO)(L)X<sub>2</sub> can occur under both photochemical and thermal conditions and in both solid and solution phases.

Two mechanisms for the solid-state photochemical isomerization reactions of ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)Re(CO)(L)X<sub>2</sub> on the surface of silica gel can be proposed (Schemes 1 and 2). Both mechanisms include interaction of the halogen ligand X of ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)Re(CO)(L)X<sub>2</sub> with the surface of silica gel. These mechanisms are different from the original proposal made by Hill<sup>7b</sup> for similar compounds, in which CO dissociation was shown to be the key step for photochemical isomerization at low temperature. However, a more recent report by Hill and co-workers has implicated metal–halogen bond cleavage in a *diag*–*lat* isomerization reaction of related rhenium complexes.<sup>22</sup>

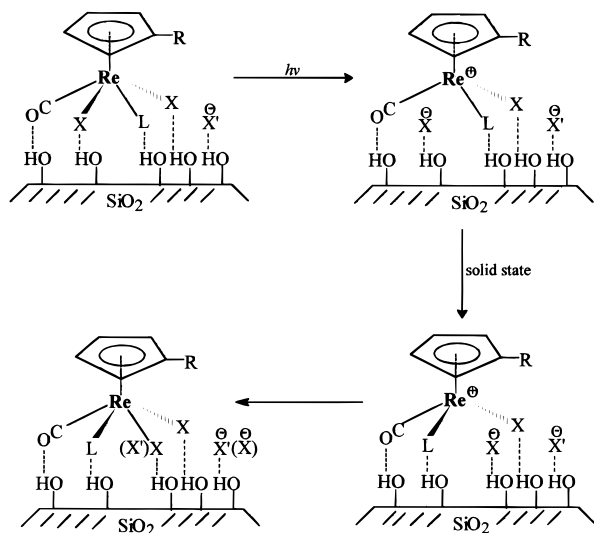
These two mechanisms are shown in diagram form in Schemes 1 and 2. In Scheme 1, upon irradiation, the

(20) Molecular iodine was separated from the isomerization products of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Re(CO)<sub>2</sub>I<sub>2</sub> on a chromatography column and confirmed by reaction with starch in water (blue color).

(21) The bond energies of NaI, NaBr, and NaCl are 72.7, 86.7, and 97.5 kcal/mol, respectively.

(22) Xia, W.; Hill, R. H.; Klahn, A. H.; Leiva, C.; Buono-Core, G. E. *Polyhedron* **1996**, *10*, 3093.

**Scheme 1. Proposed Mechanism 1 for the Solid-State Photochemical *diag*-*lat* Isomerization of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)Re(CO)(L)X<sub>2</sub> on the Surface of Silica Gel**

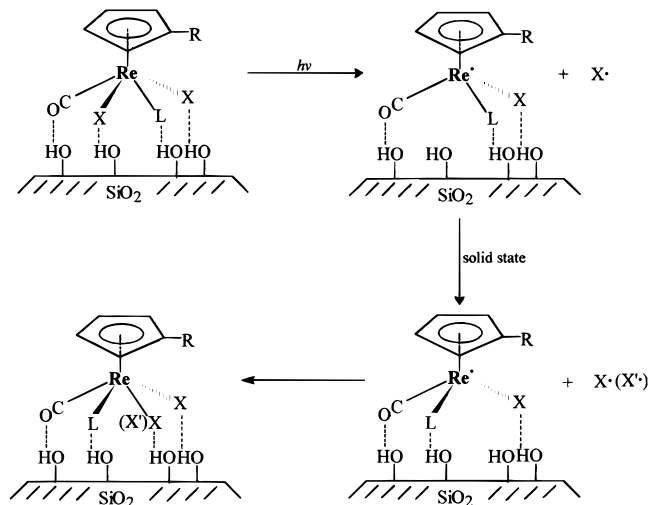


ligand X dissociates to form a halogen ion and a diagonal three-legged cation intermediate which rearranges to the lateral configuration. The later recombines with X<sup>-</sup> (or X'<sup>-</sup>) ion to form the lateral isomer. In Scheme 2, irradiation results in Re–X bond homolysis to form the halogen radical X<sup>•</sup> and a diagonal three-legged radical intermediate, which converts to a lateral radical intermediate and recombines with X<sup>•</sup> (or X'<sup>•</sup>) to form a lateral isomer. While the details of the two mechanisms proposed presently lack direct experimental support, they provide a basis for further mechanistic studies on this unusual solid-state photochemical isomerization reaction on silica gel.

### Conclusions

The solid-state diagonal to lateral isomerization of monosubstituted cyclopentadienyl four-legged piano-stool rhenium complexes ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)Re(CO)(L)X<sub>2</sub> (R = H, alkyl; L = CO, P(OR)<sub>3</sub>; X = Br, I) proceeds in good yield when the complexes are adsorbed on the surface of silica gel and irradiated with visible light. Unlike the thermal solid-state or molten-state isomerization

**Scheme 2. Proposed Mechanism 2 for the Solid-State Photochemical *diag*-*lat* Isomerization of *diag*-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)Re(CO)(L)X<sub>2</sub> on the Surface of Silica Gel**



reactions, the ring substituent has little effect on the photochemical solid-state isomerization reactions of ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)Re(CO)(L)X<sub>2</sub>. The photostationary ratio [*lat*]/[*diag*] was mainly determined by the ligands L and X. The solution and matrix isomerization reactions of ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R')Re(CO)<sub>2</sub>X<sub>2</sub> (R = H, Me; R' = Me) gave results completely different from those observed for the solid-state thermal and photochemical isomerization reactions discussed here. It was found that only monolayer adsorbed molecules on the silica surface underwent isomerization and studies showed that the hydroxyl groups on silica gel play a crucial role in the isomerization reactions. The isomerization reactions could be rationalized by a mechanism in which a halogen dissociative–associative process involving ions or radicals occurs under irradiation with visible light.

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